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ALPINE LEAD–ZINC ORES OF EUROPE.

HENRY L. JICHA, JR.

CONTENTS.

ABSTRACT.

The ore deposits of Cave di Predil (Raibl), Mezica (Miess), and Bleiberg-Kreuth, in Italy, Yugoslavia, and Austria, respectively, are representative of the Alpine lead-zinc ores of Europe and are of the "Mississippi Valley" type. In each case the upper 50 to 100 meters of the mid-Triassic (Wetterstein) limestone constitutes the chief ore horizon. The ore is in fissure veins and replacements, partly widely disseminated, and generally the bodies are not far below a relatively impervious formation (e.g., the Carditas or Raibl slate). Overturned anticlines (Mezica) and especially tear faults controlled mineralization.

Besides the usual galena, sphalerite, marcasite, dolomite, and calcite mineralization, the ores contain fluorite, barite, chalcopyrite, and some arsenopyrite, together with noteworthy quantities of wurtzite. Wurtzite shows botryoidal, concentric bands, in part alternating rhythmically with marcasite and forming the so-called "Schalenblende" of German geologists. Much of this wurtzite is markedly anisotropic, in part converted to sphalerite but most stable where darker in color and richest in iron (Ehrenberg's theory). Where light yellow it was either first formed as sphalerite or has now inverted to that mineral. Disseminated zinc sulfide, however, was apparently sphalerite when first deposited, and a later, cross-cutting sphalerite can also be distinguished, though the possibility is not excluded that all the zinc sulfide was at first wurtzite. The darker bands of the "schalenblende may have derived their iron by primary resorption from the associated marcasite.

INTRODUCTION.

In 1937–38 Dr. Charles H. Behre, Jr., made an extensive tour of the lead-zinc deposits of Europe. In the course of his studies of the deposits he acquired a large suite of ore specimens from each deposit. He provided the writer with the specimens and considerable other data collected at the time in order that a detailed paragenetic investigation might be made. Results of that study are here reported.

Three districts were chosen for this study because of their relatively close proximity to each other (within 100 miles), their geologic similarity, and their apparently related modes and times of deposition. These are Cave di Predil (Raibl) in Italy, Mezica in Yugoslavia, and Bleiberg-Kreuth in Austria.

ACKNOWLEDGMENTS.

Grateful acknowledgment is extended Professor Behre, for his advice and guidance in this study; and to Professors Paul F. Kerr, Walter H. Bucher and J. Lawrence Kulp, all of the Department of Geology, Columbia University, for their helpful suggestions and advice on some specific problems; and to the graduate students of economic geology at Columbia University, whose discussion, interest, and suggestions have also greatly helped in preparing this paper.

GENERAL DESCRIPTION.

The Bleiberg-Kreuth District is located in Western Carinthia (South-central Austria) about 12 km west of Villach and 50 km west of Klagenfurt, in the eastern end of the Gailtal Alps. The Mezica (Austrian name, Miess) district is located in Slovenia, Yugoslavia, in the eastward extension of the Carinthian Alps. The Cave di Predil (Austrian name, Raibl) mines are near the town of Raibl, in the Seebach Valley, Italy, about 8 km south of the Austro-Italian border and 16 km south of the Bleiberg-Kreuth District. Before World War I these three districts were all in the Austrian province of Carinthia (Fig. 1).

The rugged glaciated peaks and U-shaped valleys surrounding the districts are typical of the topography found throughout the southern Alpine region of Europe. Average relief is about 1,000 meters and the average elevation of the valley floors ranges from 500 to 1,000 meters.

All three deposits have a long history of development. The Cave di Predil mines have been known since Roman times and have been worked since the Fourteenth Century. Some of the Mezica mines have been worked since the Fifteenth Century and documents show that the Bleiberg-Kreuth area has been a lead producer since A.D. 1004.

GEOLOGY.

The lead-zinc deposits of Carinthia occur in fissure enlargements or other cavities in close genetic connection with soluble rocks, particularly limestone. Locally they constitute replacement bodies. These are a typically developed form of deposit, similar in many ways to the "Mississippi Valley" type of the

United States. Deposits of this kind traverse Carinthia in a broad east-west zone and are usually below an impermeable slate bed. The "Hauptschieffer," the Bleiberg or Raibl slate of the Upper Triassic, and the Werfen slate of the Lower Triassic all are such units. The ore deposits seem to be localized by the overlying argillaceous rocks (3).[1]

The three deposits under discussion fit the above general description of the Carinthian ore deposits very well. The stratigraphic environment of these ore deposits is similar. In each case, the ore-bearing horizon is the Wettersteinkalk, a limestone of upper Middle Triassic age. The ore deposition appears to have been at least partially controlled by the impounding effect of the overlying Raibl or Carditas slates. This control is demonstrated by the fact that the ore deposits invariably occur within 50 to 100 m of the top of the Wetterstein limestone and that, while ore may often appear in the basal member of the slates, the mineralization never extends any great distance into the shale layer, nor is there any mineralization found above this bed in areas where the Wettersteinkalk is mineralized.

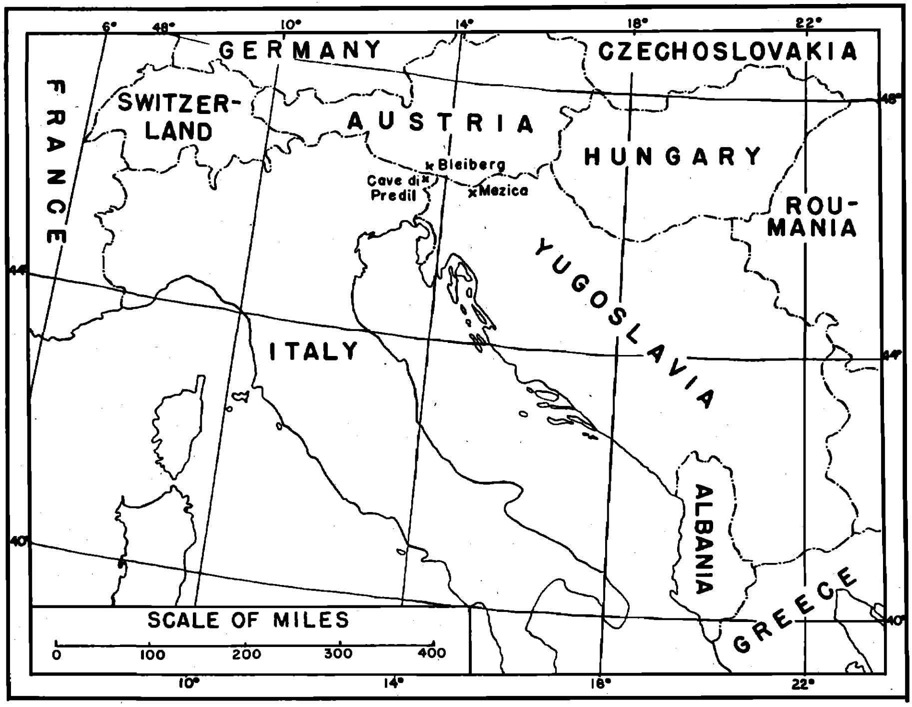

FIG. 1. Map of southern Europe showing the locations of the ore deposits discussed.

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[1] Numbers in parentheses refer to Bibliography at end of paper.

A generalized stratigraphic section for the three districts is given in Table 1 (5, 17, 20).

The overall structure of each of these three districts is different, but in a general way, the structural control of the ore deposition in each of them is the same. The ore occurs in fissures and tear faults, and along bedding planes in areas where there has been bedding-plane movement. The intersections of fractures or faults and planes of movement between beds are particularly favorable for ore deposition. Some replacement ore bodies also occur.

At Cave di Predil (Fig. 2), tear faults are the main structural features. Their close connection with the ore deposition is made clear by the fact that ore occurs only near and in these faults and mainly in an area bounded by the two major tear faults (the Fallbach and Barenklamm faults) running roughly north-south, across the major structural trends of the Alpine arc. Faulting outside the mineralized area is less marked. At Bleiberg (Fig. 3), the overall structure is a graben, formed by the downfaulting of a large syncline parallel to its length. This graben is split by a large, high-angle thrust or tear fault (the Dobratsch thrust), whose lateral movement has caused the minor faulting with which the ore deposits are associated. The minor faults and bedding-plane movements at Mezica (Fig. 5) are related to overturned anticlines. In the Mezica district, the structural highs of the anticlinal axes are additional features controlling ore deposition.

TABLE 1.

GENERALIZED STRATIGRAPHIC SECTION OF THE CARINTHIAN REGION.

Age	Formation	Description
Quaternary		Talus, glacial deposits, etc. (Missing in many areas)
Tertiary		Limestone conglomerates (Mezica)
Triassic		
Upper	Hauptdolomit (Main dolomite)	Dark brown to black dolomite 31.5–5,000 m.
	Carditas or Raibl slates	Black slates 15–500 m.
Middle	Wettersteinkalk (Ore-bearing limestone)	Chiefly limestone and dolomite; some shaly and marly beds in upper 30 m. 1,000 m.
	Muschelkalk	Various formations, including mostly marls and limestones and dolomites (Werfen and Buchenstein beds, etc.)
Lower	Notsch Carbon (Bleiberg) or Werfen schists (Raibl, Mezica)	

Paleozoic rocks are found in some areas

The ores themselves are similar in composition. In general, the predominant gangue minerals are calcite and/or dolomite, and barite. Fluorite and anhydrite, though generally present in minor amounts, are the only gangue minerals present in some parts of the Bleiberg-Kreuth district. The ore minerals are galena, sphalerite, and wurtzite, with insignificant marcasite, pyrite, and arsenopyrite. Except at Mezica, the predominant form of zinc sulfide is wurtzite. Even at Mezica there is evidence that the zinc sulfide was deposited as wurtzite and inverted to sphalerite, the more stable mineral. At Bleiberg and at Cave di Predil the wurtzite has a botryoidal banded texture, characteristic of similar ores in many of the other European deposits. This form of the mineral is the "Schalenblende" of the German geologists. Secondary minerals, predominantly cerussite, anglesite, smithsonite, hydrozincite, calamine, wulfenite, limonite, and gypsum, were found in the upper oxidized zone of the deposits. Such ores have now, for the most part, been mined out.

The ratio of lead to zinc in the ores is a characteristic peculiar to each deposit. At Bleiberg-Kreuth the ratio is 10:1, at Mezica 2:1, and at Cave di Predil 1:4.

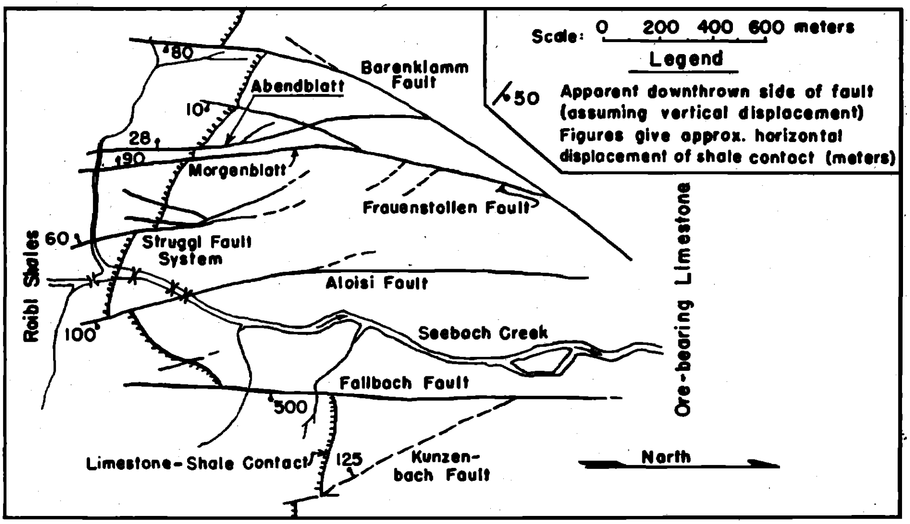


FIG. 2. The fault system at Cave di Predil (Raibl). After Radcliff (modified).

In origin these deposits are all closely related to each other in time and source, despite the slight differences between the opinions expressed by various investigators. All were associated with some deep-seated igneous mass. Evidence is furnished by the granite porphyry intrusives found at Raibl, which are of post-Jurassic, probably Tertiary age (21). The Tertiary age of the mineralization in all three districts is not disputed, but the exact times proposed vary. Tornquist (20, p. 90) gives the age of the Bleiberg-Kreuth deposits as Miocene-Pliocene. Di Colbertado (5, p. 288) considers the mineralization at Raibl to have taken place in late Oligocene and early Miocene time. The age of the Mezica deposits is given merely as Tertiary (10, p. 83–91). However, it seems reasonable to assume, as Di Colbertado (5, p. 288) has stated, that the hydrothermal solutions are related to a deep magmatic mass associated with the intrusive manifestations of the peri-Adriatic Alpine arc.

ORE DEPOSITION AND PARAGENESIS.

Bleiberg-Kreuth.

The ore deposits at Bleiberg-Kreuth belong to the mesothermal or epithermal class, more probably the latter. The mineralization appears to have occurred in several phases, with little apparent discontinuity, except in the final phase, which was probably appreciably separate from the others in time.

The first phase was calcitization on a large scale. The original limestone was brecciated and recemented, with replacement veining, by introduced carbonates. In the second phase, minor amounts of pyrite (the first sulfide) and barite were deposited, closely followed by the introduction of yellow zinc sulfide, probably as sphalerite, and later galena, which formed large euhedral crystals. A second carbonate phase that formed large scalenohedral crystals then took place. In the fourth phase the solutions were probably more acid and bright orange blend (wurtzite), botryoidal blend (schalenblende), barite, and marcasite were introduced, closely followed by fluorite. The marcasite occurs in large bladed masses that form incrustations on galena and other early sulfides and replace the late barite. Fluorite is the latest of all minerals. It is only a relatively minor accessory in most parts of the mines, but in some areas it makes up the chief gangue mineral. Cockade ore, made up of botryoidal blend around crystals of galena, with accessory barite and marcasite, appears to float in massive fluorite. It is noteworthy that fluorite is more startling in this limestone district than in others where dolomitization has been more conspicuous. For lack of adequate specimens it has been impossible to place the next two stages of the mineralization accurately. In some places anhydrite forms the chief gangue mineral and cements not only the brecciated limestone but also fragments of sulfides which were broken by

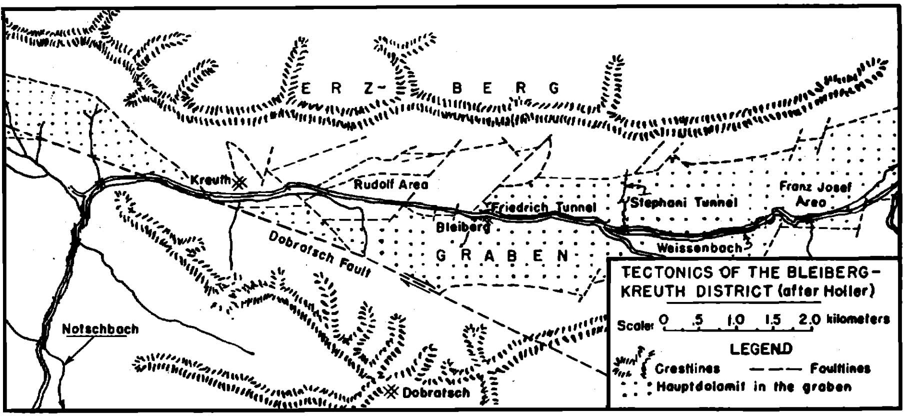


FIG. 3. Tectonics and ore deposition of the Bleiberg district (after Holler).

tectonic movements following directly upon or contemporaneous with the sulfide deposition. This tectonic effect is expressed in ores from all parts of the district, at least by minor shearing in the galena. In the areas of greatest stress the stages include brecciation and later recementation by finely crystalline anhydrite. Pyrite was deposited as the top layer on the late brown schalenblende. The last phase was another introduction of calcite, which in some cases penetrated the ores and caused secondary growth of the early scalenohedra, but for the most part formed only a coating of tiny scalenohedra on the pyrite shell of the schalenblende.

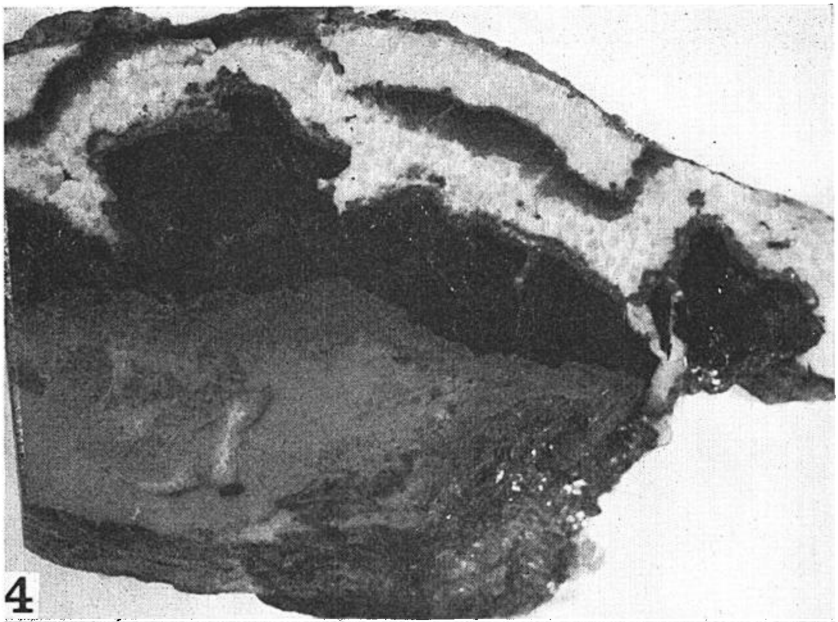
Description.

Carbonates.—Calcite occurs in three generations. The earliest generation is pre-ore, and permeated and recemented the fractured and brecciated bituminous limestone in which the deposits were formed. In some cases it replaced the original limestone with rhombohedral crystals of epigenetic carbonate. Large rhombohedral and scalenohedral crystals of the intermediate generation were introduced after the first phase of sulfide mineralization, partially replacing all the previously formed minerals. These were in turn replaced by the later sulfides and gangue. The last generation of calcite was introduced as the final stage of the mineralization sequence. This generation, in addition to forming scalenohedral crystals, most of which were of much smaller dimensions (1–2 mm in diameter) than those of the second generation, contributed to the secondary growth along the crystal faces of the second generation of calcite. This is demonstrated by replacement of the schalenblende along the faces of the second spar generation around which the zinc sulfide was originally deposited.

Iron Sulfides.—Marcasite and pyrite occur throughout the ore deposit. Pyrite was formed either in one or two generations. Euhedral and subhedral crystals of pyrite in masses of early calcite and limestone are thought to be an early generation although no evidence of the relative age of these pyrite crystals is found except on the basis of general paragenetic sequences. The second generation of pyrite, which forms a capping shell on the late schalenblende, is the last sulfide deposited. The only later mineral is calcite.

Marcasite was deposited during the third (apparently more acidic) phase of sulfide mineralization. It takes the form of thin peripheral bands of anisotropic bladed crystals around masses of galena and sphalerite (Fig. 4). The fact that it is replaced only by fluorite and late calcite favors, but does not prove, that this mineral is one of the latest of the sulfide sequence. In some specimens barite II replaces, in others it is replaced by marcasite, with little evidence of contemporaneity in either case. Since these specimens are from different and widely separated parts of the mineral district, it is assumed that the paragenetic sequence must have varied to some extent between the various areas.

Barite.—Barite occurs in two generations. Barite I, one of the early gangue minerals of the first sulfide phase of the mineralization is in tabular plates, now, for the most part, very badly corroded and replaced by all the



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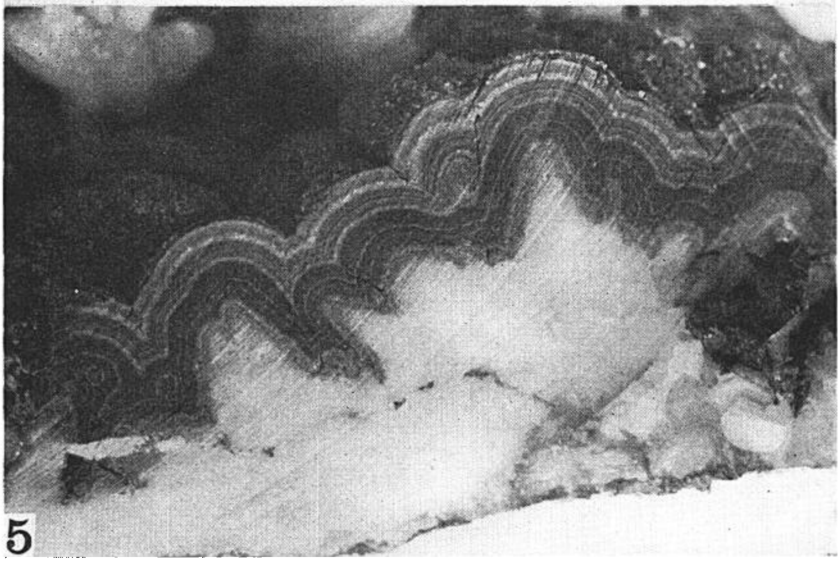

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Fig. 4. Layered ore. Base is fine-grained limestone with disseminated sphalerite increasing toward contact with later galena surrounded by marcasite. Late calcite has replaced some galena and marcasite and blende (dark bands) completed the deposition. Bleiberg. × 1.

Fig. 5. Schalenblende (banded wurtzite) surrounding slightly corroded scalenohedra of Calcite II. Outer shell of pyrite with tiny scalenohedra of calcite. Bleiberg. × 1.

later minerals. It is distinguished by the fact that in several places it has been replaced by the yellow sphalerite of the early sulfide phase, a relationship which would be impossible if the barite were later.

Barite II occurs as sheaves and masses of large bladed crystals, up to 1 cm long, which show sharply defined replacement relations toward the minerals of Phases I through IV and the orange wurtzite and early schalenblende of Phase V (see Fig. 6 a).

Zinc Sulfides.—Three forms of zinc sulfide occur in the deposits of the Bleiberg-Kreuth area. The earliest form, crystalline granular yellow sphalerite, which disseminated in the limestone and throughout the zincy ores of the district, is a product of the first sulfide phase of the mineralization.

The remainder of the blende was deposited in the form of wurtzite and schalenblende. Wurtzite forms anisotropic orange rims around the earlier yellow sphalerite crystals (Fig. 6 b). Wurtzite in this form is clearly a product of the second sulfide phase as it replaces galena, the last sulfide deposited in the first sulfide phase.

Schalenblende takes on two forms that are closely allied and may be considered best as separated parts of the same occurrence. To the earlier form, which is brownish to reddish-brown in color, wurtzitic (anisotropic) in character, and replaces the minerals of the previous phases, the name "botryoidal blend" is here applied. This blend replaces galena and is in turn replaced by later barite and marcasite. In the areas where some tectonic movement has taken place, this blend has been broken and recemented by anhydrite, fluorite, and the last generation of calcite.

The true schalenblende is a later form. It encrusts the dog-tooth spar of the second calcite generation and gives the impression of having been formed as a colloidal mass. The color of this mineral is varied in the several layers in which it is formed, but is always brown or yellowish-brown. It has a marked anisotropism. In one particularly conspicuous case the schalenblende has a layer of pyrite crystals covering the smooth curves of the last layer of blend and this, in turn, has a covering of scalenohedral calcite crystals (Fig. 5). This type of texture is clear evidence of formation in an open cavity.

Galena.—Galena occurs as large crystals, most of which have the form of cubes modified by octahedrons, and as veinlets and small masses that replace the early yellow blend and the early gangue minerals. It is itself replaced by many of the later minerals in the sequence, especially botryoidal blend, which forms cockades around the large crystals, with some replacement along the edges and cleavages. Some galena occurs as veinlets which have rounded outlines, suggesting that lines of crystals have been replaced and the "veinlets" are really remnants of these crystals.

In most of the Bleiberg ores the galena shows some shearing as the result of the late tectonic movements. The curved cleavages thus formed are often clearly visible megascopically.

Fluorite.—In most parts of the deposit fluorite is a minor gangue mineral, but in the Bellegarde ore body (in the central part of the district, just northwest of Bleiberg) fluorite is almost the only gangue mineral of any importance. In other areas fluorite is sparingly disseminated in small subhedral

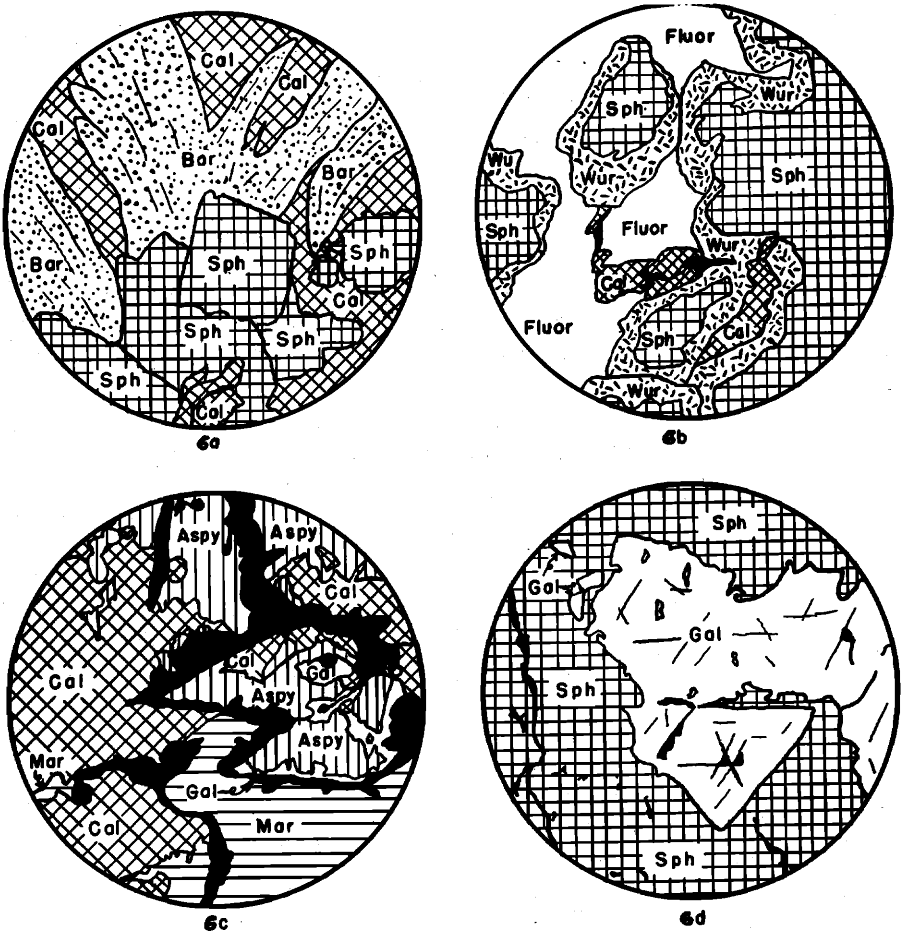

FIG. 6. Camera lucida drawings. *a.* Sheaf of late barite (Barite II) on sphalerite. Bleiberg. × 15. *b.* Anisotropic rims of wurtzite around isotropic sphalerite. Gangue is fluorite and calcite. Cross nicols. Bleiberg. × 85. *c.* Early (?) arsenopyrite surrounded and partially replaced by marcasite, galena, sphalerite, and calcite. Reflected light. Mezica. × 170. *d.* Late zinc sulfide replacing galena. Reflected light. Raibl. × 25.

masses and cubes, most commonly in ores close to the shale contact. Fluorite is considered to be late because it replaces all of the ore minerals.

Anhydrite.—Anhydrite is disseminated through most of the ore deposits in the district in the form of isolated tabular crystals. However, in the Franz-Joseph area in the eastern part of the district, and in a few other small areas where late tectonic disturbance of the ores has taken place, massive bluish anhydrite cements the breccia fragments. This mineral is considered to be primary in origin on the basis of its wide dissemination in other parts of the deposit and its perfection of crystal shape.

Mezica.

The ore deposition in the Mezica area is of the epithermal type. Mineralization is considered to have taken place in three phases which may or may not have been continuous. There is no evidence of discontinuity other than the change in mineral types. The first phase was dolomitization and baritization; the second, sulfide deposition; the third, a second deposition of barite and carbonate with minor amounts of fluorite. The mineralizing solutions were probably weakly acid as evidenced by the deposition of marcasite and wurtzite, which are believed to occur as primary minerals only under conditions of low pH. The ore deposits were then oxidized where near or at the surface.

Carbonates.—Dolomite occurs in two generations. Dolomite I is the earliest gangue mineral. It replaces the Wetterstein limestone both as a grain-for-grain replacement, retaining the original texture of the limestone, but segregating much of the bitumen present into the areas around the grain boundaries, and as larger crystals than those of the original fine-textured limestone, in the form of veinlets (Fig. 7).

Dolomite II is the last mineral deposited. It replaces all the other minerals including sulfides, with the exception of the oxidation products. In thin sections, it is easily seen that dolomite II has either replaced dolomite I almost completely or at least peripherally, the inhomogeneous crystals thus formed having a center of dolomite I. Some calcite also occurs with the late dolomite and in similar relations to the earlier minerals.

Barite.—Barite also occurs in both early and late phases of mineralization. Barite I was apparently deposited as part of the early phase of alteration, later than dolomite I or with slight overlap. The relations are partially obscured by dolomite II. Barite II shows definite replacement relations with dolomite I and the sulfides and is itself replaced only by fluorite and dolomite II. Both generations of barite occur as bladed crystals, isolated or in sheaf-like masses.

Arsenopyrite.—Arsenopyrite has been observed in only one section from the Mezica area (Fig. 6 c). In this section it is the earliest sulfide, occurring both in large masses and diamond-shaped crystals. It shows replacement by all other sulfides and late gangue minerals. Relations to the earlier gangue minerals could not be determined.

Marcasite.—Marcasite is the earliest common sulfide. It occurs as incrustations and disseminated crystals and is commonly replaced by the other sulfides and the late gangue minerals. Some of the disseminated crystals show very weak or no anisotropism and may have partially or wholly inverted to pyrite. This is evidenced by the presence of some zoned crystals in which pyrite and marcasite alternate. There is also a minor late generation of marcasite (and/or pyrite) which occurs as disseminated crystals and incrustations after the deposition of galena. Most of this material is isotropic, but as the conditions of mineralization were probably acidic, it may have been deposited as marcasite and later inverted to pyrite.

Zinc Sulfides.—Zinc sulfide occurs in several colors as both sphalerite and wurtzite. It is assumed that all zinc sulfide was deposited as wurtzite and has inverted to the more stable form with the passage of time. This conclusion is

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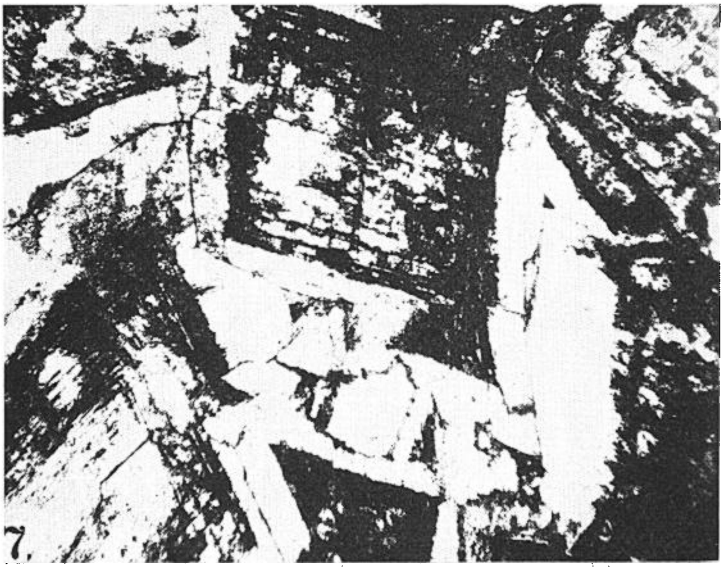

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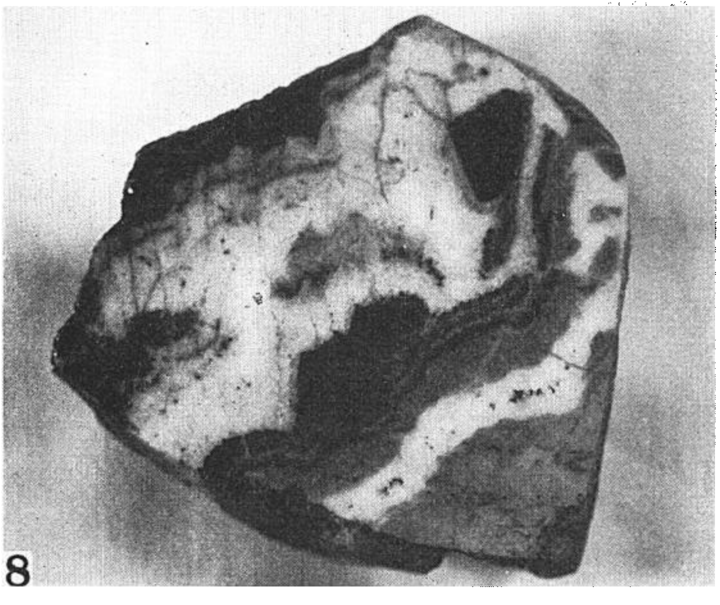


FIG. 7. Inclusions of bitumen show the shape of original calcite crystals which were replaced internally and surrounded from without by epigenetic carbonate. Mezica. × 35.

FIG. 8. One side of a "vein." Original limestone (lower right) is traversed by a vein of late calcite. Galena (black crystals) was replaced by botryoidal blend. Late calcite replaced the sulfides in some places. Note brecciation. Mezica. × 1.

derived from the fact that red zinc sulfide (wurtzite) is found replacing marcasite and is replaced, or at least succeeded by a later generation of yellow zinc sulfide (sphalerite). Apparently either (1) conditions of pH and/or temperature changed to such an extent as to allow the deposition of sphalerite after deposition of wurtzite or (2) some wurtzite has inverted to sphalerite. Ehrenberg (5) has shown that wurtzite inverts to sphalerite very slowly or not at all when over 5 percent of iron is present in the mineral, and that even a small amount of iron will inhibit this inversion to a large degree. As anticipated from that explanation, in the ores here described the more highly colored, iron-bearing form of zinc sulfide occurs as wurtzite and the least colored, pale, translucent, yellow form, presumably not iron-bearing, occurs as sphalerite.

Galena.—Galena occurs as large euhedral crystals (Fig. 8) and in veinlets of all sizes which were deposited after deposition of zinc sulfide had been completed. This is clearly shown by the fact that although galena is replaced by late iron sulfide and gangue minerals, it is in no case replaced by zinc sulfide, but rather often itself replaces sphalerite or wurtzite in veinlets. It also replaces all the other early minerals similarly. Finally, it also occurs as large crystals in dolomite. Some "steel galena"—a highly sheared form of this mineral—is also present. It is related in its origin to post-ore movement, probably along pre-existing faults in the ore zone.

Fluorite.—Fluorite occurs in minor amounts as rare, generally small crystals, which fill in between and to some extent replace the sulfides and gangue minerals.

Secondary Minerals.—Gypsum appeared in veinlets in the specimens showing incipient alteration. Its relation to the other minerals is not clearly established. It appears to be the result of secondary oxidation.

Only two other secondary minerals, cerussite and covellite, have been observed. In the literature examined, no mention was made of the presence of covellite in the Mezica area. This mineral occurs as finely crystalline masses replacing zinc sulfide and gangue minerals. It probably has its origin in very minor chalcopyrite which formed a solid solution in the zinc sulfide, a relation which is often found in lead-zinc ores. No chalcopyrite has been observed in the course of microscopic examination of the ores, however.

Other secondary minerals mentioned by Granigg (10, pp. 188–190) are smithsonite, hydrozincite, wulfenite, anglesite, leadhillite, plumbocalcite, greenockite, and limonite. Small amounts of quartz of uncertain relation to the other minerals also occur, apparently as part of the mineralization, as it shows a replacement relation to the Wetterstein limestone. However, no quartz was observed in the course of this study.

Cave di Predil (Raibl).

The ore deposits at Cave di Predil are of the epithermal type. The mineralization occurred in several phases with some apparent discontinuity in deposition. The first phase was dolomitization. The second phase introduced marcasite, followed by a generation of black crystalline zinc sulfide, sparsely distributed, and of the more common yellow crystalline and scaley zinc sulfide. This was succeeded by a generation of galena, replaced by and in part contemporaneous with a botryoidal zinc sulfide having bands of bright red, red- to orange-brown, and violet-gray. Minor replacement of this zinc sulfide by white, finely crystalline calcite then took place; locally this calcite shows almost oolitic texture. The galena which accompanied the zinc sulfide is minor. At this juncture the ores were brecciated by contemporaneous tectonic movement. Next, a light yellowish-gray generation of zinc sulfide was introduced. In many cases this replaced the breccia fragments peripherally. It was accompanied by late marcasite deposited as incrustations on the earlier sulfides and also as crystals in dolomite. The last phase was the introduction of barite and minor fluorite with further later dolomitization. The late dolomite cements the brecciated ores.

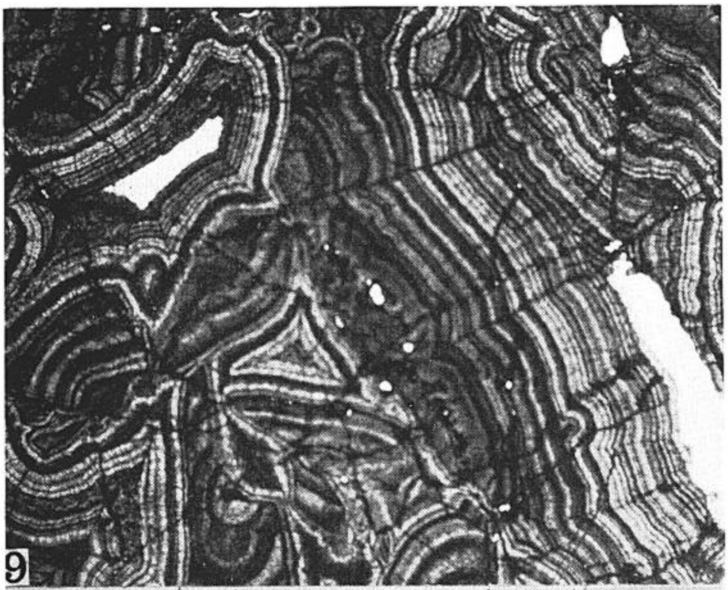
Carbonates.—Dolomite appears in two major generations, early and late. The early generation permeated the original limestone in the form of veinlets and, to a larger extent, as replacements. In many cases it is distinguishable only with some difficulty, even with the metallographic microscope, but in some cases small remnant crystals of dolomite can be found as inclusions in galena and zinc sulfide. In thin section the distinction is easily made as early dolomite shows inclusions of bitumen, whereas the replacing later dolomite is peripheral to the earlier crystals and shows no inclusions. The late generation, besides forming veinlets of white crystals up to 2 mm in diameter that transect the entire previous sequence of earlier minerals, also constitutes the matrix of the brecciated ores (Fig. 12) in the form of large crystals up to 1 cm in diameter.

Minor fine-textured calcite occurs in association with red and violet-gray zinc sulfide and to a lesser extent with the earlier yellow zinc sulfide as replacements across the banded structure, and as tiny round globules resembling oolites. This calcite appears to be clearly earlier than the late grayish-yellow zinc sulfide and the late dolomite, as it shows the brecciation that affected the ores before the deposition of the grayish-yellow blend and late dolomite.

Marcasite.—Marcasite occurs in two generations. The early generation is the first sulfide present, with the possible exception of arsenopyrite. Arsenopyrite was not observed during the course of the studies here presented but it has been reported in minor amounts by Tornquist (20, p. 165). The early marcasite occurs as botryoidal masses of large crystals, commonly bladed, which exhibit strong blue and greenish-yellow anisotropism. This is replaced by all later minerals, but especially by bands of red zinc sulfide along the interfaces between the earlier marcasite bands.

The late generation of marcasite occurs in two forms: (1) as incrustations on galena, yellow zinc sulfide, and limestone breccia fragments (Fig. 11), and (2) in irregularly shaped, rounded, zoned crystals. Both of these kinds of marcasite show very poor anisotropism, which may indicate partial inversion to pyrite. The late marcasite is in all cases replaced by late dolomite.

Zinc Sulfides.—Zinc sulfide occurs in several generations of different colors. The earliest generation is in pale yellow to orange-yellow finely crystalline disseminated platelets and is accompanied by a slightly later black form



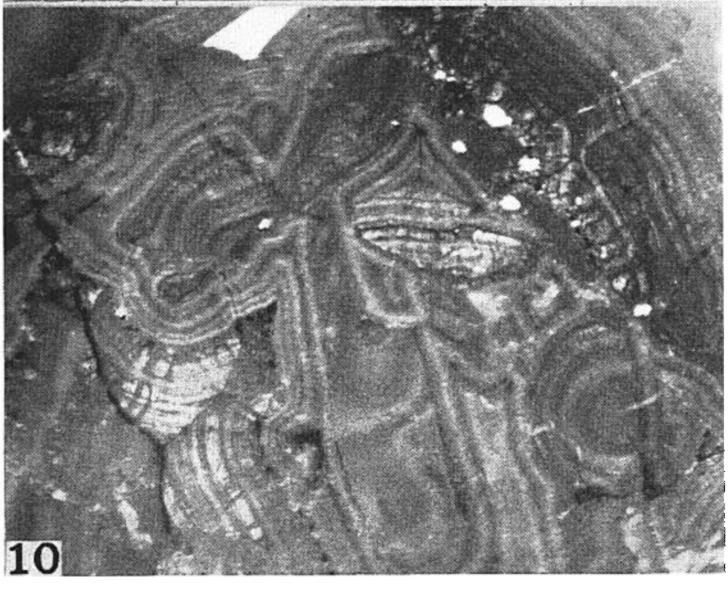
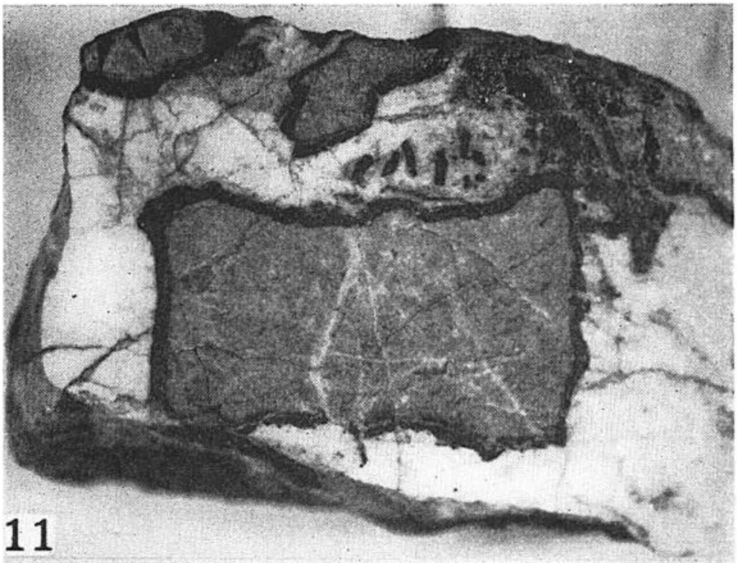


FIG. 9. Schalenblende (botryoidal wurtzite). Ordinary light. Raibl. × 17.

FIG. 10. Schalenblende. Cross nicols. Note the anisotropism showing the wurtzitic nature of the zinc sulfide. Compare with Figure 9. Raibl. × 17.

as crystals up to 2 mm in diameter. Both of these kinds of zinc sulfide show replacement by botryoidal deep red to reddish- or orange-brown and pale violet-gray zinc sulfide. The botryoidal nature of this zinc sulfide is clearly demonstrated in Figures 9 and 12. Galena was apparently deposited both



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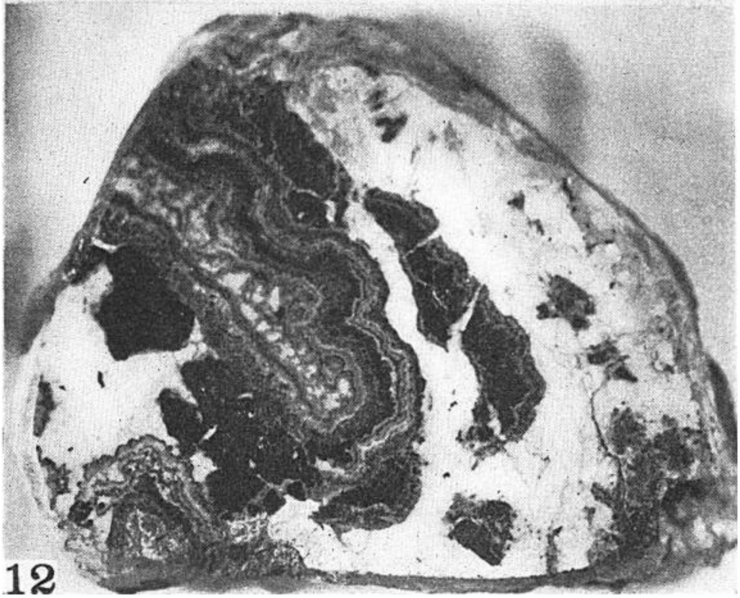

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FIG. 11. Pieces of brecciated limestone (Wettersteinkalk) surrounded by early marcasite and recemented by later carbonate. Raibl. × 1.

FIG. 12. Botryoidal blend and galena with carbonate and late barite (upper left, sheaves). Note the brecciation of the sulfides and recementation by carbonate. Raibl. × 1.

previous to and contemporaneously with the later generation of zinc sulfide, but it is definitely later than both the yellow and black forms, which it replaces. The red zinc sulfide shows replacement of the yellow plates and forms cockades around the black zinc sulfide and the galena. In some places these bands of late zinc sulfide appear cut off by the galena crystal which they encircle in an adjacent part of the periphery of the crystal, a relation which results from the bands growing against the face of the galena mass. A later generation of yellowish-gray crystalline zinc sulfide appeared after the brecciation took place as it can be demonstrated to have replaced both the early red zinc sulfide and the marcasite around the edges of the breccia fragments. This red zinc sulfide is always closely associated with marcasite and the wine red form occurs only as incrustations on or replacement bands along the planes of banding of early marcasite. Its red color is attributed to its high iron content, derived from the resorbed marcasite. This zinc sulfide is clearly wurtzite, being anisotropic (Figs. 9 and 10). In fact, most of the zinc sulfide, with the possible exception of the late yellowish-gray generation, is believed to have been deposited as wurtzite, whether now sphalerite or not. The evidence for this is the ubiquitous nature of marcasite and red zinc sulfide (wurtzite); these both could only have been deposited under conditions of low pH. As explained in discussing mineralization at Mezica, the iron-rich red zinc sulfide would invert very slowly or not at all. Thus it is always found as wurtzite, while the other botryoidal forms are only slightly wurtzitic and the crystalline forms are sphalerite. The red zinc sulfide also shows rather close association with minor late calcite, which cross-cuts it and locally forms narrow units in the banded sequence described.

Di Colbertado (5, pp. 284–285), in his description of the Raibl deposits indicates that there is a rough zoning with respect to the forms of blende. The red blende occurs mostly in the northern part of the deposit. The botryoidal blende occurs in its greatest concentration in the central part of the deposit. The crystalline forms of blende show their greatest development in the southern part of the mineralized area. In no case does Di Colbertado indicate that the division is a strict one, however; it must be assumed that all forms are found throughout the deposit in varying proportions.

Galena.—Galena appears to have been fairly early in the sequence. The most prominent form is in large cubes and octahedrons up to 3 cm in diameter (Fig. 12). These crystals are surrounded by red to violet-gray zinc sulfides and apparently replaced the earlier generations of zinc sulfide (Fig. 6 d). Galena also forms lines of small crystals which appear to be crusted vein fillings. It occurs in lesser amounts in "mutual" contacts, suggesting contemporaneity in deposition with the red zinc sulfide; in such cases it forms fine discontinuous bands between the bands of zinc sulfide and also forms tiny veinlets cutting the earlier banding of the zinc mineral. Finally, some galena is found as fine disseminations in early dolomite.

Barite.—Barite occurs here only in a late generation as white needles with characteristic sheaf-like arrangement. These typically replace the early sulfides and other early gangue minerals.

Fluorite.—Fluorite, identifiable only under the microscope, appears in small amounts as fillings in interstices between sulfides and as small blebs in dolomite. It is distinguished by its dark gray color, smooth surface, and in rare instances, by evidences of octahedral cleavage. This mineral was deposited later than all the sulfides.

Other Minerals.—Di Colbertado (5, p. 286) also mentions the occurrence of pyrite, pyrrhotite, chalcopyrite, and cinnabar in quantities of secondary importance or as rare minerals. The presence of pyrrhotite is noteworthy and surprising.

Oxidized Ores.—The oxidized products are said to be calamine, hydrozincite, cerussite, limonite, and a blue copper stain.

COMPARISON OF THE DEPOSITS.

From the comparison of the structure and mineralization (Table 2) the following conclusion is drawn:

The ore deposits appear to be of similar origin but the mineralizing solutions varied somewhat in composition and acidity. The largest similarity is found between the deposits of Raibl and Bleiberg. Their close proximity to each other is a partial confirmation of this thesis. The mineralization at Mezica is probably related to another similar intrusive. On the basis of these and structural and control features, it is believed that there is enough similarity in the sequences of mineralization and mineral suites to imply that there is a definite relationship among these three deposits.

NATURE OF THE MINERALIZING SOLUTIONS.

For many years economic geologists have been divided over the problem of whether hydrothermal solutions (or their equivalent gaseous phases) were acid or alkaline in nature. Basically, of course, some of the argument depends upon the definitions used for the terms acid and basic. Some have maintained that any solution that does not contain free strong acid is alkaline in nature, while others have defined the terms on pH. This has been brought out by Fenner (7).

The definitions of chemistry state that if pH is above 7 (i.e., if OH_3^+ concentration is less than 10^{-7}), the solution is alkaline; if pH is below 7, the solution is acid. Neutrality is defined by the pH value 7. These are the definitions used for the terms in this paper. It may be assumed that a condition near neutrality is found in solutions with pH between 6.5 and 7.5. However, it should be noted that any solution with pH other than 7 will tend to have the characteristics of an acidic or basic solution, according to the side of 7 on which the pH lies. Therefore, care should be exercised in using the term neutrality, especially since under conditions of heat and pressure such as are thought to have prevailed during the formation of mineral deposits, the chemical reactivities, solubilities, and other properties of solutions and compounds may increase; similarly, the effect of pH, which depends upon heat and pressure, may become correspondingly greater.

Since the assertion that ore deposition takes place from "alkaline" solutions has been made again and again in the literature (11, 18) while others maintain that acidic solutions were the media of mineralization in many cases (7, 13, 8), the author wishes to discuss the problem of the formation of the three ore deposits here under study from both points of view.

TABLE 2.

COMPARISON OF STRUCTURE AND MINERALIZATION.

	Mezica	Bleiberg	Raibl
1. Genesis time	Tertiary	Miocene-Pliocene	Oligocene-Miocene
2. Source	Acid intrusive	Basic? probably acid intrusive	Acid intrusive
3. Structure	Anticlines, tear faults, bedding plane movement	Syncline, large and small tears, bedding plane movement	Large tears, bedding plane movement
4. Control	Shale cover	Shale cover	Shale cover
5. Ore horizon	Wetterstein Ls.	Wetterstein Ls.	Wetterstein Ls.
6. Solutions	Moderately acid	Late highly acid, early mildly acid or neutral	Moderately to strongly acid
7. ZnS	2 forms, no schalenblende	3 forms, late schalenblende	4 forms, early sphalerite, later schalenblende
8. Galena	Before ZnS	After early ZnS, before schalenblende	After early ZnS partly contemporaneous with other forms of ZnS
9. Gangue			
a. Carbonates	Dolomite and minor calcite	Mostly calcite	Dolomite and minor calcite
b. FeS_2	Marcasite early, marcasite and/or pyrite late	Marcasite late, pyrite early(?) and late	Marcasite early and late
c. Barite	Early and late	Early and late	Late only
d. Fluorite	Minor	Important	Minor
e. Anhydrite	Minor	Important	Not noted

On the alkaline side, Smith (19) has shown that zinc and lead sulfides are soluble to a *limited extent* in solutions of sodium hydrogen sulfide and sodium polysulfide at high temperatures and that from such solutions sphalerite crystallizes out before galena on cooling. The experiments were carried out by heating the reagents and sulfur with zinc chloride and lead chloride in a graphite-lined steel bomb to a temperature of 425° C and slowly cooling them. The general order of events in the precipitation was as follows:

1. Crystallization of sphalerite (Octahedrons or cube-octahedrons).
2. Crystallization of galena (cubes).
3. Sphalerite was attacked by the solution which removed some zinc sulfide and later deposited it as small crystals, as amorphous zinc sulfide, or as hexagonal wurtzite.
4. Galena was attacked to a lesser degree and the dissolved lead sulfide deposited later as microcrystalline galena.

Colloidal dispersion was postulated to be the cause of "re-solution." Smith concluded that the fact that solution did take place and that the generally accepted paragenetic order was followed showed that this might be the method of ore deposition. This hypothesis may be examined with other evidences, especially with respect to the ore deposits of Bleiberg-Kreuth, Mezica, and Cave di Predil.

(1) It has yet to be demonstrated that such solutions may transport large amounts of zinc and lead sulfides at lower temperatures than 425° C. This scarcely fits the picture of mesothermal or probably epithermal or telethermal deposition (300° C or less) that is found in the mineralized areas in question. Also, Garrels (8) has pointed out that not only are alkaline sulfide solutions the media in which common metallic sulfides are least soluble (with the possible exception of zinc and the Group 2b metals), though colloidal dispersions may be obtained, but the concentrations of hydroxyl and sulfide ions required for solubility of any significant amount would have to be fairly large (0.3–0.4 molal). He concludes, "Therefore, since some metals do not form true solutions in an alkaline medium, and those that do require high sulfide ion concentrations, it seems that dilute alkaline solutions are a very poor medium for ore transport." The author is in agreement with this idea.

(2) It seems improbable that alkaline solutions could cause any significant solution of limestone or even enough solution to allow replacement. Of course, heat may cause decomposition of limestones. It has been argued that acid solutions should cause excess solution of the limestone, thus leaving cavities in the deposit. Such cavities are not typical of replacement deposits. Also, carbonates are not deposited from acid solutions. However, it is entirely possible that solutions with pH in the range between 6.5 and 7.0 could cause slow enough solution to prevent formation of large cavities and only enough to allow replacement. This is because neutralization of the solution when the limestone is dissolved causes simultaneous deposition of the sulfides to replace the removed limestone. Carbonate deposition would probably occur on reaction and neutralization.

(3) The presence of radicles of strong acids, such as the sulfate and fluoride radicles, in the barite, fluorite, and anhydrite commonly present in the gangue of these and many other deposits indicates the presence of solutions which would have a slightly acid reaction upon hydrolysis, even without the presence of free acid. Sodium sulfide solutions are unstable when pH is below 7. It may also be noted that deposition from alkaline sulfide solutions would probably cause precipitation of free sulfur. No free sulfur has been found in these deposits.

(4) Despite some similarities between the types of deposition in alkaline solutions and those of ore deposits, there are some discrepancies, notably the reversal of depositional order between lead and zinc sulfides in the later stages of mineralization in these deposits.

(5) The presence of wurtzite, and especially marcasite, two mineral forms which, except at very high temperatures, are stable only in acid solutions indicates that the solutions were probably of pH lower than 7.

On the acid side, Kristofferson (14) has shown that not only are lead and zinc able to be transported as volatile chlorides in the presence of hydrogen sulfide and hydrogen chloride above 300° C, but also that it is possible that such transportation may occur in solutions at lower temperature. Deposition would take place upon neutralization of the acid. In support of this, Garrels (9) has shown that transportation may take place in solution by the formation of complex chloride ions, and that in such solutions deposition of the type found in the deposits at Raibl and Bleiberg-Kreuth (i.e., with reversed order of deposition of lead sulfide and zinc sulfide) may also occur. It is not necessary that the pH in these solutions be much lower than 6, if even that low. Such soluble chloride ions might easily be removed with the removal of depositing waters. That ore deposition of this type occurs from gaseous effusions containing hydrogen chloride and hydrogen sulfide has been demonstrated by Allen and Zies in their studies in the Valley of Ten Thousand Smokes (2). Lead and zinc sulfides were deposited there from fumarolic emanations of this type. Newhouse (16) has shown that inclusions in galena and sphalerite in deposits of the "Mississippi Valley" type throughout the world contain calcium and sodium chlorides. Thus, the probable presence of the chloride ion in such deposits as well as the acid nature of the gaseous emanations that deposited similar minerals in the Valley of Ten Thousand Smokes has been established.

In the case of acid solutions, most of the above objections to alkaline solutions are overcome. It may also be demonstrated on chemical grounds that the later phases of the ore deposition, in which apparently colloidal deposition occurs (formation of late schalenblende) at Bleiberg is the result of acid solutions.

Figure 13 shows that wurtzite and amorphous zinc sulfide form at low temperatures in acid environments. The wurtzitic nature and colloidally deposited appearance of this schalenblende may thus be explained. That the solutions could not have been strongly acid is shown by the extremely small amounts of resorption of the calcite scalenohedra on which the schalenblende has been deposited. Late pyrite, also formed at about this time, may indicate that neutralization of the solutions had proceeded to a very high degree of completion, or that at this stage, the solutions may even have been slightly on the alkaline side. This pyrite is slightly later than the schalenblende.

Graton (11) has indicated that the original solutions separated from the magma were necessarily basic. This may well be, as Butler (4) has shown that oxidation may cause the formation of sulfuric acid and deposition of primary sulfate minerals from sulfide ions. However, as Garrels (9) has suggested, it is not necessarily so that, because solutions are rich in ions of strong alkalies such as sodium and potassium, they must necessarily be alkaline in nature. These ions are capable of existence with halogens or sulfate ions in acid solutions. Thus the solutions need not be basic (i.e., of high pH) at all.

In conclusion, on the basis of the evidences here presented and the relations of the ores, it must be assumed that the solutions which formed these deposits,

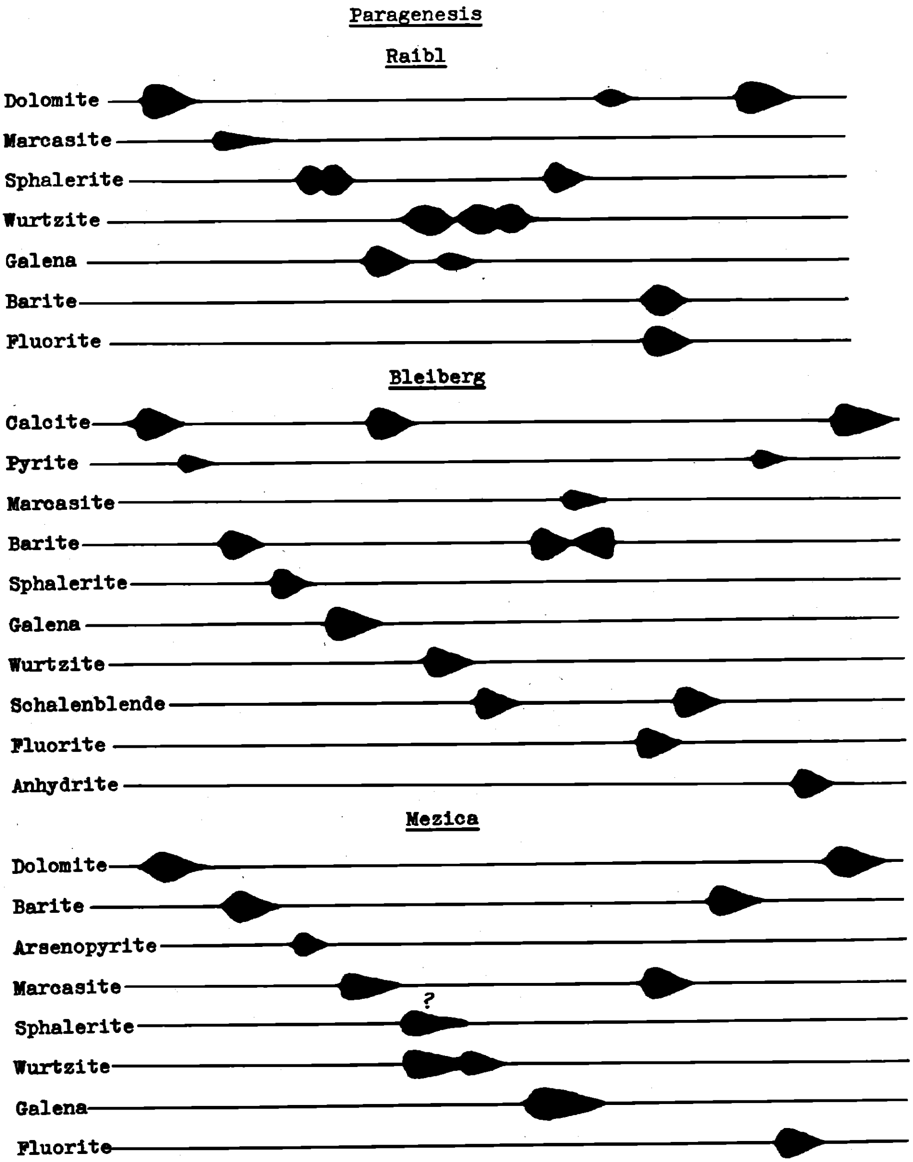
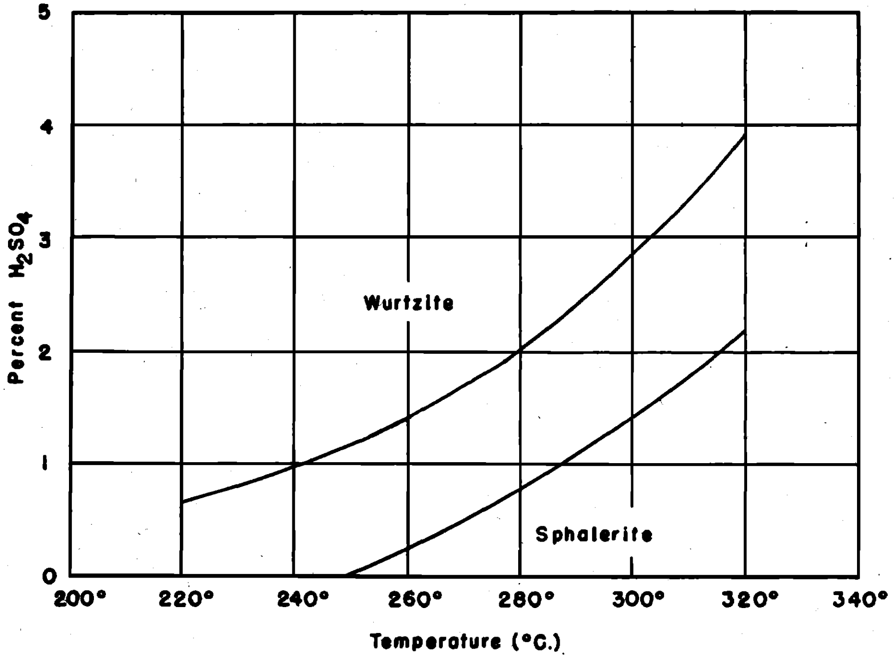


FIG. 13. Paragenetic relations at Raibl, Bleiberg, and Mezica.



Fields of Precipitation of Sphalerite and Wurtzite

	Percent H_2SO_4					
Temp.(°C.)	1.0	2.5	4.0	5.0	7.5	10.0
250	S & W	W & A		W & A		
300	No W Little A	No W	70% W&A	5% W	90% W	All W
350		70% W		30% W		80% W

S = Sphalerite W = Wurtzite A = Amorphous zinc sulfide

FIG. 14. Fields of precipitation of sphalerite and wurtzite (after Allen and Crenshaw, and Mellor).

regardless of their past history, were acidic in nature during the time of formation of these mineral deposits. This means only that the solutions had a pH less than 7, regardless of their original composition of strong or weak acid anions or basic cations.

With regard to other deposits, it is difficult to make a statement covering all types, but in any event, the author is convinced on the basis of the above arguments that lead-zinc deposits of the "Mississippi Valley" type, at least, were formed from solutions whose pH was less than 7.

CONCLUSIONS.

1. On the basis of age relations of the deposits, structural and control features, and the similarity in the sequences of mineralization and mineral suites, there is a definite relationship among these three deposits.
2. The ore deposition in all three districts has been from acid solutions.
3. The ore deposition in similar deposits (Mississippi Valley type) throughout the world has probably been from acid solutions (solutions whose pH is less than 7).

Department of Geology,
Columbia University,
New York City,
April 12, 1951.

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