

MICROSCOPIC INVESTIGATION OF FRIEDENSVILLE, PENNSYLVANIA, ZINC ORE

DONALD M. FRASER, *Lehigh University, Bethlehem, Pa.*

INTRODUCTION

The zinc mines at Friedensville, Pennsylvania, are situated south of Bethlehem in Saucon Valley, which is developed on a down-faulted block of limestone lying between ridges of pre-Cambrian gneiss to the northwest and southeast. The valley is irregular in outline but is approximately ten miles long and three and one-half miles wide. It is bounded on the northwestern side almost entirely by faults and the southeastern boundary is in part marked by fault lines. In addition, faults cut the limestone of the valley proper both longitudinally and crosswise. The ore is concentrated along these crushed zones.

ACKNOWLEDGMENTS

This paper deals primarily with the microscopical features of the ores, and the writer is indebted to Dr. Benj. L. Miller, whose papers¹ and helpful discussion have contributed much of the information regarding structural relationships and general features of the deposit.

Dr. H. V. Anderson and Mr. E. B. Frazee kindly collaborated and furnished the writer with the results of an x -ray examination of certain specimens. Dr. Warren Ewing also assisted the writer by helpful discussion in the application of the laws of physical chemistry.

During the preparation of this paper, the writer learned that Robert D. Butler was examining a variety of sphalerite and associated pyrite found at Friedensville. Mr. Butler sent the writer an abstract of his paper, "Mylonitic Sphalerite from Friedensville, Pa.," which has aided in the understanding of the fractured ore.

PREVIOUS WORKERS—ORIGIN OF ORE

Previous workers concerned primarily with the mineralogy or

¹ Miller, B. L., Topographic and Geologic Atlas of Pennsylvania: No. 206, Allentown Quadrangle, *Penna. Geological Survey*, 1925.

Miller, B. L., Lead and Zinc Ores of Pennsylvania: *Topographic and Geologic Survey*, Bulletin **MS**, 1924.

the origin of the ore include F. A. Genth,² H. S. Drinker,³ J. P. Lesley,⁴ F. C. Clerc,⁵ and J. F. Kemp.⁶ The most comprehensive discussion of the area is given by Benj. L. Miller, who lists a complete bibliography⁷ of the Friedensville mines and also summarizes the views of other workers regarding the origin of the ore in the following manner:

Drinker supposes, "that the zinc was originally disseminated through the dolomite in the form of carbonate or sulphide." Later the small particles were dissolved by water that contained carbonic acid, converted into zinc sulphate by coming in contact with sulphuric acid that was formed by the decomposition of pyrite, and later precipitated in their present location as zinc sulphide through the action of the organic matter contained in the limestone.

Lesley held somewhat similar views and said that, "it is probable that they (lead and zinc minerals) were deposited with the limestone in far greater abundance in ancient ages and were originally brought into the Appalachian sea as soluble salts, together with the lime and magnesia waters of the primeval rivers," and that, "the dissolution of the lime rocks has produced concentrated masses of zinc ore."

Clerc suggested a deep-seated origin in his published statement that "they belong to a class of deposits which seem to warrant a belief in their continuance to a considerable depth."

Kemp states that "the veins were evidently filled by circulation from below that brought the zinc ore to its present resting place in the shattered and broken belt."

Miller regards the ore as having resulted from the following sequence of events:

a. "During . . . Cambrian and Ordovician time zinc minerals . . . (were) precipitated in minute disseminated particles in the limestone as sulphides and carbonates."

b. "The waters that concentrated the sphalerite and pyrite were doubtless mainly of meteoric origin, . . ."

² Genth, F. A., Contributions to Mineralogy—Lanthanite: *Am. Jour. Sci.*, 2nd Ser., vol. **XXIII**, pp. 425-426, 1857.

Genth, F. A., Preliminary report on the mineralogy of Pennsylvania: *Pennsylvania Second Geol. Survey*, Rept. **B**, pp. 15, 18-20, 57, 69, 106, 107, 120-122, 149, 161-163, 165, 166, Harrisburg, 1875.

³ Drinker, H. S., The mines and works of The Lehigh Zinc Company (abstract): *Trans. Am. Inst. Min. Eng.*, vol. **I**, pp. 67-75, 1871.

⁴ Lesley, J. P., The Saucon zinc mines in Lehigh County: *Pennsylvania Second Geol. Survey*, Summary Final Report, vol. **I**, pp. 436-443, 1892.

⁵ Clerc, F. C., The mining and metallurgy of zinc in the United States,—Pennsylvania: *U. S. Geol. Survey*, Mineral Resources, 1882, pp. 361-365, **1883**, *Eng. & Min. Jour.*, vol. **XXXVI**, pp. 148-149, 1883; *Pennsylvania Second Geol. Survey*, Summary Final Report, vol. **I**, pp. 439-443, Harrisburg, 1892.

⁶ Kemp, J. F., Ore deposits of the United States and Canada, second edition, pp. 250-251, **1906**.

⁷ Miller, B. L., *loc. cit.*

c. ". . . ascending waters must have brought the sphalerite and pyrite to their present position unless the ground-water level formerly lay at much greater depths than now."

He thus concludes that the ore is due to circulating meteoric water which on ascending deposited zinc sulphide that had been picked up by the solutions in their descent through the limestones.

Magmatic solutions have been suggested as the source of the ore minerals and the presence of Triassic diabase outcropping a few miles south of the ore district must not be disregarded in a consideration of the source of the solutions.

The writer has not found additional facts pertinent to the origin of the solutions which deposited the zinc ore and therefore must regard the deposit to be the result of ascending solutions of unknown origin.

The primary ore is found as disseminated particles and as replacement masses in the limestone, as fissure and cavity fillings and as the cementing material of brecciated areas. Secondary minerals occur as fillings and encrustations along steeply inclined bedding planes, in transverse joints, in solution cavities and as replacements of the limestone.

MICROSCOPIC FEATURES

PRIMARY MINERALS. The primary sulphides occurring chiefly below the water table, though sometimes above, are sphalerite and pyrite. Greenockite is found in the oxidized ore and it is thought, therefore, that cadmium, probably as a sulphide, is present in the sphalerite.

Sphalerite appears in two distinct types. One, the more common black-jack variety, is coarse-grained and massive with the broken surfaces showing cleavage faces with random orientation. The other type is chert- or flint-like in appearance, ranging from gray-brown to black in color, is dense, massive, and breaks with a conchoidal fracture.

In thin-section the coarser-grained variety is dark brown in color and shows a complete network of fractures traversing the mineral. Between crossed nicols it is noted that the mineral has a clouded appearance not only adjacent to the fracture planes but also for a distance inward equal to several times the width of the apparent fracture zone. Also when the clearer, less prominently fractured parts of the sphalerite are examined, it is found that their

diaphaneity is conditioned by countless smaller breaks which appear to be mainly cleavage planes and by numerous granule or rod-like inclusions having diameters of only a few microns. Some of these may be cadmium, probably in the form of the sulphide, but they have not been proven to be such. X-ray studies in progress at the present time may give more definite information on this point.

Inasmuch as the clearer, more yellowish sphalerite found in the oxidized ore shows numerous cleavage cracks but is lacking in inclusions and in the network of fractures with crushed borders, it is suggested that the black-jack variety found in the primary ore may be less diaphanous and of a darker color due to these features as well as its probable higher iron content.

The finer-grained sphalerite is described by R. D. Butler⁸ as having been formed by crushing; the result being a mylonitic sphalerite. This description is based on observations on polished surfaces. A description of this material in thin-section is given here.

In plane polarized light this yellow brown to dark brown sphalerite is seen to be a granular mass wherein the individual grains are more or less indefinable. This is due to the presence of fractures even in what are apparently the more distinct grains, and also to the overlapping of grains. In a thin-section of the material whose grain size is of the order of several microns in diameter, a few grain-thicknesses are necessary to build up the thin-section which is close to thirty microns thick.

Between crossed nicols two types of material are evident. Brownish material appears in a network of anastomosing wavy bands whereas blacker material lies as elongated areas within the network. The former is interpreted to be the more intensely broken material which is similar in appearance to the crushed areas bordering the fractures in the coarser grained sphalerite. The latter are thought to be "augens" of sphalerite which escaped the minute fracturing of the neighboring material. If this is a correct interpretation, it might be preferable to speak of these specimens of sphalerite as being mylonitized and possessing flaser structure, to indicate the incomplete crushing.

Pyrite is abundantly distributed through the primary ore. The great majority of the pyrite is present as irregular masses or as

⁸ Butler, R. D., Mylonitic Sphalerite from Friedensville, Pa. Abstract, *Am. Mineral.*, vol. 20, p. 203, 1935.

euohedral to subhedral crystals which were deposited on sphalerite layers in fissures or as replacements of sphalerite (figure 1A). In some places pyrite has been fractured and the fractures filled with sphalerite similar in every respect to the primary vein sphalerite. These relations indicate the deposition of pyrite both prior to and after the formation of some of the sphalerite.

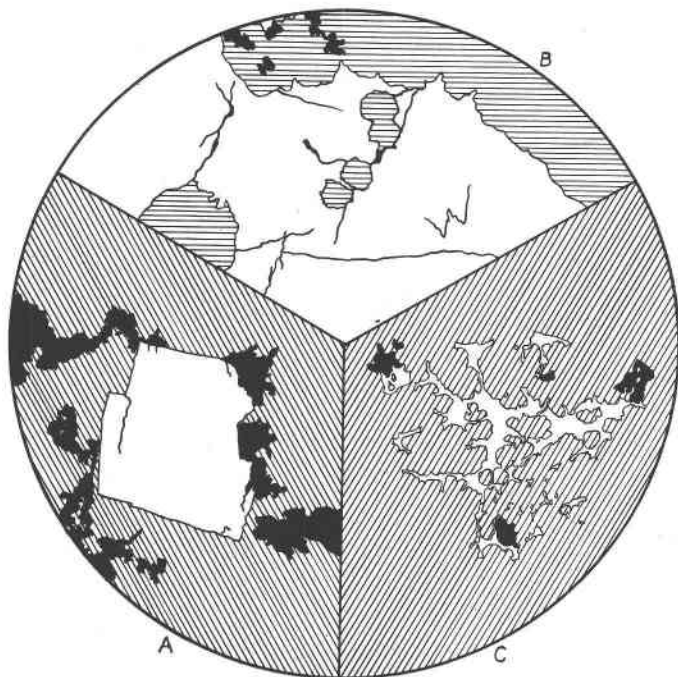


FIG. 1. Sketches traced from photomicrographs of polished surfaces showing the relations of pyrite (unruled), sphalerite (ruled) and carbonate and silica (black). A. Pyrite replacing sphalerite. B, C, Sphalerite replacing pyrite, leaving in "C" only the skeleton of a former grain. Magnification 40X.

Another relationship between sphalerite and pyrite, an unusual one, is found in the fine-grained chert-like sphalerite (figures 1B, 1C). Here pyrite crystals show numerous included circular areas of sphalerite and equally abundant concave-inward protuberances of sphalerite into the pyrite. In places the sphalerite has so nearly eliminated the pyrite that the remnant of the latter closely resembles, in plan, the connected aretes of mountain cirques.

Furthermore, between crossed nicols the circular areas of sphalerite within the pyrite, near their borders, have a more grayish color than the remaining part. This grayish zone fades gradually in passing toward the center of each patch, and commonly has a rude radiating appearance from the less affected center to the more grayish outer zone which is in contact with pyrite.

These relationships are interpreted as evidence of the encroachment and replacement of pyrite by sphalerite. The grayish zone bordering the circular sphalerite areas may well indicate the area of sphalerite still containing some dissolved iron sulphide either in solid solution or as submicroscopic disseminated inclusions.

This relationship may be similar to that described by N. W. Buerger⁹ between sphalerite and chalcopyrite where the latter is thought to have been dissolved in the former. In any event, this grayish zone differs from the central part. Since the sphalerite areas are undeformed and the surrounding pyrite is undisturbed, structural differences are eliminated and a compositional difference is favored.

Marcasite has been reported as occurring at Friedensville but to the writer's knowledge marcasite has never been definitely determined by *x*-ray analysis, polished surface examination or chemical analysis. Two specimens of iron sulphide were submitted to Dr. H. V. Anderson for *x*-ray examination. One of them had a crude radiating structure and was associated with similar material showing marked decomposition. This material was thought to be more likely marcasite than pyrite and in the past has been so named. The second specimen was part of a typical cube of pyrite. Both were found to be pyrite.

MICROSCOPIC EVIDENCE OF CONDITIONS OF PRIMARY REPLACEMENT

Fibrous and mosaic quartz in some specimens replaces the limestone, and in other places fibrous quartz is the vein material cutting both sphalerite and pyrite, and in still other cases fibrous and mosaic quartz is replaced by pyrite and (or) sphalerite.

Much of the sphalerite replacing limestone is present in irregular masses but in places subhedral grains showing zonal growth are observed (figure 2). These have small arm-like projections reaching

⁹ Buerger, N. W., The unmixing of chalcopyrite from sphalerite: *Am. Mineral.*, vol. 19, no. 11, pp. 525-530, 1934.

into the limestone from the solid sphalerite. These projections may join and form an irregular network around the solid limestone core. They are the evidences that the zinc sulphide solutions failed before the inter-arm areas could be completely replaced. The zoning is probably due to unequal distribution of inclusions some of which were very likely derived from the replaced limestone.

The grains of the limestone are normally clouded by numerous inclusions of carbonaceous matter, clay minerals and sericite. Where cut by veinlets of quartz, the carbonate adjacent to the introduced material has recrystallized and has eliminated the inclusions (figure 3).

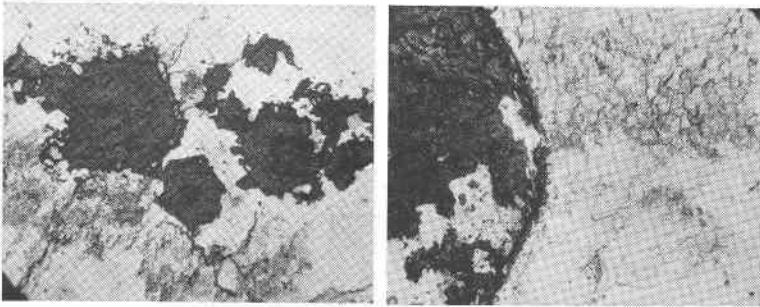


FIG. 2. Zoned crystals of sphalerite metasomatically replacing a fine grained limestone containing areas of mosaic quartz. Note the lace-like margins and the projecting nodes showing the incomplete development of the crystals. Magnification 120 \times .

FIG. 3. Silica solutions have entered the lower right part of the field depositing quartz and recrystallizing the limestone. Sphalerite has later replaced both quartz and carbonate. Magnification 120 \times .

Such inter-relationships together with those indicating no absolute priority of deposition of sphalerite or pyrite might indicate the ore forming solutions were silica-bearing and at the same time carried iron and zinc sulphides. An alternative explanation would be the postulation of a changing composition of the invading solutions. Radical changes in the composition of invading solutions may not be easily accepted but one might well imagine the earliest liquid to be more siliceous and therefore depositing silica dominantly, while later sphalerite might be the active replacing material from a solution richer in zinc sulphide than the first. The importance of solutions of changing composition as a cause of banding in veins is questioned by B. M. Shaub.¹⁰

In the case under discussion, however, the writer is inclined to think a change in the composition of the invading solutions most easily explains the replacement of limestone in one place by silica and in an adjacent area by sphalerite. Also, sphalerite is found in some instances to encroach, by replacement, upon both the limestone and quartz which itself had previously replaced limestone.

It is interesting to note that often a cleaner, purer zone of carbonate lies immediately in front of the encroaching sphalerite (figure 4). In other places a much darker narrow zone (figure 5) of material lies adjacent to the sphalerite. In the former case the structure of the original limestone and the cleaner zone is the

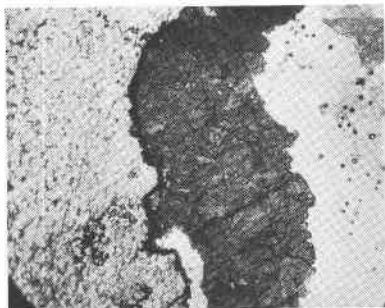
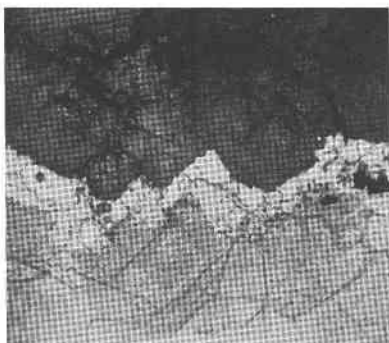


FIG. 4. Sphalerite replacing limestone. A cleaner zone has been formed just ahead of the sphalerite by the removal of soluble inclusions or the filling of openings in the carbonate. Magnification 160 \times .

FIG. 5. Sphalerite deposited in the space from which limestone has been dissolved. The dark band between sphalerite and limestone made up of the accumulated carbonaceous inclusions from the latter indicates that here metasomatic replacement was absent. Recrystallized calcite forms the material to the right. Magnification 120 \times .

same. Some larger grains may even be partly clear and partly clouded, and extend from the original into the altered rock. This cleaner zone is thought to have been formed by the diffusion of solutions through the carbonate which removed soluble inclusions or filled openings, either or both of which may have caused the darker color. This zone is not dominantly due to recrystallization because then one would expect it to have a structural break with the original mass.

¹⁰ Shaub, B. M., The cause of banding in fissure veins: *Am. Mineral.*, vol. 19, pp. 393-402, 1934.

The dark band adjacent to the sphalerite in some of the specimens is formed by the accumulated inclusions removed from the limestone. Some of this material is incorporated within the zinc sulphide but much of it is pushed ahead of the mass. We must infer from this that in these places there was hindered circulation, or else that materials were introduced and removed by diffusion and hence discrete particles could not be carried. Their concentration in an advanced zone however necessitates the suggestion of the presence of a small amount of liquid ahead of the sphalerite, otherwise all inclusions from the limestone would be contained in the sulphide.

CONCLUSIONS REGARDING CONDITIONS OF PRIMARY REPLACEMENT

We may conclude that silica solutions, later richer in sulphides, invaded the limestone. Quartz first intimately replaced the limestone and was deposited in veinlets; later, sphalerite replaced the carbonate and in places quartz. This was accomplished through two processes: first, by metasomatic replacement evidenced by small sphalerite arms or veinlets penetrating carbonate grains, and second by simple solution and deposition. By this is meant the dissolving of a discrete part of the limestone and the subsequent deposition of sphalerite from solution. This latter process is thought to have resulted in the concentration of the dark band of inclusions discussed above. These inclusions were carried along by the solution which on one side of the inclusion band dissolved carbonate and on the other side deposited sphalerite.

Much of the primary sphalerite is found as vein and cavity fillings where replacement was at a minimum.

SECONDARY MINERALS. The most abundant secondary ore mineral is calamine, although smithsonite and sphalerite are also present. Associated minerals in the oxidized ore are limonite, greenockite, quartz, calcite, dolomite, melanterite, and probably goslarite.

Calamine characteristically occurs in porous masses built up of successive irregular spongy encrustations of calamine chiefly but also containing some smithsonite and secondary sphalerite.

Above the water-table in places sphalerite has been protected by a layer of quartz which in turn has been coated by calamine. In thin-section a contact zone of calamine and quartz showed the

following relations (figure 6). An euhedral crystal of quartz containing numerous smaller dust-like inclusions (probably chiefly carbonaceous matter from the limestone) exhibits an outer zone about .15 mm. thick in which mineral inclusions of calamine and carbonate grains from eight to ten microns in diameter are distributed. The interior limit of these is sharply defined and is a line parallel to the trace of the face of the crystal in which they are found. Calamine deposited on the quartz crystal has in places penetrated and replaced the silica to a depth of .03 mm. to .08 mm.

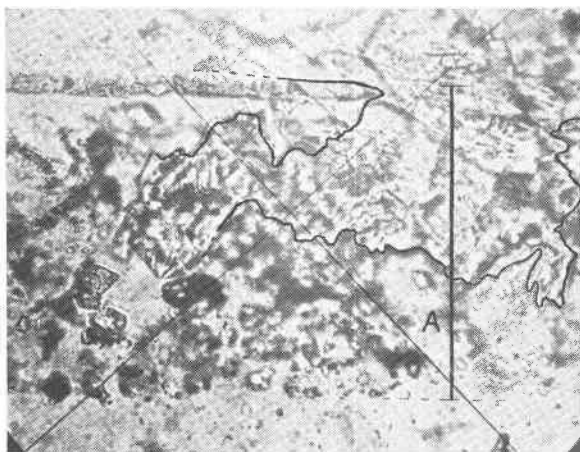


FIG. 6. Calamine replacing quartz. The quartz crystal shows an outer zone (A) of numerous inclusions which extends below the depth of calamine replacement and indicates the incorporation of the inclusions during the growth of the crystal. Magnification 215X.

We may infer from the above that the solutions depositing silica at first contained in suspension dust-like particles of other materials, while later larger fragments of calamine and calcite probably loosened by some minor movement were included in the silica as it was deposited. Following the deposition of quartz, zinc-bearing solutions entering the channels caused the partial replacement of quartz by calamine and elsewhere deposited a coating of the latter mineral.

Calamine in thin-section possesses strong relief in contact with quartz and balsam. It occurs in radiating and sheaf-like aggregates and as granular masses. Single larger crystals sometimes show a

great number of yellow to red-brown granules as inclusions. These are thought to be greenockite but may be in part iron oxide.

Smithsonite is found intimately mixed with calamine in the highly porous vein and solution cavity fillings. It also forms drusy surfaces on the walls of joints or other openings and with other oxidized ores replaces limestone. It is less abundant than calamine.

Sphalerite in the oxidized ore is found with calamine and smithsonite on drusy surfaces, in porous masses encrusting surfaces and filling cavities and as a replacement of limestone. In thin-section, as stated above, it is brown to yellow or in some cases grayish in color but is distinctly lighter than the dark gray to black zinc sulphide of the primary ore. As has been discussed, it is thought that this lighter color is due as much to the greater freedom from fractures and inclusions as to the lower iron content.

Greenockite is found as a yellow dusty deposit on the surface of fractures or as aggregates of minute grains deposited along sheer planes in the limestone. It is thought to be one of the minerals appearing as inclusions in sphalerite and calamine.

Under the microscope the fine-grained, dusty greenockite is yellow to red-brown in color and has very strong relief. Individual granules are rarely more than a few microns in diameter and only the larger ones show double refraction. Aggregates of several hundreds of these granules are nearly opaque to transmitted light and except for their higher index of refraction closely resemble aggregates of limonite granules.

Melanterite occurs as a bluish-green to white earthy coating associated with weathered pyrite. Under the microscope it appears as fibrous and granular masses which are colorless and have a low index of refraction and weak birefringence.

Goslarite has been reported in the oxidized ore. A white deposit found on a smithsonite surface and thought to be goslarite is not readily identified. Further work will be done on this material.