

DEPARTMENT OF THE INTERIOR

FRANKLIN K. LANE, Secretary

UNITED STATES GEOLOGICAL SURVEY

GEORGE OTIS SMITH, Director

BULLETIN 690—A

ZINC CARBONATE AND RELATED
COPPER CARBONATE ORES
AT OPHIR, UTAH

BY

G. F. LOUGHLIN



Contributions to economic geology, 1918, Part I

(Pages 1-14)

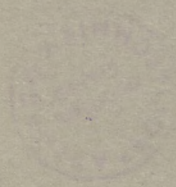
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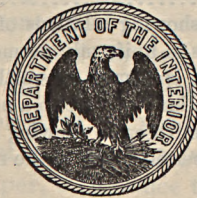
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UNITED STATES GEOLOGICAL SURVEY
GEORGE F. SMITH

CONTENTS.

	Page.
Introduction.....	1
Metal content.....	1
Occurrence.....	2
Mineralogy.....	2
Zinc minerals.....	3
Smithsonite.....	3
Ferruginous variety.....	3
Drusy variety.....	6
Hydrozincite.....	6
Minor zinc minerals.....	6
Copper minerals.....	7
Malachite.....	7
Azurite.....	8
Aurichalcite.....	8
Other copper minerals.....	8
Associated minerals.....	9
Deposition of copper carbonates.....	9
Summary of deposition processes.....	12
Economic considerations.....	13

ILLUSTRATIONS.

	Page.
FIGURE 1. Sketch showing relation of lamellae of smithsonite to open part of a fracture.....	3
2. Diagrammatic sketch showing relations of curved lamellae to two intersecting fractures in uniformly permeable limestone.....	4
3. Simplified sketch of a specimen of smithsonite showing extreme complication of lamellar structure in a network of fractures.....	5
4. Sketch of a piece of smithsonite showing irregularities in lamellae due to variation in permeability of the replaced limestone.....	6

NOTE.—The Survey's annual volumes entitled "Contributions to economic geology" are issued in parts, and the last part will include a volume title-page, table of contents, and index for the use of those who may wish to bind the separate parts. A small edition of the bound volume will also be issued, but copies can not be supplied to those who have received all the parts.



ZINC CARBONATE AND RELATED COPPER CARBONATE ORES AT OPHIR, UTAH.

By G. F. LOUGHLIN.

INTRODUCTION.

Although the Ophir mining district, Utah, has long been an important source of lead carbonate and of lead and zinc sulphide ores, zinc carbonate ore was not shipped from it until 1913. On July 23, 1914, the writer visited the two mines, the Cliff and Hidden Treasure, that were shipping zinc carbonate ore. The output of this ore from each mine was small, but the deposits presented some very interesting features, the principal of which were the marked lamellar structure of the zinc carbonate in contrast to that in other deposits studied by the writer,¹ the prevailing absence of calamine, and the intimate association of the zinc carbonate with copper carbonates. The present paper is devoted mainly to these features and is offered as a further contribution to the literature on the genesis of oxidized zinc ores.

METAL CONTENT.

As oxidized zinc ore has been shipped from only two mines no figures showing the quantity and value are presented here, as this might disclose individual returns given in confidence. It is probable that these ores yielded only a minor fraction of the total quantity of zinc from the district during 1913 and later years.

Some idea of the metal content of the ore from the Hidden Treasure mine may be obtained from the following data on carload shipments, supplied by Mr. Keith, of the Empire Zinc Co., through C. W. Henderson, United States Geological Survey: 36.09 per cent zinc and 2.3 per cent lead; 40.2 per cent zinc and 1.5 per cent lead; 35.84 per cent zinc, about 1 per cent copper, 0.75 ounce to the ton of silver, and no lead or gold. The ore, as a rule, is said to contain no gold, 1 ounce to the ton of silver, and 1 per cent each of lead and copper. In view of the relation of copper to zinc described on page 10, the low content of copper is noteworthy and indicates careful sorting of the ore. No

¹ Loughlin, G. F., The oxidized zinc ores of the Tintic district, Utah: *Econ. Geology*, vol. 9, pp. 1-19, 1914; The oxidized zinc ores of Leadville, Colo.: U. S. Geol. Survey Bull. — (in preparation).

determinations of copper, lead, silver, or gold were made on the oxidized zinc ore from the Cliff mine. At the time of visit, in 1914, ore containing less than 35 per cent zinc could not be shipped at a profit.

OCURRENCE.

Both of the deposits studied lie at shallow depth and close by the summit of the ridge and are typically associated with lead deposits. The wall rock is rather coarse grained bluish-gray limestone, probably of Mississippian age, cut by numerous vertical veinlets of calcite, 1 to 3 inches thick, which are genetically associated with the original sulphide ore of the district. The lead ore bodies are in part pipe-like form along fissures and in part deposits formed by replacement along the bedding. They consist of galena, partly oxidized to cerussite and minor oxidation minerals. Their lower parts are incased by shoots of oxidized zinc and copper ore. As in other lead-zinc districts, the material in some of these shoots was formerly regarded as waste and used to fill up old lead stopes, but in 1913 and 1914 its value was recognized, and it was sorted into zinc and copper ores and shipped along with newly broken ore obtained around recently mined lead stopes. The zinc and copper carbonate minerals in these ores as seen in ore piles were intimately associated, and the two kinds of ore graded into each other. The writer was informed that occasionally pieces of ore were broken in two and one part thrown on the pile of copper ore and the other on that of zinc ore.

Observations made underground and at the ore piles indicated that the zinc carbonate ore was deposited by replacement of limestone prior to the deposition of the copper carbonates and was later in part replaced by the copper carbonates. Mr. D. W. Lynch, lessee at the Hidden Treasure mine in 1914, stated that zinc and copper ores in a part of the mine which the writer could not visit lay along the foot-wall of an old bedded lead stope; that copper carbonates lay nearest to the lead stope and graded downward, both along and normal to the dip of the wall rock, into zinc carbonate. These statements accord with evidence gained by paragenetic study of material in the ore piles.

MINERALOGY.

The principal ore minerals present are ferruginous smithsonite, aurichalcite, malachite, and azurite. Calamine, hydrozincite (?), and a zinc-bearing clay have been noted in very small quantity on a few specimens. A little cuprite was seen in the copper ore but not in association with zinc minerals, and one specimen showed remnants of chalcopyrite. The principal minerals associated with the ore are limonite and psilomelane or wad. Calcite and quartz are present in small quantity.

ZINC MINERALS.

SMITHSONITE.

The smithsonite (zinc carbonate) is principally the ferruginous variety, deposited by replacement of limestone. Some cavities in it are lined with druses of purer smithsonite.

FERRUGINOUS VARIETY.

The ferruginous smithsonite is medium to dark gray where free from oxidation but is mostly stained from light to dark brown by hydrous oxides of iron and manganese. It is very fine to microgranular, and nearly all of it has a marked lamellar structure. The lamellae are from 1 to 7 or 8 millimeters thick and are separated by thinner spaces, lined with films or well-developed druses of copper, zinc, iron and manganese minerals, and, in a few places, calcite. The lamellae range in shape from nearly perfect planes to intricately contorted forms that are closely related in position to fractures preserved from the original limestone.

This relation indicates that the zinc solution, after invading the limestone along the fractures, was diffused laterally and produced a rhythmic replacement of the limestone. Where a single fracture was of uniform width and the limestone of uniform permeability replacement formed lamellae with little or no curvature. Where a fracture contained a relatively open part between tight or sealed portions the solution spread like a fan into the rock and the replacement lamellae assumed concentric positions concave toward the open part of the fissure, as shown in figure 1. Where the solution spread from two intersecting fractures and the adjacent rock was of uniform permeability the lamellae became locally convex to the junction line of the fractures and curved in either direction to positions parallel to each fracture, as shown in figure 2. Where a network of fractures was present the shapes of the lamellae were correspondingly complicated (fig. 3), and any variations in permeability produced still further complications (fig. 4).

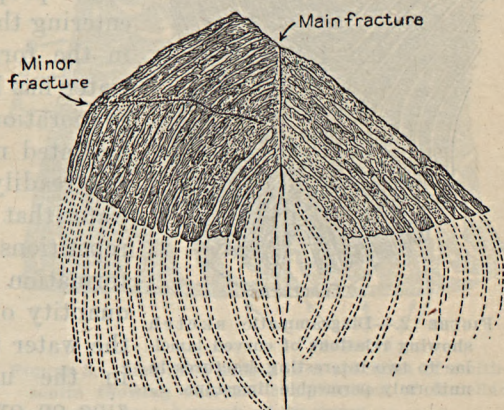


FIGURE 1.—Sketch showing relation of lamellae of smithsonite to open part of a fracture. Solution spreading in fan shape from the opening produced concentric lamellae concave to the opening. Part inclosed in solid lines sketched from a specimen.

This prominent lamination is a feature that distinguishes the smithsonite at Ophir from the bulk of that in the Tintic district, Utah, and at Leadville, Colo., which is massive or contains only cavities due to leaching. The difference is believed to be explainable by the influence of geologic conditions on the chemistry of deposition.

In the Tintic and Leadville districts the waters that deposited the zinc as carbonate in limestone first descended through a considerable thickness of rhyolitic rocks and became charged with material leached from them, notably alkali carbonates or bicarbonates and silica, together with other compounds of no importance in the present discussion. Carbon dioxide forms a small proportion of the rain water entering the earth, but it is held there in the form of carbonates after the water has become exhausted either by evaporation or by the formation of hydrated minerals. These carbonates are readily soluble in the next rain water that reaches them, and by many repetitions of this process in a thick formation of porphyry a considerable quantity of carbonate accumulated in the water that reached the ore bodies in the underlying limestone. The zinc on oxidation from sulphide was

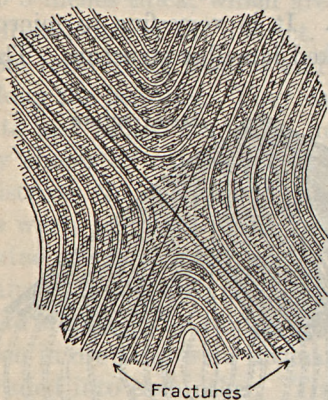


FIGURE 2.—Diagrammatic sketch showing relations of curved lamellae to two interesting fractures in uniformly permeable limestone.

carried in solution largely as sulphate and also as bicarbonate, the latter due to reaction with alkaline bicarbonates or with any excess of carbon dioxide present in the solution. The extent to which such reaction took place depended upon the relative concentrations of the different constituents, but the effect was to form the least soluble compound. Were such a solution to become supersaturated or to lose excess carbon dioxide, zinc carbonate, the least soluble mineral that could be formed from the solution, would crystallize.

When a zinc sulphate solution attacks limestone, the limestone goes into solution as sulphate and is replaced by a molecularly equivalent quantity of zinc as carbonate. The formation of a deposit by this simple molecular interchange would involve a shrinkage of 37 per cent; but with a sulphate-bicarbonate solution of zinc this loss of volume could be in part or wholly compensated by deposition of the zinc that was already available as carbonate, and the zinc carbonate actually formed could thus replace the limestone volume for volume instead of molecule for molecule.

In the Ophir district there is no evidence to suggest that volcanic rocks or sedimentary rocks of similar chemical composition ever over-

lay the limestones which now form the crest of the ridge. Furthermore the ore bodies lie close to the crest of the ridge, where there has been a minimum amount of erosion, and water from the surface would therefore not take noteworthy quantities of alkalis and silica into solution. Any carbon dioxide present would aid in the conversion of limestone into soluble bicarbonate. This solution, after converting the zinc blende in the sulphide ore body to sulphate and passing downward into limestone, would cause reaction between zinc sulphate and calcium carbonate, with the resultant replacement of limestone by smithsonite—a replacement molecule for molecule. Additional zinc carbonate could be deposited from a combination of zinc with carbon dioxide already in solution, but the quantity available from this reaction was not sufficient to approximate a replacement volume for volume.

The shrinkage due to the molecular replacement is expressed, approximately at least, by the quantity of voids in the lamellar smithsonite. The occurrence of a lamellar rather than

any other arrangement may be attributed to a rhythmic process of deposition, analogous to that forming the Liesegang rings.¹ After deposition of the first lamella the solution permeated onward and attacked the area represented by the second lamella and the intervening space. Replacement followed, the intervening space representing the amount of resulting shrinkage. Continued permeation of the rock alternated with successive stages of replacement, until the supply of available zinc was exhausted.

It may also be suggested that the position of the ground-water level, general or perched, is a factor in determining whether replacement goes on volume for volume or molecule for molecule. If limestone is replaced by smithsonite in the relatively stagnant water at or a little below ground-water level, as it evidently was at Leadville, the entire quantity of rock to be replaced may become saturated with solution before the slow process of replacement has progressed ap-

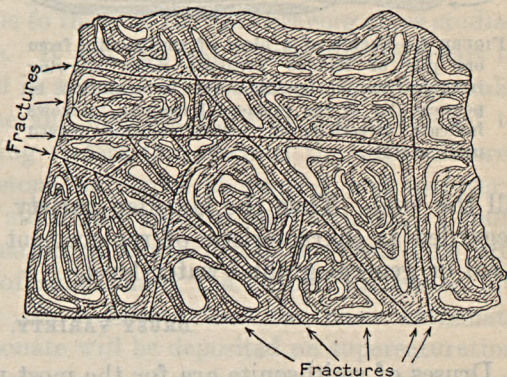


FIGURE 3.—Simplified sketch of a specimen of smithsonite showing extreme complication of lamellar structure in a network of fractures.

¹ Liesegang, R. E., *Geologische Diffusionen*, p. 180, 1913. Review by A. Knopf in *Econ. Geology*, vol. 8, p. 803, 1913.

preciably, and the rock may be replaced volume for volume if enough zinc is available and enough carbon dioxide in solution is present to supplement that derived from the replaced limestone. If a locally impervious stratum impounds water above the general ground-water level, as occurred in the Tintic district, the opportunity for replacement volume for volume is likewise favorable. Away from either of

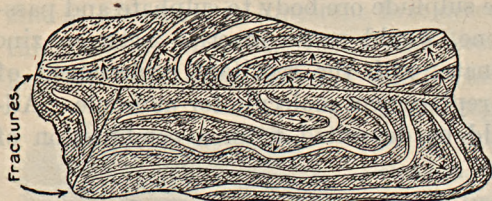


FIGURE 4.—Sketch of a piece of smithsonite from ore pile of Hidden Treasure mine, showing irregularities in lamellae due to variation in permeability of the replaced limestone. Arrows indicate directions in which solution moved most rapidly.

these levels, where the solution is moving in successive installments, the supply at any one time is less and may become exhausted before it permeates any considerable distance from the main course of travel or has opportunity to deposit enough additional zinc carbonate to fill the void. Thus the lamellar variety of zinc carbonate may be regarded as characteristic of replacement along watercourses above local or general ground-water level.

DRUSY VARIETY.

Druses of smithsonite are for the most part very inconspicuous in this district. The most prominent noted were not over 1 millimeter thick and ranged from pale brown to light gray and pale green. All the druses noted are separated from the ferruginous smithsonite by films of limonite, a relation suggesting derivation through decomposition from the ferruginous variety. The drusy smithsonite was deposited before any of the copper carbonates. These relations are the same as those noted in the Tintic and Leadville districts.

HYDROZINCITE.

The only material resembling hydrozincite noted was a few white streaks along or across lamellae of smithsonite. None could be separated with sufficient purity for identification. The relations of this material to the smithsonite are apparently the same as those of the malachite described on page 9. Although it has been found close by malachite, its relation to that and the other copper carbonates is uncertain.

MINOR ZINC MINERALS.

The scarcity of calamine is a characteristic feature of the Ophir deposits; it was noted only in a few small white patches along cavities in smithsonite. These patches consisted of microscopic crystals

that could not be separated cleanly from smithsonite. No typical flat prismatic crystals of calamine were found. Small quantities of gelatinous silica obtained by dissolving material composed principally of earthy hydrous oxides of iron and manganese suggest the presence of a little calamine in these decomposition products of smithsonite. The meager evidence at hand indicates that some calamine formed on smithsonite before oxidation of the smithsonite, and that some formed after or as a result of oxidation. No calamine of later origin than any of the copper carbonates was noted.

A few films of gray to pale-brown clay were found coating cavities in smithsonite. This clay has an index of refraction of about 1.58 and is decomposed by hydrochloric acid, with the separation of silica—properties analogous to those of the zinc-bearing clays studied by the writer at Leadville. It was the last of the zinc minerals to form but was not identified in specimens containing copper minerals.

The scarcity of calamine and zinc-bearing clay are attributed to the fact that the descending waters that formed the oxidized ores passed only through limestone, as shown on page 4, and had very little opportunity to take silica and alumina into solution. Conditions controlling the formation of hydrozincite, the basic zinc carbonate, by the alteration of smithsonite, the normal carbonate, are only vaguely understood. It is known that the basic carbonate instead of the normal carbonate will be deposited on supersaturation from solutions containing no excess of carbon dioxide, and it may be assumed that such solutions can take carbonic acid from smithsonite, replacing it with an equivalent quantity of hydroxyl, and form the basic carbonate—hydrozincite. The question why hydrozincite and malachite form close by each other and also close by aurichalcite, whose chemical formula is equivalent to the sum of the formulas of these two minerals, will be considered after the copper carbonate minerals have been described.

COPPER MINERALS.

MALACHITE.

Malachite, the green basic carbonate of copper, has two modes of occurrence in association with the zinc carbonate ores at Ophir—as a deposit formed by the replacement of lamellar smithsonite and as druses lining cavities in smithsonite.

The degree of replacement varies, there being all gradations from smithsonite containing a few scattered green spots or streaks to practically pure malachite in which only the lamellar structure of the former smithsonite is preserved. Thin sections of the spotted or streaked facies show the malachite to consist of typical radiating

groups of needles penetrating and completely replacing grains of smithsonite and a few inclosed grains of calcite. The variety in which replacement is complete is seen with a lens or in thin section to consist of minute radiating groups of malachite needles, each group showing in the center a few specks of ferric oxide or highly birefracting granules that may be remnants of smithsonite. Each group has a polygonal outline, whose straight sides are due to interference in growth with adjacent groups. The microscopic texture as a whole resembles that of the coral *Goniatites*.

The drusy variety lines cavities both in the replacement variety of malachite just described and in smithsonite that shows no replacement by copper minerals. In the latter occurrence it has formed both before and after partial decomposition of smithsonite. In a few specimens it is coated by azurite, but more commonly it coats azurite. In one specimen a small druse of malachite was found on aurichalcite.

AZURITE.

Azurite, the blue carbonate of copper, also both replaces smithsonite and occurs, much more abundantly, as drusy growths. Replacement of typical smithsonite by azurite has been noted only in a few small spots, most of which are close by or directly connected with druses of azurite. The druses of azurite reach 2 millimeters or more in thickness and are typical in appearance. They were formed later than the replacement malachite and at the same time as the replacement azurite. Where azurite is associated with other drusy copper carbonates it was generally the first deposited, and only one specimen was found in which it was preceded by malachite.

AURICALCITE.

Aurichalcite, the double basic carbonate of copper and zinc, is probably the most widely distributed of the copper minerals in the zinc carbonate ores at Ophir. It ranges from typical soft druses and tufts of light bluish-green crystals to thin films of pearly white color. It occurs almost exclusively as a lining to cavities. The only exception noted was a small spot where aurichalcite appeared to replace ferruginous smithsonite. In all the specimens studied it was deposited after both malachite and azurite, with the one exception noted above, and the only mineral of persistently later origin was the zinc-bearing clay.

OTHER COPPER MINERALS.

The only other copper minerals noted were chalcopyrite and cuprite. The chalcopyrite was found as scattered grains in a carbonate gangue—presumably limestone originally but now replaced in part

by smithsonite. The cuprite was not found in contact with zinc carbonate ore, but a few small patches of it were closely associated with azurite and malachite in copper ore mined close by the zinc ore in the Hidden Treasure mine. These copper minerals were in a gangue of rusted replacement quartz.

ASSOCIATED MINERALS.

The minerals associated with the ore include limonite, psilomelane, calcite, and quartz. The limonite and much of the psilomelane occur as brown and black stains on weathered smithsonite and for the most part appear to be residues of leached smithsonite. The psilomelane, however, has in a few places distinctly replaced laminae of smithsonite. Whether residual or due to replacement, both minerals appear to have been formed in part prior to the deposition of the copper carbonates. Later oxidation processes have of course been continually increasing the amount of both minerals.

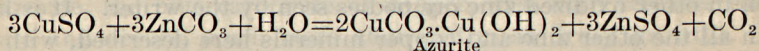
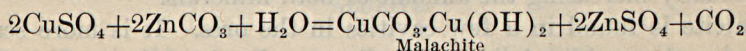
Calcite is found in a few cavities in the ores. It is more scarce than in other oxidized zinc ore bodies seen by the writer. It is later than all the other zinc and copper minerals here described, with the possible exception of the zinc-bearing clay, none of which was found in contact with calcite.

Quartz is mainly present as the unreplaced portion of siliceous limestone. A few cavities containing well-developed crystals were noted in the ore piles, but these also were older than the carbonate ores. The microscope revealed a very small amount of opal and chalcedony deposited later than the smithsonite.

DEPOSITION OF COPPER CARBONATES.

It has been generally recognized that in the oxidation of mixed sulphide deposits zinc blende is completely oxidized and removed before chalcopyrite, pyrite, and galena have become very much affected. The resulting smithsonite bodies should therefore be expected to have formed before bodies of copper carbonates and of residual lead carbonate and limonite. As copper sulphate, derived directly by the oxidation of chalcopyrite, is, like zinc sulphate, readily soluble in water, it may also be removed by descending waters from the original ore body, and by reaction with carbonates or with carbon dioxide in solution it may be deposited as one of the copper carbonates. The problem presented by the Ophir deposits is to ascertain what conditions determined the deposition of a part of the two copper carbonates (malachite and azurite) by replacement of smithsonite and of the remainder by simple crystallization from a saturated solution.

The solution that contained copper sulphate on reaching the zinc carbonate ore replaced smithsonite with malachite or to a small extent with azurite, but the reaction involved was not a simple interchange of metals between sulphate and carbonate, as simple carbonate of copper is not known among natural minerals. Azurite and malachite are basic carbonates, the former containing two parts of cupric carbonate (CuCO_3) to one of cupric hydrate (CuO_2H_2) and the latter one part of the carbonate to one of the hydrate. Both minerals have a greater specific volume than smithsonite (ratio $\frac{4.3}{4.0}$ for malachite; $\frac{4.3}{3.8}$ for azurite), and a replacement volume for volume therefore necessitates the removal of a somewhat greater molecular quantity of smithsonite than the quantity of copper minerals deposited. Without allowance for this additional quantity of smithsonite, the reaction is similar to that given by Lindgren¹ for cupric sulphate and limestone:



Solution of the small additional quantity of smithsonite to make room for the copper minerals would be aided by the carbon dioxide (CO_2) set free by the reactions just cited, which would form the relatively soluble bicarbonate of zinc.

The conditions determining whether smithsonite is replaced by malachite or azurite have not been determined experimentally. It may be suggested (from the chemical formulas of the two minerals) that replacement by malachite was effected by sulphate waters that contained little or no carbon dioxide and therefore allowed the hydroxyl radicle (OH) to form a more conspicuous part of the mineral, and that replacement by azurite was effected by waters that contained a relatively large amount of carbon dioxide, which combined more readily with copper than the hydroxyl radicle.

According to this suggestion, if all the copper were deposited by replacement from waters low in carbon dioxide, malachite would be formed until the quantity of carbon dioxide set free by the reaction above cited became sufficient to cause the deposition of azurite. So far as the material studied is concerned, there is nothing to refute this suggestion, but the quantity of replacement azurite found is too small to lend it much support.

The order of deposition of the copper carbonates in openings, however, agrees well with the suggestion. Where malachite is the

¹ Lindgren, Waldemar, Mineral deposits, p. 791, 1913.

only conspicuous replacement mineral the earliest mineral deposited in adjacent openings is azurite, followed successively by malachite and aurichalcite. Azurite evidently was deposited until the ratio of carbon dioxide (made available by the replacement process) to water or hydroxyl diminished to a certain point, when malachite was deposited. Continued depletion of copper and carbon dioxide from solution finally established a ratio of copper to newly dissolved zinc and of carbon dioxide to water that caused the formation of the double basic carbonate, aurichalcite. It is possible that if changes of this kind progressed further the proportion of carbon dioxide would become too small for the continued formation of aurichalcite, and that the still more basic hydrozincite could be deposited in small quantity; but owing to the scarcity of hydrozincite and the failure to find it in contact with copper carbonates, there is no evidence to support this suggestion.

The order of deposition outlined in the preceding paragraph applies where all the minerals mentioned are represented and where the solution moved very slowly or was stagnant. Several variations are to be expected when it is realized that waters in the oxidized zone might have been moving at an appreciable rate of speed. The following examples illustrate the range of variation possible in the association of these minerals. (1) Water charged with carbon dioxide taken from the overlying limestone may move along open fractures and penetrate the smithsonite body only very slightly. On becoming supersaturated, it deposits first azurite, at some lower point malachite, and at a still lower point aurichalcite. (2) If the solution replaces no smithsonite it may not contain enough zinc to yield any noteworthy quantity of aurichalcite. The azurite or the malachite may later be covered by one of the other minerals if the composition or concentration of a later supply of water is correspondingly different. (3) The amount of copper and carbon dioxide in the attacking solution may be so small that replacement by malachite adds enough zinc to cause the deposition of aurichalcite without first passing through the azurite and malachite stages. The occurrence of aurichalcite at many places resting directly on malachite surfaces implies that the set of conditions last mentioned was of common occurrence at Ophir. Other exceptional associations could be appropriately attributed to further variations in the conditions controlling the composition and concentration of the copper-bearing waters and the extent to which they could permeate smithsonite bodies; but they do not conflict with the explanation offered to account for the paragenesis of the zinc and copper carbonates where all are present.

SUMMARY OF DEPOSITION PROCESSES.

The principal processes active in the deposition of the zinc and copper carbonate deposits at Ophir may be summarized as follows:

1. Ferruginous zinc blende was removed by oxidation from mixed sulphide ore bodies, and the resulting zinc sulphate solution migrated downward into the adjacent limestone, which became replaced by smithsonite.

2. The replacement was accompanied by a considerable shrinkage in volume, expressed by the open lamellar structure of the smithsonite.

3. The lamellar structure bears a direct relation to fractures or other openings along which the zinc solutions invaded the limestone. The lamellae tend to parallel these openings or to lie concave to the more open parts of fractures. Where the openings were far apart the lamellae present simple forms, but where there was a network of fractures and the permeability of the limestone was not uniform the forms of the lamellae are very complicated.

4. The expression of shrinkage in lamellae rather than in a honeycomb structure is attributed to a rhythmic order of replacement, similar to the process proposed by Liesegang to account for diffusion banding—a process referred to in the last few years by several investigators to account for banded structure in numerous ore bodies.

5. The contrast between the large amount of shrinkage that accompanied replacement at Ophir and the small amount that took place in other districts studied by the writer is attributed to difference in geologic conditions. In the other districts there is reason to believe that the waters that cause the replacement had already taken in considerable carbon dioxide before replacement of the limestone or related carbonate rock began, and that more zinc carbonate could therefore be deposited than would have resulted from simple reaction between zinc sulphate and carbonate rock; furthermore, that replacement took place near and even below the general or local ground-water level, where the rock could become thoroughly permeated with the zinc solution. At Ophir the opportunity for descending water to obtain carbon dioxide in considerable quantity before depositing zinc carbonate was relatively small, and there is no evidence that downward circulation of the water was impeded at the level of the smithsonite deposits. Such conditions permitted direct molecular reaction between zinc sulphate and limestone, but they were not favorable to replacement volume for volume.

6. A small amount of ferruginous smithsonite was changed under oxidizing conditions into limonite and drusy smithsonite low or lacking in iron. Psilomelane and associated drusy smithsonite had an analogous origin.

7. The scarcity of calamine and zinc-bearing clay at Ophir is attributed to the fact that no volcanic rock formerly overlay the limestone in the vicinity of the zinc carbonate deposits. It is believed that in districts where calamine is abundant the silica of the calamine was derived from the decomposition or alteration of igneous rocks (or other silicate rocks) above the ore horizons. The fact that in the Ophir district calamine is of later origin than both varieties of smithsonite shows that silica does not combine with zinc to form hydrous silicate until the carbon dioxide in solution has been reduced to a very small quantity.

8. Oxidation of chalcopyrite, or cupriferous pyrite, did not take place extensively until after the smithsonite bodies had been formed. The resulting copper sulphate solution migrated downward and doubtless replaced in part smithsonite and in part limestone. The replacement of limestone, which received no special study, was doubtless effected by reactions similar to those involved in the replacement of smithsonite, summarized in the next paragraph. Where replacement was complete copper carbonate ore was formed. This graded downward into smithsonite ore or limestone.

9. Whether smithsonite is replaced by malachite or azurite is thought to depend on the relative amount of carbon dioxide in the sulphate solution. If little is present, replacement by malachite occurs until the carbon dioxide resulting from this reaction is sufficient to cause the deposition of azurite. If much carbon dioxide is originally present in the attacking solution, the smithsonite is replaced at once by azurite, no malachite being formed. Malachite was the principal mineral that replaced smithsonite at Ophir.

10. Where the copper carbonate minerals were deposited in openings carbon dioxide was also the determining factor. Where it was relatively abundant azurite was deposited first, followed, when the supply decreased beyond a certain undetermined point, by malachite. If zinc was present, derived through the replacement of smithsonite, deposition of malachite would continue only until a certain copper-zinc ratio was reached, beyond which the double basic carbonate aurichalcite would be deposited. This ideal order, represented in several of the Ophir specimens, may vary according to variations in the solutions at different times and to other changes in the zone of oxidation.

ECONOMIC CONSIDERATIONS.

From the processes of deposition here described it is to be expected that bodies of lamellar zinc carbonate like those at Ophir will prove to be of high grade, owing to the complete removal of limestone, but of small dimensions and confined to the immediate vicinity of frac-

tures and open bedding planes. Such small bodies are not likely to lead to larger bodies of massive ore, unless they lie near to ground-water level, or to some impervious stratum or fault that impounded the waters containing the oxidized compounds of zinc.

In districts where mixed sulphide deposits in limestone contain both copper and zinc in considerable quantity the resulting carbonate ores of both metals are to be expected in the oxidized zone, the copper carbonate immediately below the position of the original sulphide body or its siliceous casing, and the zinc carbonate below the copper carbonate. The details of these relations, as well as the richness and size of the carbonate bodies, depend on such local factors as the purity and permeability of the limestone replaced and the relative openness of bedding planes and fractures, which must be determined for each deposit or group of deposits.



