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THE OXIDIZED ZINC ORES OF LEADVILLE COLORADO

BY

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CONTENTS.

Varieties of ore—Continued.

ILLUSTRATIONS.

THE OXIDIZED ZINC ORES OF LEADVILLE, COLORADO.

By G. F. LOUGHLIN.

INTRODUCTION.

Oxidized zinc ores were first exploited in the Leadville mining district, Colorado, after the Geological Survey's field study of the other ores had been completed. In the summer of 1913 the writer was detailed to study these ores and spent four weeks in the district during July and August. The present report was completed early in 1914 and transmitted to form a chapter in a monograph on the geology and ore deposits of the district, but owing to continued delay in the completion of the monograph it has been decided to publish this chapter in advance.

The mine operators and engineers in the district gave the writer all possible assistance in his work. Thanks are especially due to Messrs. Nicholson, MacDonald, and Dalrymple, of the Western Mining Co.; Messrs. Platt and Kleff, mine surveyors and lessees of the New Dome property; Messrs. Davis and Pendery, of the Yak Co.; Messrs. Argall and Aicher, of the Iron Silver Co.; the officers of the Ibex Co.; Mr. Warren F. Page, of the Luema Mining Co.; and Mr. John R. Curley, State inspector of mines. To the several other lessees, foremen, and miners who rendered assistance at different times the writer here expresses his hearty thanks. Thanks are also due to Mr. R. C. Wells, of the United States Geological Survey, for criticism of the discussion of chemical processes involved in the deposition of the oxidized zinc ores.

DISCOVERY.

After it was realized, in 1910, that large deposits of oxidized zinc ores were present in the Leadville district, considerable discussion arose over the fact that these ores had been so long overlooked both by the mining engineers and geologists who had made frequent visits to the mines and by the mine officers and assayers who had been working in the ore and handling samples of it for several years. It must be admitted that the ore had been exposed both on dumps and underground and all who have had an opportunity of finding it must share the blame of having overlooked it. Very few of those who have written on the subject realized that silicate and carbonate of zinc had been known to exist from the earliest days, when only a comparatively small part of the oxidized lead ores had been worked.

EARLY ACCOUNTS OF ZINC CARBONATE AND SILICATE.

The following paragraph was published as long ago as 1882:[1]

> Mr. Garrison (of St. Louis) makes the prediction that at an early date Colorado will be made tributary to the western spelter industry. Probably the first call will be made for carbonates, calcined before shipping. This class of zinc ores often so closely resembles limestone that the ordinary prospector would not detect its value. If we remember correctly, Prof. König, of Philadelphia, has found calamine, or carbonate ore, in the vicinity of Leadville. Should a closer search, which we trust will be made at an early date, reveal the presence of larger bodies of this ore, zinc mining might soon be added to the list of Colorado industries.

It was thus early known, therefore, that oxidized zinc ores occurred in the Leadville district, but zinc was then evidently of insufficient interest to stimulate prospecting for bodies of high-grade zinc ore.

In 1886 Emmons, in his famous monograph,[2] noted the occurrence of calamine at Leadville and mentioned zinc blende and calamine as accessory minerals. He evidently had considered the problem of the disposition of the zinc in the oxidized zone, as he shows in his description of the old Iron mine:

> In the body of the limestone, on the eighth level, not far from the north incline, a natural jointing plane forming one wall of the drift was observed to be coated with fine, silky white crystals which chemical examination proved to be calamine or silicate of zinc. If the sulphureted ores, which will undoubtedly be found when the mine workings shall have reached the limits of the zone of oxidization, are as rich in blende as those which have been found in the A. Y. mine, it seems singular that little or no zinc has hitherto been found associated with the oxidized ore. This occurrence would seem to show that, owing probably to greater solubility, the alteration products of blende have been removed during secondary deposition to a greater distance from their original location than those of the other sulphurets.

Again, he writes:

> Zinc occurs in the lead carbonate ores in very small proportion and probably in the form of silicate (calamine), since this is the only mineral of zinc that has been observed in the Leadville deposits. It is rarely visible and generally form fine, needle-like silky-white crystals, lining drusy cavities and cracks or joints in vein material and limestone. There is little doubt that it originally occurred as zinc blende, and, from analogy with the Tenmile deposits, it may be presumed that it formed a much larger proportion of the deposit than it does

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[1] Eng. and Min. Jour., vol. 34, p. 16, 1882.

[2] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, pp. 376, 389, 398, 547, 550, 556, 557, 560, 1886.

now. The much greater solubility of its sulphate than that of the other metals would account for its more thorough removal by surface waters.

He noted the absence of zinc in analyses of samples of basic ferric sulphate, a feature in accordance with the observation, quoted above, that the zinc had been further removed from the original ore bodies than the other metals, owing to the more ready solubility of its sulphate, and he states that in spite of the comparative absence of zinc this metal was "quite uniformly detected in the products of smelting."

The analyses of different vein materials show little or no zinc. A siliceous hematite from the Chrysolite mine, carrying 2.56 per cent of zinc oxide, was said to contain "a rather unusual percentage of zinc." As these vein materials were in large part similar in color and other visible features to the reddish-brown zinc ores now mined, the absence in all of them of any considerable amount of zinc may well have diverted Emmons's attention, both then and in later years, from such iron-stained bodies as possible oxidized zinc ores. Very little drifting or other work beneath the old lead stopes had been done at the time, and no ground with abundant pockets of calamine, such as characterize much of the oxidized zinc ore now mined, had been exposed. Even after some of the extensive zinc ore bodies had been exposed along drifts and other workings the strong resemblance of the reddish-brown ore to iron ore at one extreme and iron-stained limestone at the other and the close resemblance of the gray ore to partly leached but unstained limestone were hardly likely to lead one to suspect the presence of high-grade zinc ore. These ores are in general so different in color and texture from the more crystalline and brilliant specimens from other districts, so common in museums and other collections, that failure to recognize them without chemical examination is not surprising.

Emmons, however, did recognize the rather exceptional occurrences of small quantities of the dense white zinc ore that is identical in appearance with "Chinese talc," as shown by his discussion of the analyses. He regarded this material as a mixture of hydrated silicates of alumina and silicate of zinc and remarked that "the occurrence of the zinc was somewhat unexpected." In the extensive mining of oxidized zinc ores during the last few years, ore of this type has been found only in small quantities and of a grade too low for shipment except during a short time when the price of zinc was abnormally high. It is indeed striking that none of the many specimens of ores and vein matter taken during the extensive study of the ores in the earlier days proved to contain any considerable quantity of zinc carbonate.

In 1889, after a period of extensive development, during which many of the oxidized lead bodies had been followed down to the sulphide zone, Blow[1] called attention to the abundance of zinc blende just below the zone of oxidation and offered the conclusion that it was the result of downward sulphide enrichment. In his own words,

> The zinc sulphides are the most widely disseminated and show plainly the result of their more ready solubility than the other sulphides and the redeposition of a large portion of the zinc which has thus been removed from the carbonate ores. This fact is clearly shown in many ways, but most satisfactorily just at the line of transition. The sulphides first encountered are invariably heavy sulphides of zinc, carrying a little iron and very little lead. They have a close crystalline structure and lie in a laminated form, the lines of fracture being nearly vertical. Upon these cleavage planes crystals of cerusite are found, and often a small incrustation of native silver. Such deposits, where first encountered in passing from oxidized to unoxidized ores, are always lowest in silver. In their further extension the zinc gradually grows less and the laminated structure disappears. Beyond this, again, the zinc sulphides appear to predominate along cleavage and contact planes with the gray porphyry, or along the lines of minor faults and cracks in the limestone. Such characteristics are also universally observed in other instances besides those of Iron Hill. * * *
>
> In advancing further within the ore shoots the zinc appears to lose its preponderance over the other sulphides. * * * It seems probable that a large proportion of the zinc, which was totally removed from the carbonate ores, has beeen redeposited as a sulphide, and principally just below the line of complete oxidation, by surface waters, and such redeposition has advanced and increased pari passu with the limit and extent of such oxidizing action.
>
> As a corollary of the above, it is believed that at the present stage of development in Leadville, the sulphide of zinc forms a larger part of the unoxidized ores than will be found in future and deeper exploration.

This conclusion, in view of the fact that no zinc carbonate ore bodies had then been discovered or recognized, seemed very plausible from the evidence in hand. It was evidently adopted by Emmons and Irving,[2] who wrote in 1907:

> The hydrous zinc sulphate is presumably more soluble and less stable than the corresponding iron sulphate. In Leadville, like gypsum, which should have been formed by the reaction between iron sulphate and limestone, it is practically absent from the oxidized zone and must have been carried away in solution or redeposited as a sulphide below the zone of oxidation. It has, in fact, been observed that the sulphide ores are much richer in zinc blende immediately below the limit of oxidation than elsewhere.

This hypothesis of downward enrichment of zinc blende tended to delay the search and discovery of the zinc carbonate ores, as the possible existence of such ores must have been dismissed from the minds of the geologists and consequently from the minds of the operators.

The field evidence, however, on which this hypothesis was based may be interpreted in another way, as will be shown later; further-

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[1] Blow, A. A., The geology and ore deposits of Iron Hill, Leadville, Colo.: Am. Inst. Min. Eng. Trans., vol. 18, pp. 168–172, 1890.

[2] Emmons, S. F., and Irving, J. D., The Downtown district of Leadville, Colo.: U. S. Geol. Survey Bull. 320, pp. 32–33, 1907.

more, later developments have shown that rich bodies of zinc blende are not limited to the top of the sulphide zone; and finally, recent experimental evidence and field observations in other parts of the world have shown that such deposition of secondary zinc blende is very unlikely.

After the large shipments of ore in 1910 had attracted wide attention Emmons addressed a letter from Dinard, France, to the Leadville Herald-Democrat,[1] in which he said:

> At the time of my first study of the Leadville district, in 1880, I was much puzzled to know what had become of the zinc. * * * I assumed then that owing to the superior solubility of the zinc sulphate, the oxidation products of that metal had been carried much further than those of lead before being transformed into the now stable carbonate, and had possibly been entirely removed in the run-off.
>
> Blow's observation that on Iron Hill secondary zinc blende had accumulated in the upper part of the sulphide zone seemed to account for some of the missing zinc, and from accounts published by you, it is evident that much of it has accumulated as calamine in the zone of change from sulphide to oxide.
>
> Though I have particularly desired to study the zinc of Leadville, I have never been able to, because in 1880 mine workings had not yet reached it, and when I next visited the district (1890) they had gone beyond it, and owing to the soft nature of the ground in that zone the drifts leading to it were for the most part caved and inaccessible.
>
> It certainly seems rather strange that those in charge of mines, when this zone was exploited, did not notice such bodies of calamine as you describe, but it must be borne in mind that calamine is generally a white-brown earthy-looking material, which would not attract attention unless especially sought for, and that it was pay ore rather than material of only mineralogical interest that they were seeking, and at that time zinciferous ores were a particularly undesirable product.

Another reason, mentioned by several writers,[2] for the failure to recognize oxidized zinc ores is the fact that in the earlier days the presence of zinc in the lead-silver ores and also in the iron ores was a decided detriment, and miners in consequence avoided points where assays showed a considerable percentage of zinc. According to G. O. Argall and E. W. Keith, the presence of zinc was especially noticeable in shipments from the Carbonate Hill and Fryer Hill mines. The object of search in those days was lead-silver ore, and as there was then no market for zinc there was no incentive to look for it, even though some of the early operators may have recognized its character. Argall further states that it was after the gradual depletion of the sulphide ores and in consequence of the increasing expense of deep operations that exploitation turned again to the

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[1] This letter, dated Oct. 11, 1910, has been quoted by the Engineering and Mining Journal (Nov. 12, 1910, p. 954) and by H. E. Burton in Mines and Minerals (February, 1911, p. 436).

[2] Mining World, Dec. 17, 1910, p. 1147. Keith, E. W., Leadville Herald-Democrat, Sept. 20, 1910, p. 1. Argall, G. O., Oxidized zinc ores at Leadville: Eng. and Min. Jour., Aug. 26, 1911, p. 399.

upper levels in search of ore that might not have been profitably mined when first opened and thus led to the discovery of the character and value of the oxidized zinc deposits.

RECENT DISCOVERY OF OXIDIZED ZINC ORE BODIES.

Accounts of the recent discovery of oxidized zinc ores in extensive bodies at Leadville are not in accord.[1] Some state that the discovery was made through the curiosity of a Leadville assayer, who took the time and trouble to determine the contents of a sample of high specific gravity, which had been shown by assays to contain little or no lead, silver, or gold; others state that the character of the material was recognized by those who had discovered and worked oxidized zinc ores elsewhere in the State. According to J. B. McDonald,[2]

> the first silicate of zinc shipped from the State was from the old Madonna mine, at Monarch, Chaffee County, in 1902. * * * Several hundred tons of the ore were shipped. * * * The first carbonate of zinc ever shipped from the State came from the Monarch Pool mine, at Monarch, and the two highest-grade cars of carbonate of zinc ever shipped out of the State to this day came from this mine. One car ran 46.7 per cent and the other 47 per cent zinc.

The following year (1903) Mr. McDonald and Mr. Harry Paul procured a lease on the Eclipse mine at Monarch and shipped a mixed carbonate and silicate ore almost identical in character with that discovered in Leadville seven years later. Mr. McDonald states that in the spring of 1906 he found the first carbonate and silicate of zinc ever found in commercial quantities in the Leadville region. This was at the Hilltop mine, in the Horseshoe district, which adjoins the Leadville district on the divide between Lake and Park counties.

The first discovery of ore of this kind within the Leadville district in recent years was made in 1909 by W. E. Jones, a lessee in the Robert E. Lee mine, who found a large body of zinc carbonate. Shipments were made from this body and also from the Penrose dump but were of too low grade for treatment and failed to arouse much interest in oxidized zinc ores. In the following year (1910) the first high-grade zinc ore, reported as calamine, was discovered by H. E. Burton, H. K. White, and Alfred Thielen in a lease at the Hayden shaft of the May Queen mine. This property was the first to ship high-grade calamine ore. After this discovery S. D. Nicholson, manager of the Western Mining Co.'s properties, began a search for oxidized zinc ores in the old workings of the Wolftone and adjoining claims and discovered in them the largest bodies yet found

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[1] Leadville Herald-Democrat, Sept. 11, 1910, and Jan. 1, 1911; Eng. and Min. Jour., Nov. 12, 1910, p. 954, and Aug. 26, 1911, p. 399; Min. World, Dec. 17, 1910, p. 1147; Mines and Minerals, Feb. 11, 1911, p. 436; Min. Sci., July 27, 1911, p. 85.

[2] Personal interview with the writer. A similar account is given in Min. Sci., July 27, 1911, p. 85.

in the district. This discovery resulted in a general search for the ore throughout the district, with the result that smithsonite and calamine in varying amounts were found in a number of properties from Fryer Hill on the north to Weston Pass on the south.

PRODUCTION.

These discoveries were made at a time when there was an increasing demand for zinc, and although shipments of oxidized zinc ores began only at the end of 1910, they became very large in 1911, as shown in the table on page 14, offsetting a marked decline in the production of zinc sulphide ore and increasing the output of metallic zinc in Lake County by 15,243,011 pounds. This increase, in spite of a decrease of 7,996 tons in total shipments of zinc ores from the Leadville district, was due to the higher grade of the oxidized ores. At first only oxidized ores that averaged 30 per cent or more in zinc were shipped, but the increasing price, which culminated at 7 cents a pound late in 1912 and early in 1913, allowed profitable mining of ore containing as low as 17 per cent, and the production of oxidized zinc ores in 1912 greatly increased. Some ore containing as low as 15 per cent was shipped but at a loss. Most of the ore shipped, however, averaged about 30 per cent, and some contained as high as 40 per cent. The average for all shipments was 29.2 per cent.

Owing largely to this increase in price, which allowed several small producers of low-grade ore to ship at a profit, many enthusiastic estimates were made of the vast quantity of ore in reserve; but the rapid decline in price to about 5 cents a pound in the spring of 1913 forced most of the small producers to stop work, and the production for 1913 was less than that for 1912. During the writer's visit to the district in July and August, 1913, only a few properties besides those of the Western Mining Co. at Carbonate Hill were being worked. Ore containing as little as 24 per cent of zinc, however, could be shipped at a profit during the summer, and in October of that year it was stated that 22 per cent ore could be marketed.[1]

In January, 1914, new smelting rates made it possible to ship carbonate ore containing only 18 per cent of zinc. The average content of ore shipped during that year was 24.3 per cent, and in 1915 the average was 22.48 per cent. In spite of this opportunity to ship lower-grade ores, and in spite of the reported opening of a large body of zinc carbonate ore averaging 25 per cent zinc in the upper levels of the Wolftone mine in 1915,[2] the production of oxidized zinc ores, as shown in the accompanying table, continued to decrease during 1914 and 1915, the decline more than offsetting substantial

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[1] Eng. and Min. Jour., Oct. 18, 1913, p. 761.

[2] Mining Press, Mar. 20, 1915, p. 455.

increases in output of zinc sulphide ore. Owing to the extraordinarily high price of zinc in 1915, however, the total value of zinc from Lake County was more than 100 per cent greater than in 1914.

Depletion of the immense deposits in Carbonate Hill was evidently far from compensated during these years by discovery and development of oxidized zinc ore bodies elsewhere in the district. The production of both zinc carbonate and zinc sulphide ore in 1916, however, showed an encouraging increase, though the zinc content of the carbonate ore continued to decrease slightly.

The following figures[1] show the quantities of oxidized zinc ore produced in the Leadville district from the time of the first shipments in 1910 to the end of 1916 and the corresponding quantities of zinc sulphide shipments in the district, the total zinc for Lake County (most of which is from Leadville), and the total zinc for the whole State.

Zinc produced in the Leadville district, in Lake County, and in Colorado, 1909–1916.

Year.	Leadville.				Lake County.		Colorado.	
	Oxidized ores.		Sulphide ores.		Total zinc (pounds, in spelter and oxide).	Value.	Total zinc (pounds, in spelter and oxide).	Value.
	Quantity (short tons).	Per cent of zinc.	Quantity (short tons).	Per cent of zinc.				
1909							51,210,260	$2,765,354
1910	8,059	30+	163,218		56,367,445	$3,043,842	77,089,648	4,162,841
1911	83,905	31.1	79,376	23.3	71,610,456	4,081,796	94,607,456	5,392,625
1912	142,782	29.2	104,148	24	105,945,783	7,310,259	132,222,812	9,123,374
1913	135,760	27.45	97,704	23	93,842,857	5,255,200	119,346,429	6,683,400
1914	113,881	24.3	111,947	21.2	78,763,334	4,016,930	96,774,960	4,935,523
1915	82,592	22.48	136,555	22.09	72,493,170	8,989,154	104,594,994	12,969,779
1916	85,513	21.52	147,295	21.69	76,785,567	10,289,266	134,285,463	17,994,252

Most of the ore thus far mined has come from the immense body in Carbonate Hill, which extends through the claims controlled by the Western Mining Co. and a few adjoining claims. Smaller amounts have come from Fryer, Breece, Iron, Printer Boy, and Rock hills, showing that the oxidized zinc ores, like the oxidized lead ores, are distributed throughout the district. There is, however, a striking contrast between these two classes of ore, for although large bodies of oxidized lead ore have been mined in all of these hills, the correspondingly extensive bodies of high-grade oxidized zinc ore thus far discovered are limited to the northern part of Carbonate Hill.

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[1] Henderson, C. W., Gold, silver, copper, lead, and zinc in Colorado: U. S. Geol. Survey Mineral Resources, 1909 to 1916.

Mines producing oxidized zinc ores, 1910 to 1916.

	1910	1911	1912	1913	1914	1915	1916
Blind Tom	......	......	......	......	×	×	......
Bullion	......	......	×	......	......	......	......
Blonger	......	......	×	......	......	......	......
Chrysolite	......	×	×	......	......	......	×
Dolly B	......	......	......	×	×	×	......
Eliza	......	......	......	......	×	×	×
Elk	......	......	......	......	×	×	×
Fannie Rawlings	......	......	×	......	......	......	......
Gambetta	......	......	×	×	......	......	......
Highland Chief	......	......	×	×	×	×	......
Ibex (Little Johnnie)	......	×	×	×	×	×	......
La Plata (Rickard)	......	......	×	×	×	×	......
Lilian	......	×	×	×	×	×	×
Little Chief	......	×	×	×	×	×	×
Little Ellen	......	......	......	......	×	×	×
May Queen	×	×	×	......	×	×	......
Mikado	......	......	×	×	......	......	......
Minnie Lee	......	......	......	......	......	×	......
New Dome (Nisi Prius)	......	×	×	×	......	......	......
Penrose	......	......	......	......	......	......	×
Polaris	......	......	......	......	......	×	......
Pons	......	......	×	......	......	......	......
Rattling Jack	......	×	×	......	......	×	×
Robert E. Lee	......	......	......	×	×	×	×
St. Louis tunnel	......	......	......	......	×	×	......
Sardine and Seneca	......	......	×	×	......	......	......
Sierra Nevada	......	......	......	......	×	......	......
Smuggler	......	......	×	×	×	×	......
Star Consolidated	......	×	×	×	×	×	×
Tucson	......	×	?	......	......	......	......
U. S. Smelting, Refining & Mining Co	......	......	......	......	......	......	×
Western Mining Co.:							
Adams	......	?	×	×	......	......	......
Big Chief	......	×	×	×	×	×	×
Brookland	......	?	×	......	......	......	......
Castleview	......	×	×	×	×	×	×
Evalyn	......	......	......	......	×	×	......
Henrietta	......	×	×	×	......	......	......
Maid of Erin	......	×	×	×	×	×	×
Waterloo	......	?	×	×	......	......	......
Wolftone	......	×	×	×	×	×	×
Yak tunnel:							
White Cap	......	......	×	×	×	×	......

Among recent developments in the district wholly or partly induced by the mining of oxidized zinc ores are the establishment of a plant at Leadville for the treatment of low-grade oxidized zinc ores and the unwatering of the Downtown, Fryer Hill, and Carbonate Hill sections of the district. In the spring of 1914 the Western Zinc Mining & Reducing Co. began the erection of a zinc oxide plant to treat the oxidized ores.[1] This plant, which had a capacity of 50 tons a day and was designed to treat zinc carbonate ore containing 16 per cent or less of zinc, was put into operation in the fall of 1914[2] but was operated for only a short time. In 1915, however, it was successfully operated by the Western Zinc Oxide Co. on low-grade zinc carbonate ores, mainly from the Robert E. Lee mine, and was reported in July of that year to be yielding 150 tons a month of a product containing 70 to 80 per cent zinc and realizing $100 a ton.[3] The plant was operated steadily during 1916. In April, 1917, it was reported to be capable

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[1] Eng. and Min. Jour., Mar. 28, 1914, p. 676.

[2] Min. and Eng. World, Nov. 14, 1914, p. 92.

[3] Min. Press, July 24, 1915, p. 144.

of treating 60 tons of zinc carbonate a day, and the company was said to be considering an enlargement of the plant to include equipment for roasting sulphide ores.[1]

The unwatering of the Downtown section of the district was begun in 1914 with the installation of pumps at the Penrose shaft. It proved an immense undertaking and was not completed until 1916. During that year the projects to unwater the Fryer and Carbonate hills sections were begun. In 1917 they were completed, and shipments of ore, including zinc carbonate, were made from the newly unwatered ground in all the three sections.[2] Trial shipments of zinc carbonate ore from the Penrose mine yielded 25 per cent of zinc.[3]

LITERATURE.

Although several short articles, already referred to, have been written on the oxidized zinc ores of Leadville, they deal mostly with history. Only three papers have discussed the occurrence and genesis of these ores at any length. G. O. Argall[4] in 1911 gave brief descriptions of the mineralogy and occurrence of the ore and discussed the process of oxidation by which the zinc ore was concentrated. Butler[5] in 1913 described the occurrence and nature of the ore in somewhat more detail and announced the occurrence of two mineral varieties not previously recognized in the district. One of these was an aragonite containing variable proportions of zinc and named by Butler nicholsonite, after S. D. Nicholson, manager of the Western Mining Co., in whose mine the mineral was found. The other mineral was at first thought to be a new species and was named wolftonite, from its discovery in the Wolftone mine. Further study, however, proved this mineral to be hetaerolite, although the Leadville specimens are different in appearance from the type material.[6] Butler also discussed the origin of the ore and the results of experiments on the determination of the grade of ore and on its concentration.

Philip Argall visited the deposits on Carbonate Hill a few months after the writer's visit and in 1914 published a very interesting paper,[7] laying special emphasis on the occurrence of gray zinc carbonate ore along fissures in the lower part of the White limestone of

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[1] Min. Press, Apr. 14, 1917, p. 519.

[2] Hoskins, A. J., Unwatering projects at Leadville: Eng. and Min. Jour., Mar. 24, 1917, pp. 483–487. Henderson, C. W., U. S. Geol. Survey Press Bull. 325, p. 3, July, 1917.

[3] Min. Press, Mar. 24, 1917, p. 424.

[4] Argall, G. O., Oxidized zinc ores at Leadville: Leadville Herald-Democrat, Jan. 1, 1911, p. 6. The same article in condensed form appeared in Eng. and Min. Jour. Aug. 26, 1911, p. 399.

[5] Butler, G. M., Some recent developments at Leadville, second paper, The oxidized zinc ores; Econ. Geology, vol. 8, pp. 1–18, 1913; reprinted with addendum in Colorado School of Mines Quart., vol. 8, pp. 9–21, 1913.

[6] Written communication by G. M. Butler to the writer.

[7] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag. (London), vol. 10, pp. 282–288, 1914.

the Maid of Erin mine—places not exposed at the time of the writer's visit. The zinc carbonate ore there grades into manganiferous siderite a short distance from the fissures. Argall's descriptions supplement and his conclusions are in accord with those of the writer.

A paper of general interest on the formation of oxidized zinc ores by Wang[1] was published in 1915, over a year after the present report was completed. In this paper several experiments were described, some of which confirmed conclusions stated by the present writer regarding the genesis of the Leadville ores and none of which offered conflicting evidence. Wang's conclusion, however, that there is no definite order in the formation of smithsonite and calamine is not confirmed by study of the Leadville ores, in which smithsonite everywhere precedes calamine. The only specimen from Leadville described by Wang is one composed mostly of calamine with some smithsonite, in which hematite and limonite are concentrated along the partings and cleavage cracks of calamine.

MINERALOGY.

The zinc-ore and associated minerals noted in the oxidized zinc deposits of the Leadville district are given in the following lists:

Zinc-ore minerals.

Smithsonite.
Hydrozincite.
Aurichalcite.
Nicholsonite (zinciferous aragonite).
Calamine.
Hetaerolite ("wolftonite").
Chalcophanite.
Zinciferous clay.
Deschenite.

Associated minerals.

Iron oxides.
Manganese oxides (?).
Dolomite.
Manganosiderite.
Calcite.
Aragonite.
Barite.
Plumbojarosite.
Opal or chalcedony.
Chert.
Quartz.
Sericite.
Kaolin.
Sulphides.
Native silver.

ZINC-ORE MINERALS.

SMITHSONITE.

Smithsonite, the zinc carbonate ($ZnCO_3$), is by far the most abundant of the oxidized zinc minerals. The pure mineral should contain 52 per cent of metallic zinc, but owing to the presence of impurities, the percentage in shipping carbonate ore of the better

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[1] Wang, Y. T., The formation of the oxidized ores of zinc from the sulphide: Am. Inst. Min. Eng. Bull., September, 1915, pp. 1959–2012.

grades is rarely above 40 and commonly not much above 30. Smithsonite occurs in two varieties, deposited in different stages. Both may commonly be noted in a single specimen. The older variety (Pls. I, *A;* II, *A*) contains isomorphous mixtures of iron, magnesia, and manganese carbonates. It forms a dense gray to pale-brown mass of microscopic grains, in part relatively massive and in part containing numerous small cavities or pockets. The younger varieties (Pls. III, *A;* IV, *A*) is a fine drusy growth, colorless to white or locally pale greenish where free from foreign matter but usually of brown appearance, owing to the brown iron oxide to which it is attached. The dusty smithsonite has a weaker absorption and a lower index of refraction than the dense variety, properties which indicate a higher percentage of zinc, whereas the dense variety is correspondingly high in iron. Individual grains of the dense material, however, are so extremely fine and so complex in composition that measurements of their indices can not be made with sufficient accuracy to give more than a rough approximation to the percentage of zinc. The drusy variety lines small pockets and minute fractures in the dense variety, and close inspection shows that in several places it forms minute layers alternating with layers of a black manganese mineral (hetaerolite?) and locally with ferric oxide. (See Pl. IV, *A.*) Many if not most of the cavities containing calamine have a narrow rim of drusy smithsonite. The crystals of the drusy variety have for the most part curved or corroded faces, but here and there minute though nearly perfect unit rhombohedrons may be found. Occasionally pockets are found containing minute isolated rhombs, more or less corroded, scattered over a surface of brown iron oxide.

No coarsely fibrous or botryoidal smithsonite was seen by the writer, and only one occurrence—in the lower beds of the White limestone in the Maid of Erin mine—has been reported, to his knowledge.[1] In this respect the Leadville smithsonite is sharply contrasted with that in many well-known deposits of oxidized zinc ores, and the absence of these more familar forms of the mineral may go far toward explaining the failure to realize earlier the position and extent of the oxidized zinc ores in the Leadville district.

HYDROZINCITE.

Hydrozincite, a basic zinc carbonate ($ZnCO_3.ZnO_2H_2$), has been reported to occur here and there as a dull-lustered white, soft, earthy alteration product of smithsonite.[1] In the workings accessible to the

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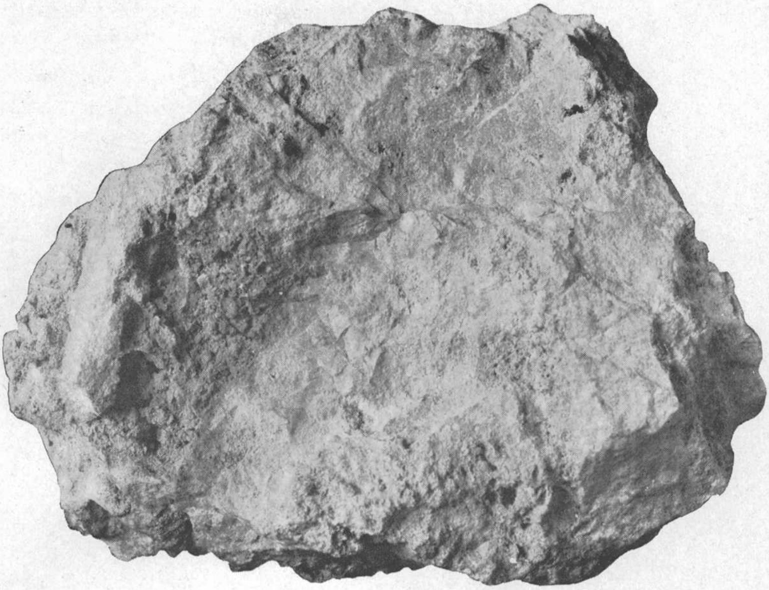
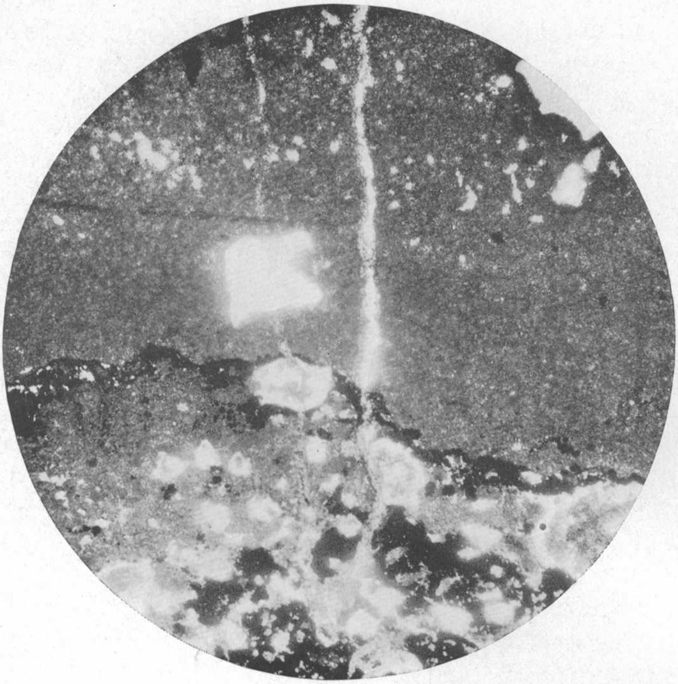
[1] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag. (London), vol. 10, p. 284, 1914.

[2] Butler, G. M., Some recent developments at Leadville, second paper, The oxidized zinc ores: Econ. Geology, vol. 8, p. 8, 1913; reprinted in Colorado School of Mines Quart., vol. 8, April, 1913.

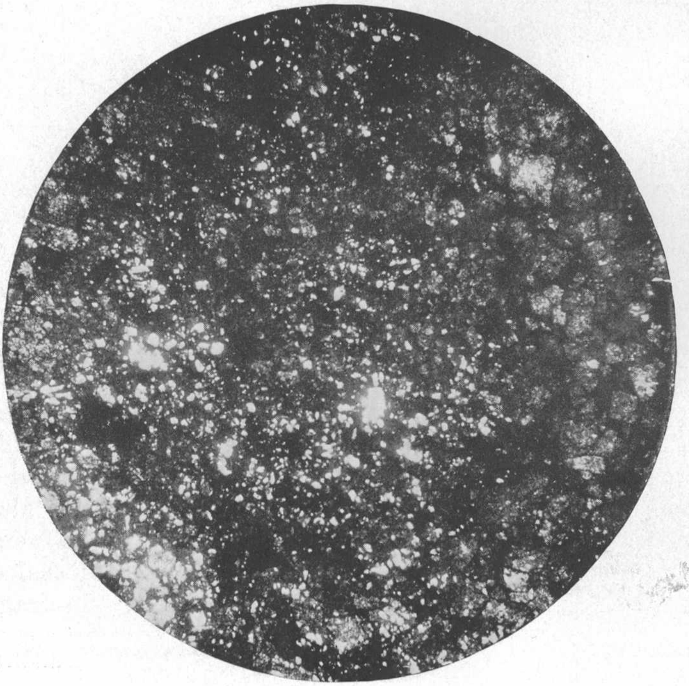


A. GRAY ZINC CARBONATE ORE.

B. CHALCOPHANITE AND CALAMINE COATING BROWN ZINC CARBONATE ORE.



A. PHOTOMICROGRAPH OF GRAY ZINC CARBONATE ORE INCLOSING REMNANTS OF SULPHIDE ORE.



B. PHOTOMICROGRAPH OF ZINC CARBONATE REPLACING MANGANOSIDERITE.

writer, however, the only earthy white material found in the oxidized zinc ores proved, on testing, to be the zinciferous clay, described on pages 24–28.

AURICHALCITE.

Aurichalcite is a basic carbonate of zinc and copper, $2(Zn,Cu)CO_3.3(Zn,Cu)(OH)_2$, whose zinc content ranges, according to different analyses, from 50 to 59 per cent, and whose copper content ranges from 15 to 22 per cent. The pure mineral, according to Penfield,[1] contains 53 to 54.4 per cent of zinc and 20 to 21.2 per cent of copper. The pure mineral is of pale-green to sky-blue color, of pearly luster, and very soft and occurs in drusy coatings or divergent tufts of columnar or needle-like crystals.

The only deposits of aurichalcite noted by the writer in Leadville were in two small stopes above the first level of the Ibex No. 1 (Little Johnny claim). Here the aurichalcite occurs as pale bluish-green crystals forming druses or cavity fillings in light-brown zinc carbonate ore. (See Pl. V, *A*.) In thin section (Pl. V, *B*) the pocket fillings were found to consist of a mixture of aurichalcite and calamine. The calamine predominated, forming diverging groups of bladelike crystals, in and through which were scattered tufts of fine needle-like to fibrous crystals of aurichalcite. A thin rim of drusy smithsonite separated the calamine and aurichalcite in places from the massive brown ore. One of the pockets was found to have a matrix of nearly or quite isotropic silica, in which the crystals of aurichalcite and calamine were embedded. The silica preserved to some extent the granular texture of the massive carbonate ore, proving that the "pocket" had grown in part, or been enlarged, by replacement of the massive ore, and indicating that the zinc in the calamine and aurichalcite had been, at least in part, derived from the zinc in the massive ore. The source of the copper is not apparent. It is said that ore of this type from the Ibex No. 1 has run as high as 4 per cent copper, but that no allowance for the copper is made by the ore buyers. Ore of a similar kind is said to have been mined in the Rattling Jack claim, whose shaft is a short distance southeast of the Ibex No. 1 shaft.

A few microscopic needles of aurichalcite were found in a thin section (Pl. V, *C*) of a calamine-quartz vein cutting low-grade reddish-brown zinc ore in the Belgian mine (Fenton's lease in 1913). Here also the aurichalcite grew simultaneously with the calamine; the two zinc minerals grew inward from the sides of the vein, and their terminations are embedded in a central filling of chalcedonic quartz. Some of the aurichalcite needles are bent, and fragments

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[1] Penfield, S. L., One the chemical composition of aurichalcite: Am. Jour. Sci., 3d ser., vol. 41, pp. 106–108, 1891.

of calamine blades, which may have been broken from the margins, are inclosed in the central portion of the vein, suggesting that there was a sluggish flowing of fluid (or gelatinous) silica during or just after the growth of the aurichalcite and calamine crystals.

The fact that these were the only occurrences of aurichalcite noted in the district indicates that the mineral is a very minor constituent of the general run of the oxidized zinc ores. Its relative abundance in the Ibex, which lies in the copper-gold belt, is significant, and its occurrence in considerable quantities is doubtless limited to this belt.

CALAMINE.

Calamine is a hydrous silicate of zinc, whose formula may be written $H_2Zn_2SiO_5$, $(ZnOH)_2.SiO_3$, or $H_2O.2ZnO.SiO_2$. The pure mineral contains 54.2 per cent of metallic zinc. It occurs typically in fine to coarse druses of white to colorless bladed crystals (Pl. IV), or in aggregates of diverging crystal groups, which may partly or completely fill cavities (fig. 2, p. 42). Sheaf-like aggregates, composed of crystals welded along their brachypinacoids, are occasionally found. The crystals in these cavities are tabular parallel to the brachypinacoid, which is vertically striated. Many of the crystals are terminated by a blunt point formed by two macrodomes; others by a sharper point where the blunt macrodomes are subordinate to steep macrodomes. Less commonly the nearly flat brachydomes predominate, producing a blunt chisel-like termination, and in a few specimens the "chisel edge" was seen to be truncated by the basal pinacoid. One small pyramid face was noted by Butler.[1] Prism faces are present but not conspicuous. The calamine also fills small fractures, in a few of which it is accompanied by amorphous or microcrystalline silica. In one exceptional specimen, found by R. S. Fitch on the dump at the Adams shaft, August, 1913, calamine crystals are coated with minute quartz crystals. The calamine crystals have grown upon both massive and drusy smithsonite, and on red and brown iron oxides and black manganese oxides. (See Hetaerolite.) They may inclose small particles of the iron and manganese minerals and be correspondingly darkened in color. They are also found in pockets or fractures in limestone near zinc carbonate ore bodies, and some veinlets cut hetaerolite and zinciferous clay ore, both of which are described below. One specimen, found on the May Queen dump, was so filled with brown oxide of iron as to have a brown opaque appearance, and only its crystal habit gave a clue to its identity. In this and certain other specimens the calamine appears to have grown, at least in part, by the replacement of brown massive smithsonite ore

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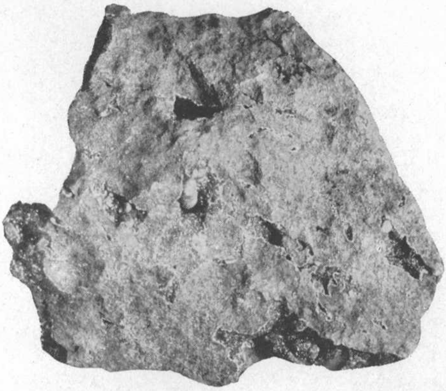
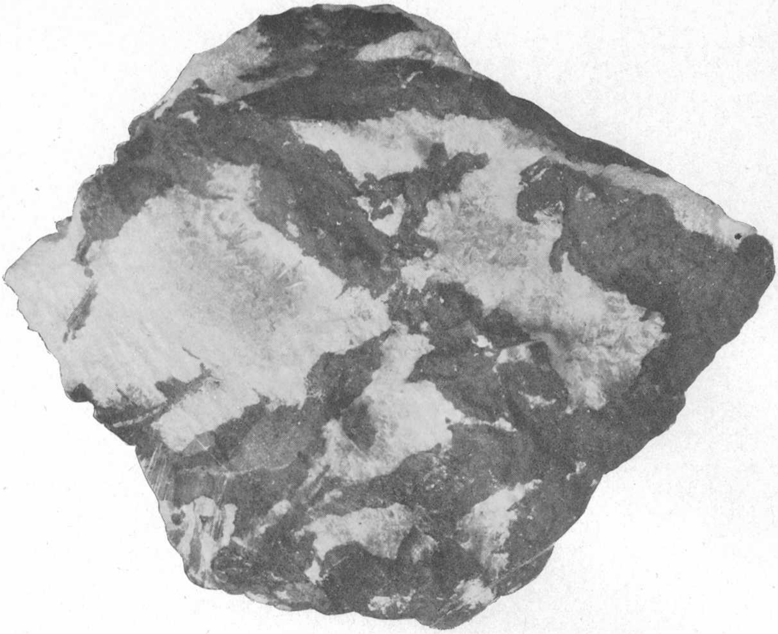
[1] Butler, G. M., Some recent developments at Leadville, second paper, The oxidized zinc ores: Econ. Geology, vol. 8, p. 7, 1913.

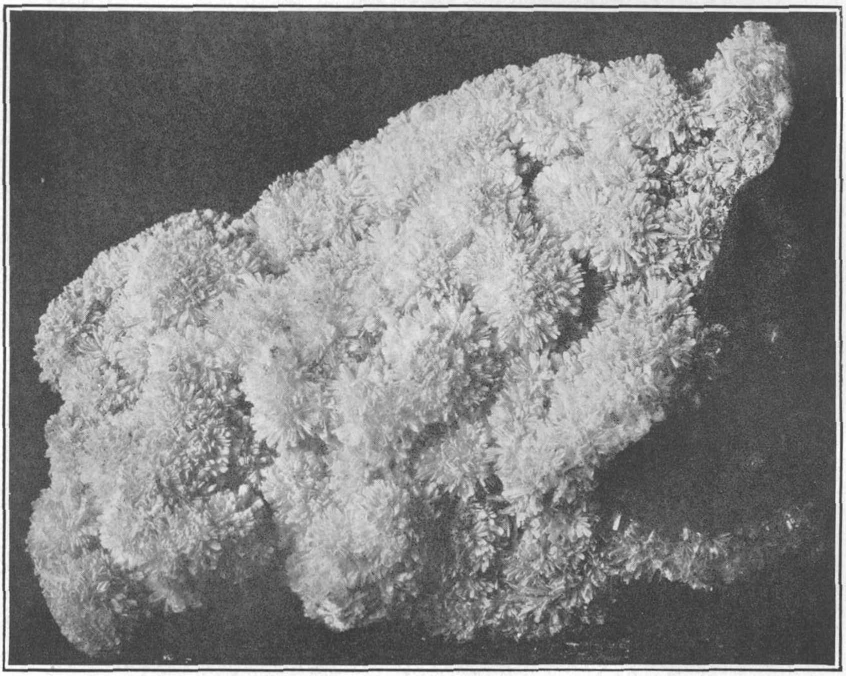


A. BROWN ZINC CARBONATE ORE WITH FINE DRUSES OF SMITHSONITE

B. PHOTOMICROGRAPH OF SPECIMEN SHOWN IN *A.*



A. BROWN ZINC CARBONATE ORE WITH DRUSES OF CALAMINE.



B. CALAMINE DRUSE COATING BROWN ZINC CARBONATE ORE, along cavities or fractures. In still other specimens, where the calamine rests upon other drusy minerals or fills a network of fractures inclosing sharply angular fragments of brown carbonate ore, the calamine was unquestionably deposited by infiltrating waters without detectable replacement.

HETAEROLITE ("WOLFTONITE").

The mineral hetaerolite was not recognized at Leadville until the development of the oxidized zinc ores was begun. It was at first believed to be a new species and was therefore named wolftonite,[1] after the mine in which it was found, but further study proved it to be hetaerolite. It is composed principally of oxides of zinc and manganese, with smaller amounts of silica and water. Opinions differ as to its chemical formula. The mineral was first described by Moore[2] in 1877 from a specimen found at the Passaic zinc mine, Sterling Hill, near Ogdensburg, Sussex County, N. J. Moore described the physical properties and occurrence of the mineral and stated it to be a zinc hausmanite ($ZnO.Mn_2O_3$)[3] but published no analyses. It occurred in association with chalcophanite in ocherous limonite, the chalcophanite usually forming a thin coating over it.

In 1910 Palache[4] studied a new lot of material from Franklin Furnace, N. J., and agreed with Moore that the hetaerolite was a zinc hausmanite. He assigned it to the tetragonal system of crystallization and stated that it had an indistinct cleavage. The material was analyzed by W. T. Schaller, of the United States Geological Survey (see column 1 on p. 23), and shown to contain small amounts of silica and water, the latter being attributed to a slight admixture of chalcophanite.

In 1913 Ford and Bradley[5] published a description and analysis of a specimen of the Leadville hetaerolite, taken from the Wolftone mine. They described it as a rare vug-filling mineral, found with a radiating mammillary structure, whose outer surfaces are generally smooth and rounded. The mineral showed a splintery fracture, and individual splinters showed a prismatic structure. Under the microscope the finest fragments were birefringent and had an extinction parallel to the prism edges, but no further indication of its crystal form could be discovered. Its hardness was found to be between 5.5 and 6, and its specific gravity was determined as 4.6. Its luster was

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[1] Butler, G. M., op. cit., p. 8.

[2] Moore, G. E., Preliminary notice of the discovery of a new mineral species: Am. Jour. Sci., 3d ser., vol. 14, p. 423, 1877.

[3] The formula for hausmanite is Mn_3O_4 or $MnO.Mn_2O_3$.

[4] Palache, Charles, Contributions to the mineralogy of Franklin Furnace. N. J.: Am. Jour. Sci., 4th ser., vol. 29, pp. 177–187, 1910.

[5] Ford, W. E., and Bradley, W. H., On hetaerolite from Leadville, Colo.: Am. Jour. Sci., 4th ser., vol. 35, pp. 600–604, 1913.

submetallic, its color dark brownish to black locally, with a bright varnish-like exterior, and its streak dark chocolate-like brown. It was infusible, but on charcoal with sodium carbonate gave the characteristic zinc oxide coating and with fluxes gave the color reactions indicative of manganese. It was easily dissolved in hydrochloric acid, giving off chlorine gas. In the closed tube it yielded water but did not give off oxygen gas. The index of refraction of hetaerolite was determined by Ford and Bradley to be above 1.78. It was determined by E. S. Larsen, of the United States Geological Survey, from material collected by the writer to be 2.19 and 2.22.

The writer can add to the above description that the mineral is of widespread occurrence in the oxidized zinc deposits of Leadville, though he found no specimens equal in size to those found in one part of the Wolftone mine. It has also been recently found by Philip Argall on the fourth level of the Tucson mine, filling small fractures in manganosiderite, well below the levels where oxidized zinc ores have been mined.[1] The mineral occurs mostly as thin drusy bands, alone or alternating with smithsonite, around cavities; also as fillings of small fractures, or as linings of fractures that are centrally filled with calamine or zinciferous clay. Its surface may be exposed, or it may be covered by calamine druses, the crystals of hetaerolite appearing to end abruptly where those of calamine begin. In some specimens small central clusters of distinct hetaerolite crystals grade outward into black stains that spot or mottle a considerable part of the brown carbonate ore. This relation leads to the suggestion that all the black manganese oxide stains and spots in the zinc carbonate ores may be incipient segregations of hetaerolite and not of psilomelane, as would at first be supposed. Wherever seen these black stains bear the same paragenetic relations to the later smithsonite and to calamine as the undoubted occurrences of hetaerolite. Locally hetaerolite may be the most conspicuous mineral in the ore, giving it a black or brownish-black color. In one specimen of this character, from the Tucson mine, the hetaerolite crystals are very distinct, having grown along intersecting fractures and inclosing dark-brown soft, earthy material of low grade. In other specimens of similar color the mineral is not visibly crystallized. The Tucson specimen strongly indicates that the hetaerolite was formed by the segregation of zinc and manganese from the massive carbonate ore, which left a residue composed largely of iron oxides. This origin is also suggested by several other specimens, some of which contain undoubted hetaerolite and others only the black stains.

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[1] Specimen taken in June, 1914, and sent to the writer for identification.

In column 1 below is an analysis made by W. T. Schaller[1] of hetaerolite from Franklin Furnace, N. J.; in columns 2 and 3 are analyses of the Leadville hetaerolite made respectively by Bradley[2] and by Chase Palmer, of the United States Geological Survey; and in column 4 a partial analysis by Haigh.[3]

Analyses of hetaerolite.

	1	2	3	4
Mn_2O_3	60.44	MnO 50.34	49.13	45.9
O	....	5.99	5.50	....
Fe_2O_3	.77	....	.67	5.9
ZnO	33.43	37.56	37.66	37.1
CaO	....	Trace.	Undet.	....
SiO_2	1.71	2.69	2.91	[a] 2.0
H_2O-	2.47	4.36	3.78	4.7
H_2O+	1.42			
	100.24	100.94	99.65	95.6

[a] Insoluble.

In discussing analysis 2, Ford and Bradley state that the structure of the mineral was such as to suggest that the silica is due to the presence of calamine, and that if so about 10 per cent of calamine is present—a large amount to escape discovery; but they thought that the fibrous structure of the hetaerolite might well conceal this amount. By recalculation, with allowance for the calamine, analysis 2 is found to correspond closely to the formula $2ZnO.2Mn_2O_3.H_2O$. Recalculation of analysis 1, including H_2O but not SiO_2, yielded the same formula, which Ford and Bradley conclude should be the formula for hetaerolite, instead of $ZnO.Mn_2O_3$, as stated by Moore and later by Palache; but they add that "it may be that the exact composition of hetaerolite can not be settled until purer material can be analyzed."

The best specimens collected by the writer show the hetaerolite to be a distinctly earlier growth than calamine, and the purest material, when crushed to a fine powder and examined under the microscope, gave no indication of calamine, even fine specks of which should be easily distinguishable from the hetaerolite. Chemical analysis (column 3 in the preceding table) shows it, however, to be practically identical with the material analyzed by Bradley (column 2). G. M. Butler[4] has expressed the conviction that the silica is an essential constituent of the mineral but has not suggested a corresponding formula. Nevertheless, the fact that silica and the excess of ZnO over that necessary for the ratio $2ZnO.2Mn_2O_3.H_2O$ are in the same ratio as in calamine is certainly significant, although just what the significance is must for the present be left to speculation.

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[1] Palache, Charles, op. cit., p. 180.

[2] Ford, W. E., and Bradley, W. M., op. cit., p. 602.

[3] Haigh, G., partial analysis quoted by Ford and Bradley.

[4] Written communication.

CHALCOPHANITE.

Chalcophanite, like hetaerolite, is a manganese-zinc oxide, with the formula $(Mn,Zn)O.2MnO_2.2H_2O$, containing about 21 per cent of zinc oxide.[1] It is closely associated with hetaerolite, both at Franklin Furnace, N. J., and at Leadville, Colo. It differs from hetaerolite in certain physical and chemical properties. In some specimens collected by the writer at Leadville it forms druses of minute tabular crystals of the rhombohedral system, coating botryoidal surfaces and filling occasional cracks in hetaerolite. In others it forms foliated crusts coating brown smithsonite and covered in turn by calamine druses. (See Pl. I, *B*.) Dana states that it also forms stalactitic and plumose aggregates. Its hardness, as given by Dana, is only 2.5; its specific gravity 3.91. Its luster is metallic and brilliant; its color bluish black to iron-black; and its streak chocolate-brown. In the closed tube it gives off water and oxygen and exfoliates slowly, and its color changes to a golden bronze. Before the blowpipe a similar change of color takes place, accompanied by slight fusion on thin edges, and it is this bronzy appearance that has given rise to the mineral name.

Since the above paragraph was written specimens of Leadville chalcophanite collected by F. B. Laney have been studied by Ford,[2] whose description verifies the properties above mentioned. He found that very thin plates under the microscope are sufficiently transparent to give a negative uniaxial interference figure.

ZINCIFEROUS CLAY.

Three varieties of zinciferous clay have been recognized in the Leadville mines—white, brown, and black. The white and brown are the most abundant. The white clay (Pl. VI, *A*) is very similar in appearance to kaolin and is one of the materials included under the local name "Chinese talc." The fresh material, however, is harder (about 3) and of more waxy luster than kaolin and does not slake or become plastic even when immersed in water for several days. Its fracture is conchoidal. Weathered or leached portions of it are of earthy appearance and slake readily in water. It has been found at the base of porphyry sheets in the Waterloo[3] and New Dome mines, forming in the latter a layer 1 to 2 feet thick that separates the sill from an underlying body of reddish-brown zinc carbonate ore. It has also been found in the Yankee Doodle mine, where it forms a layer about 2 feet thick immediately beneath a thin bed of silicified

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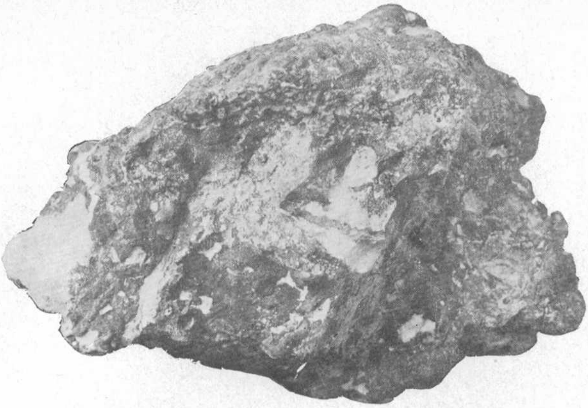
[1] Dana, J. D., System of mineralogy, 6th ed., p. 256.

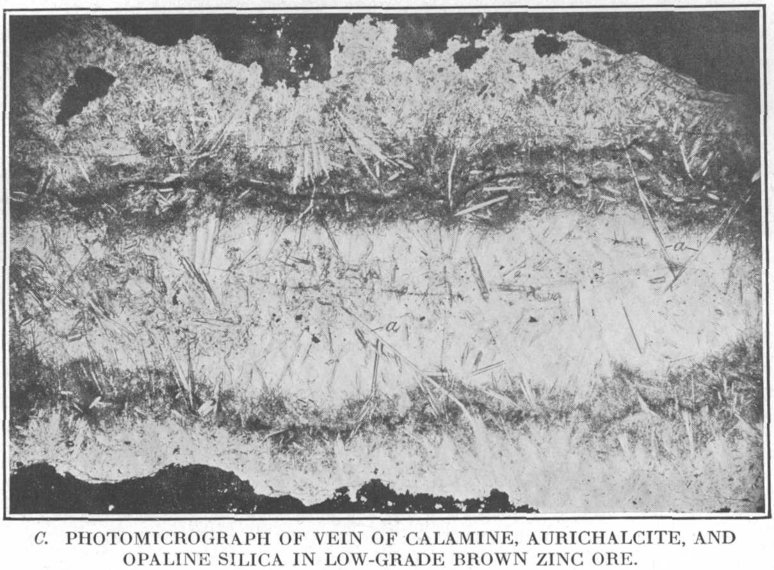
[2] Ford, W. E., Mineralogical notes: Am. Jour. Sci., 4th ser., vol. 38, p. 502, 1914.

[3] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 560, 1886. Hillebrand, W. F., idem, p. 605.

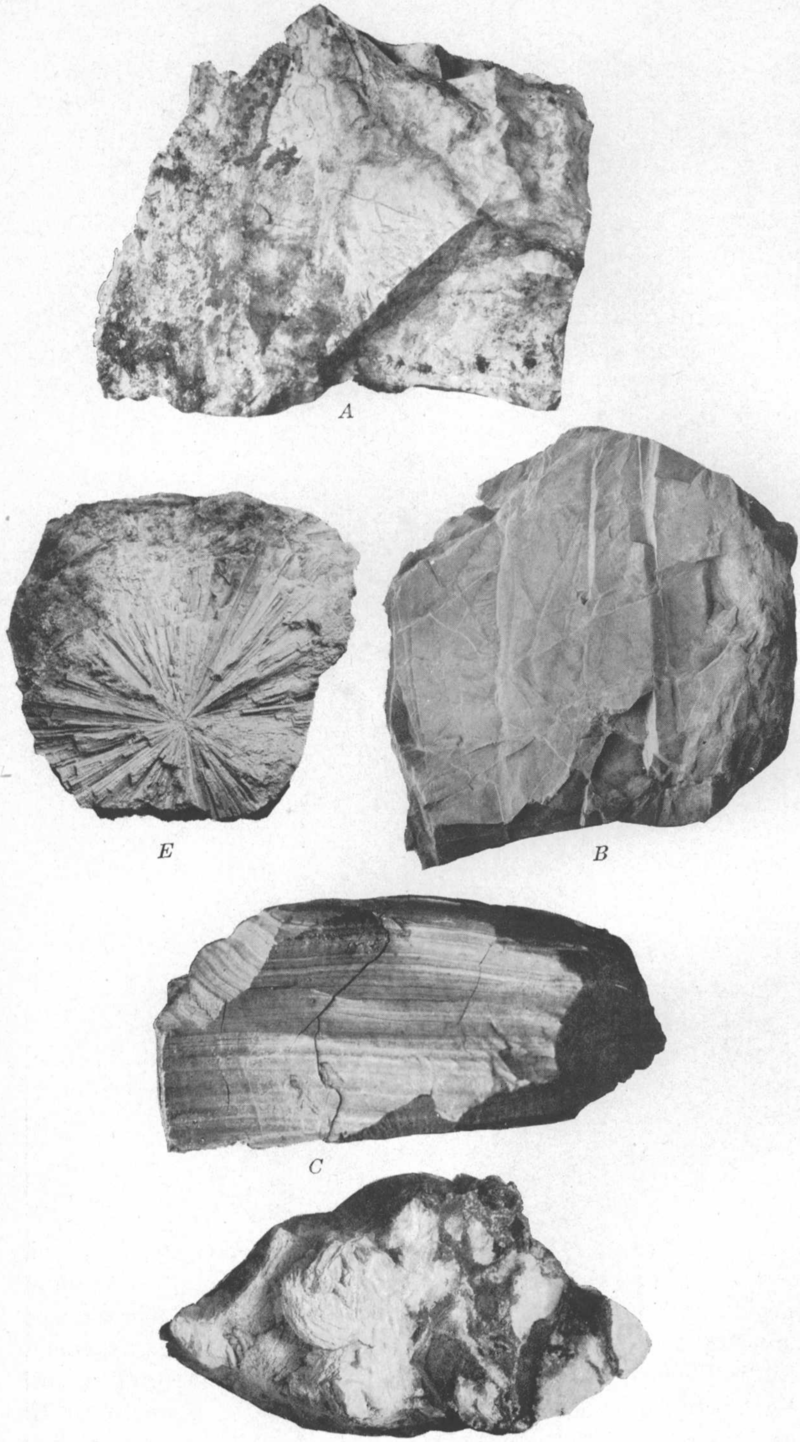


A. BROWN ZINC CARBONATE ORE WITH DRUSES OF AURICHALCITE.

B. PHOTOMICROGRAPH SHOWING AURICHALCITE AND CALAMINE FILLING CAVITY IN BROWN ZINC CARBONATE ORE.



C. PHOTOMICROGRAPH OF VEIN OF CALAMINE, AURICHALCITE, AND OPALINE SILICA IN LOW-GRADE BROWN ZINC ORE.



A. WHITE ZINCIFEROUS CLAY.
B. BROWN DENSE ZINCIFEROUS CLAY.
C. BROWN BANDED ZINCIFEROUS CLAY.
D, *E*. ARAGONITE FILLING CAVITIES IN BROWN IRON OXIDE.

shale. These occurrences are of sufficient size to be called small ore bodies. Here and there are fissure deposits and small patches and pocket fillings of clay in the zinc carbonate ore bodies.

One specimen found on the New Discovery dump contains calamine veinlets, locally expanded into drusy pockets, so distributed as to suggest that the calamine was formed in shrinkage cracks from material extracted from the clay.

Under the microscope the clay from the Yankee Doodle appears as an interlocking aggregate of minute fibers, of pale-brown color, nonpleochroic, with rather strong birefringence and positive elongation. Its mean index of refraction is a little above 1.58. The general appearance of the fibers is very similar to that of sericite fibers. Clay of similar megascopic appearance, from a pronounced fissure in the Maid of Erin mine, has optical properties more like those of kaolin, being traversed by a network of sericite-like fibers of higher birefringence and containing a few small calamine crystals. These features, together with the relatively low specific gravity of the material, suggest that it is kaolin containing a small percentage of zinc, mostly in the form of the sericite-like mineral.

The brown variety is more widely distributed but is nearly all limited to small deposits, such as the light-brown seams along bedding and joint planes and a few cavity fillings. Those along bedding and joint planes are of bright waxy luster and of uniform dense texture (Pl. VI, *B*), those filling vugs are of more or less waxy luster and may have a pronounced finely banded structure (Pl. VI, *C*), strongly resembling that of a sedimentary clay. Both varieties slake rapidly in water but lack the high degree of plasticity so characteristic of ordinary clays. The bright waxy material slakes into small chips or splinters but does not become plastic; material somewhat softened and dulled by weathering has a tendency to become plastic but lacks the stickiness of ordinary clay, as well as the characteristic odor.

An exceptional occurrence of the brown variety, sufficiently large to be called a small ore body, was seen in the Belgian mine (Fenton's lease in 1913), replacing limestone along fissures just beneath a sheet of Gray porphyry. It was identical in appearance with low-grade zinc carbonate ore but yielded no effervescence when immersed in hydrochloric acid. In this section it was found to consist of aggregates of the minutely fibrous sericite-like mineral, more or less stained and obscured by iron and manganese oxides. Microscopic vugs contained growths of the same mineral with radial arrangement around the borders. The larger of these vugs, or local enlargements of veinlets, contain calamine and the sericite-like mineral so intimately mixed as to indicate that the two must have grown at the same time, though the sericite-like mineral evidently began first, giving rise to the radial borders. It was traversed by many short veinlets of calamine with black borders of manganese oxide. Other manganese spots and streaks were also present.

A partial analysis by R. C. Wells shows the presence of 17.8 per cent of insoluble matter and 18.7 per cent of zinc oxide (or 15 per cent of zinc). The remainder, as shown by qualitative tests, contained a large amount of iron oxide and small amounts of magnesia and lime. The insoluble matter doubtless indicates the amount of silica in the sericite-like mineral, or zinciferous clay. The zinc oxide represents a little calamine as well as the sericite-like mineral. The material evidently consists essentially of zinciferous clay, a little calamine, iron oxide, and a little manganese oxide.

The black variety was noted in conspicuous amount only at one place, where the white clay in the Yankee Doodle mine was locally stained by manganese oxide.

The chemical composition of the zinciferous clays is shown by the following analyses:

Analyses of zinciferous clays.

	1	2	3	4	5
SiO_2	37.54	35.97	35.33	35.57	36.49
Al_2O_3	24.76	8.81	10.38	10.80	7.09
Fe_2O_3	.64	....	....	.40	2.48
FeO	....	....	....	Undet.	Undet.
MgO	.71	.80	.71	.82	.97
CaO	.63	1.87	1.62	.48	1.44
ZnO	18.43	35.40	33.05	31.49	33.46
PbO	....	....	....	None.	Undet.
Na_2O	.36	....	....	Undet.	Undet.
K_2O	.66	....	....	Undet.	Undet.
H_2O+	[a] 11.07	[a] 7.20	[a] 7.42	6.32	7.06
H_2O-	5.03	10.26	11.64	Undet.	Undet.
CO_2	....	....	....	None.	Undet.
P_2O_5	....	....	....	Undet.	Undet.
	100.10	100.31	100.15	[b] 86.88	88.99
Zn	....	....	....	25.30	26.88

[a] Hillebrand's analysis as tabulated gave only total water, but the amount of hygroscopic water in each analysis is stated in the text (op. cit., p. 605).

[b] By comparison with analyses 1, 2, and 3, the deficiency appears to be chiefly hygroscopic water.

1, 2, 3. "Alteration product of porphyry," Lower Waterloo mine. W. F. Hillebrand, analyst. U. S. Geol. Survey Mon. 12, p. 603, 1886.
4. White zinciferous clay, Yankee Doodle mine. George Steiger analyst.
5. Brown zinciferous clay, New Discovery mine. George Steiger, analyst.

The first three analyses represent material obtained directly under porphyry; the fourth represents the Yankee Doodle deposit, beneath a silicified shaly bed; the fifth represents the brown, finely banded type. In spite of variations in the mode of occurrence and appearance, the five analyses are very similar to one another in many respects, but attempts to calculate the mineral composition of the ore yield varying and only inconclusive results. The Yankee Doodle material (No. 4), after kaolin and calamine are calculated, has still an excess of silica and zinc, the molecular proportion of the former being a little more than double that of the latter. In the brown banded variety (No. 5) the alumina and all the zinc can be assigned to kaolin and calamine, respectively, leaving an excess of silica and combined water in the approximate ratio of 11 to 2. Attempts to find some definite relations between certain constituents by plotting their percentages on a diagram (fig. 1) do not give very definite evidence, except that the percentage of zinc oxide (ZnO) varies inversely as that of alumina (Al_2O_3). The birefringence of the clays shows that crystalline matter is present, and it may be suggested that they contain kaolin or some closely related aluminum silicate, its optical properties changed by dissolved impurities, but if it were suggested that such an aluminum silicate held the other constituents in solid solution, it would be necessary to assume that one molecule of it could hold in solution several molecules of each of the other substances—a questionable property. The low-grade clays, furthermore, show in thin section that the higher birefringent mineral forms a network impregnating a mass with optical properties like those of chalcedonic silica and kaolin. If the highly birefringent portion could be analyzed separately it would probably show as high a ratio of zinc oxide to alumina as the high-grade clays. The fact that the percentage of zinc oxide varies inversely as the percentage of alumina suggests replacement by zinc of aluminum in the kaolin molecule. The low-grade deposits indicate that such replacement has occurred in

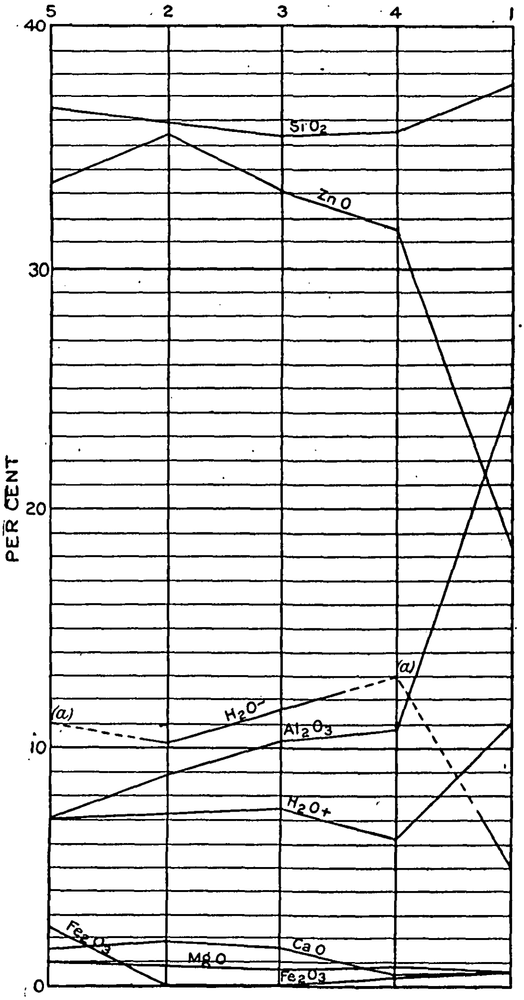


FIGURE 1.—Diagram showing percentages of constituents in zinciferous clays, arranged in order of increasing alumina.

clays previously deposited, but at least some of the high-grade clays indicate that zinc has taken the place of aluminum in solution and that the zinciferous clay has resulted from direct chemical precipitation.

Whatever its true nature, the zinciferous clay has certain relations to definite minerals, as is shown by its contemporaneous deposition with calamine, described on page 20. This relation may suggest that when zinc is above a certain ratio to alumina its excess may crystallize as calamine, but analyses of Missouri "tallow clays"[1] hardly bear out this suggestion. The veinlets and pockets of calamine in the clay, mentioned on page 20, suggest that under favorable conditions the clays that were formed first may later separate into calamine, silica, and kaolin, the silica and kaolin remaining as a microscopic mixture. The fact that zinc and silica, in the absence of alumina, crystallize readily as calamine and opal or chalcedony or quartz is demonstrated by the intimate association of these minerals in several places in the Leadville district. The presence of alumina therefore seems the critical factor in causing the deposition of the clays instead of calamine and other distinct minerals.

DESCHENITE.

According to Emmons and Irving,[2] deschenite, or the vanadite of lead and zinc, is found as an accessory and rather rare mineral associated with the ore bodies, but no description of its mode of occurrence is given. This mineral was not found by the writer.

ASSOCIATED MINERALS.

IRON OXIDES.

By far the greatest part of the oxidized zinc ores, of both high and low grade, are colored brown or reddish brown by oxides of iron. The ores contain both limonite and turgite, as suggested by their colors and by calculation of the analyses given on page 47, and perhaps also goethite and earthy hematite. Besides coloring the ores, these oxides form large masses of siliceous iron ore of varying grades, some of which have been found above and others beside bodies of oxidized zinc ore. Small masses or segregated deposits of brown iron oxide containing negligible amounts of zinc are also found here and there within the zinc ore bodies and even, rather exceptionally, under them. Iron oxide appears to have been deposited at all stages, from the earliest carbonate ore stage down to

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[1] Seamon, W. H., The zinciferous clays of southwest Missouri and a theory as to the growth of calamine of that section: Am. Jour. Sci., 3d ser., vol. 39, pp. 38–42, 1890.

[2] Emmons, S. F., and Irving, J. D., The Downtown district of Leadville, Colo.: U. S. Geol. Survey Bull. 320, p. 33, 1907.

the present time. In a thin section of a specimen from a zinc stope on the Tucson No. 1 level the iron oxide preserves the texture of the original dolomite (Blue limestone) and was evidently deposited together with silica before or quite as early as any zinc carbonate ore. The bodies of iron oxide accompanied by kaolin and silica, which are commonly found in layers from 6 inches to 5 or 6 feet in thickness between overlying lead carbonate stopes and underlying zinc carbonate stopes, were also probably deposited during or just before the first zinc carbonate stage, but they may be in part residual, having been produced by re-solution and downward migration of the topmost parts of the zinc carbonate ore bodies. The iron oxide ores of shipping grade, so far as they have been seen in contact with or in close proximity to the oxidized zinc ores, appear to have been deposited as early as the first stage of zinc carbonate. The iron oxides in the brown zinc ores have been for the most part derived from the oxidation of ferrous carbonate, which was a constituent of the zinc carbonate of the first stage. There was evidently more or less migration in solution of some of this iron before oxidation, thus accounting for the local segregated deposits within and below the zinc ore bodies. Gray zinc-iron carbonate ore may be seen to-day partly stained by iron oxide that is evidently still in process of formation.

MANGANESE OXIDES.

Black oxide of manganese occurs in much the same variety of ways as the red and brown oxides of iron and needs no detailed description. Although much or all of the black manganese oxide occurring outside of the zinc ore bodies is psilomelane, accompanied by small amounts of pyrolusite, it seems probable that the black stains and coatings in or on the zinc ores is the zinc-manganese mineral hetaerolite, accompanied in places by chalcophanite, both of which have already been described. (See pp. 21–24.)

DOLOMITE.

Dolomite occurs only as unreplaced portions of wall rock (Blue or White limestone), either as inclusions within the zinc ore bodies or as incomplete replaced walls. Analyses of different ore samples show varying but small amounts of magnesia, usually or always in too great a ratio to lime to form dolomite. It appears that during the replacement of dolomite, the lime content was nearly or quite all removed, whereas a small amount of magnesia remained with the ore.

MANGANOSIDERITE.

Manganosiderite, like dolomite, has been found as inclusions or replaced remnants in the oxidized zinc ore bodies of the Maid of

Erin mine. These inclusions are of especial interest, as they prove that manganosiderite, as well as dolomite, has been replaced by the zinc carbonate ores. Thin sections of specimens from these manganosiderite inclusions show small amounts of chalcedonic quartz and sericite accompanied by small grains of pyrite, zinc blende, and galena, all of which may be seen preserved in gray zinc-iron carbonate which has replaced the manganosiderite. The manganosiderite can be distinguished from dolomite by its lighter color and higher specific gravity and in thin section by its much stronger absorption. It differs from the gray zinc-iron carbonate ore in its distinctly coarser texture, having a fine to medium grain, whereas the zinc-iron carbonate is microgranular.

CALCITE.

Calcite in the oxidized zinc ores occurs for the most part as colorless to white crystals, here and there lining pockets in ore of all grades and associated iron oxide. Its most common crystal form is the flat rhombohedron of disklike appearance, the sharp edges lying normal to the walls of the cavity. These crystals rest on calamine and in one specimen on hetaerolite and appear to represent the latest mineral growth in the oxidized zinc ore bodies, except, of course, any oxides of iron and manganese that may be forming to-day. Calcite also occurs in small to microscopic veinlets cutting zinc carbonate ore.

ARAGONITE AND NICHOLSONITE.

Aragonite, the orthorhombic form of calcium carbonate ($CaCO_3$), is occasionally found in close association with the oxidized zinc ores but has not been noted in direct contact with zinc ore minerals. It forms diverging to spherical radiating columnar aggregates, or groups of such aggregates (Pl. VI, *E*), usually if not invariably white. The one occurrence found by the writer formed pockets in brown siliceous iron oxide. So far as its general appearance and mode of occurrence are concerned, aragonite may be mistaken at first glance for calamine; but it lacks the characteristic bladed form of calamine and can further be distinguished by its brisk effervescence in very dilute hydrochloric acid.

The aragonite studied by the writer proved to contain little or no zinc, but a variety containing as much as 10 per cent of zinc was studied by G. M. Butler, who gave it the name nicholsonite. According to Butler,[1]

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[1] Butler, G. M., Some recent developments at Leadville, second paper, The oxidized zinc ores: Econ. Geology, vol. 8, pp. 8 and 9, 1913.

The nicholsonite is identical with aragonite in all but three particulars. Those specimens with high percentages of zinc have a higher specific gravity than aragonite, show a decided adamantine rather than a vitreous luster, and have a better cleavage (good pinacoidal and poor prismatic) than pure aragonite. The variety was found in the oxidized iron-manganese ore in the blue limestone and was named after S. D. Nicholson, of the Western Mining Co., who brought it to the attention of the writer.

BARITE.

Only one occurrence of barite was noted in connection with the oxidized zinc ores. This was in the Little Giant mine, near the boundary between that mine and the Yankee Doodle. The barite formed a rather coarse grained aggregate of crystals, originally white, whose cleavage cracks and boundaries, as well as other fractures, were filled with a yellowish-brown powdery material that effervesced weakly in dilute hydrochloric acid. The material was said to have a low zinc content, but its noticeably high specific gravity was due to the barite rather than to any iron, zinc, or lead.

PLUMBOJAROSITE.

Plumbojarosite, a hydrous sulphate of lead and ferric iron ($PbO.3Fe_2O_3.4SiO_2.6H_2O$), was found in the Yankee Doodle mine in the bottom of an old lead stope, just above a small oxidized zinc stope. It was called "contact matter" but was known to contain considerable lead. The mineral occurs as a yellowish-brown soft, earthy mass, with a rather shiny luster and a smoother feel than is characteristic of iron oxide or iron-stained lead carbonate. Under the microscope the material is essentially homogeneous and consists of minute grains, some of which show a partial to complete six-sided outline under very high magnification. It is much finer grained than the material from Beaver County, Utah, figured by B. S. Butler.[1] Material of the same kind was found by Emmons under Gray porphyry in the Lower Waterloo mine during the first survey of the district and was analyzed by Hillebrand[2] as follows:

SiO_2	0.36	Bi_2O_3	None.
FeO_3	44.4	As_2S_5	0.39
Al_2O_3	.23	P_2O_5	.11
CaO	None.	SO_3	25.07
MgO	None.	Cl	.04
K_2O	.15	Ag	.075
Na_2O	.37		
H_2O	8.99		99.685
PbO	19.5		

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[1] Butler, B. S., Occurrence of complex and little known sulphates and sulpharsenates as ore minerals in Utah: Econ. Geology, vol. 8, p. 313, 1913.

[2] U. S. Geol. Survey Mon. 12, p. 606, 1886.

Emmons and Hillebrand, however, did not recognize this material as a distinct mineral species, owing doubtless to its earthy appearance and close resemblance to other materials of varying though similar composition. Plumbojarosite was determined as a distinct species six years later by Hillebrand and Penfield.[1]

OPAL, CHALCEDONY, AND QUARTZ.

Silica, usually in a dense form, has been found in small amounts at several different places, usually associated with calamine. The occurrence of amorphous (opal) to chalcedonic silica as the middle of a veinlet with marginal bands of calamine in the Belgian mine and the occurrence of amorphous silica in a vug with calamine and aurichalcite in the Ibex mine have already been described (p. 19; Pl. V, *A* and *B*). On the Mikado dump was found a specimen containing vugs lined with microscopic to visibly crystalline quartz and calamine. A few minute crystals of quartz were seen perched on the sides of calamine crystals. R. S. Fitch, of Leadville, found a similar but much better specimen in which calamine crystals were almost completely coated with fine druses of minute but typical quartz crystals.

What appears to be an exceptional microscopic occurrence was noted in two thin sections of gray zinc carbonate ore from the Chrysolite dump. Here minute crystals were found in the middle parts of veinlets and as central fillings of certain vugs, in each veinlet bordered by smithsonite of the later stage. In a single thin section some vugs may be filled with smithsonite and quartz, and others with calamine with or without quartz. No explanation is offered to account for the failure of silica and zinc to combine in certain places when they did in others within an area not more than half an inch square.

Silica is also present in considerable amount with the iron oxide bodies in or adjacent to the zinc ores. As a rule this silica is completely concealed by the iron oxides, but in one thin section from the walls of a zinc stope on the Tucson first level it was found to be present as minute quartz grains mingled with the iron oxide and also as minute agate-like growths in microscopic vugs.

Microscopic quartz with sericite and sulphide grains has been seen in thin sections of gray zinc carbonate which has replaced manganosiderite. It was originally present in the manganosiderite and has escaped replacement.

Chert has been found in reddish-brown zinc ore at a few places, where it forms the only unreplaced remnants of the original limestone or dolomite.

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[1] Hillebrand, W. F., and Penfield, S. L., Some additions to the alunite-jarosite group of minerals: Am. Jour. Sci., 4th ser., vol. 14, p. 213, 1902.

SERICITE.

The only sericite noted in the oxidized zinc ores is the small amount which, with quartz and sulphide grains, was originally in manganosiderite and has escaped replacement.

KAOLIN.

Kaolin is present as an abundant constituent of the material that separates many lead carbonate stopes from zinc carbonate stopes. It is for the most part stained with iron or manganese oxides but has its typical white color in patches away from which the iron and manganese oxides have segregated. Kaolin is also present as the principal filling of strong fissures, one of which in the Maid of Erin mine was found to be bounded on both sides by oxidized zinc ore. This kaolin was also more or less stained by iron and manganese oxides and was practically identical in general appearance with the zinciferous clay ore but differed in its relatively low specific gravity. In thin section, as stated on page 25, it was found to contain a network of streaks and patches of rather high birefringence, resembling sericite and also the zinciferous clay, its appearance suggesting that a small percentage of zinc had been introduced. A few small calamine crystals were also present in it.

At the base of a porphyry sheet in the Belgian mine was seen a kaolin mass which was stained bluish green by some copper salt. A low zinc content was also found in this mass, and it seems probable that the presence of both copper and zinc was due to adsorption by the kaolin.

SULPHIDES.

At several places in the Western Mining Co.'s workings (Pls. VII and VIII) the oxidized zinc ores have been found almost or quite in contact with bodies of sulphides, chiefly pyrite, but at no place examined by the writer could more than a small face exposure of sulphides be seen. The sulphides where exposed were clean and fresh and showed no evidence of having reacted with zinc solutions to produce secondary zinc sulphides.

In the winze about 180 feet north of the south end of the lower Maid of Erin ore body (Pl. VII) a small streak of galena was noted along a preserved bedding plane within a mass of brown zinc carbonate ore. Calamine crystals, abundant in the brown ore, were also present within the galena streak, filling cavities formed by the removal of either limestone or zinc blende.

Small amounts of sulphides were also noted in gray zinc carbonate ore. These sulphides were originally in manganosiderite but escaped replacement. They were chiefly pyrite but included a few scattered grains of sphalerite (not wurtzite) and galena.

NATIVE SILVER.

The only occurrence of native silver noted was seen in a small stope on the Maid of Erin first level, at Crowell's raise. The silver formed small flakes and wires in a small mass of siliceous iron oxide veined and sprinkled with calcite about 1½ feet in diameter which lay between an old lead stope above and a zinc stope below. The silver flakes for the most part were scattered through the iron oxide, but some were closely associated with visible spots of calcite.

PARAGENESIS.

The paragenesis of the minerals, or the order in which they were formed, may be summarized from the foregoing descriptions as follows:

Dolomite or magnesium limestone, manganosiderite, barite, chert, the quartz-sericite aggregates, and the sulphides existed before oxidation of the original ore bodies began. The iron oxide and kaolin masses that separate the lead carbonate from the zinc carbonate bodies may, from analogy with zinc deposits in other districts, have been the first of the oxidized minerals to form, but their origin in the Leadville deposits is not so clear. They may also be due in part to the leaching away of zinc minerals originally deposited with them. They will be further considered in the discussion of the genesis of the ores. The one occurrence of native silver noted was evidently formed at the same time as the iron oxide.

The first oxidized zinc ore mineral to form was the massive gray smithsonite, containing varying but considerable amounts of iron and manganese carbonate. This mineral replaced manganosiderite and dolomite (Blue and White limestone). It is believed to have formed at the same time as or immediately after the iron oxide and kaolin masses just mentioned.

Later, through oxidation, the iron and manganese present began slowly to oxidize, forming the red or brown iron oxides and the zinc-manganese oxide hetaerolite, with a corresponding amount of the later and purer drusy smithsonite, which, as shown in thin section, alternated with the iron oxide and the hetaerolite, suggesting a rhythmic alternation in deposition. The largest growths of hetaerolite, however, followed the drusy smithsonite. The inconspicuous growths of chalcophanite may be the result of the alteration of hetaerolite by further oxidation, or they may have been precipitated from solutions of different concentration from that which yielded the hetaerolite.

Oxidation of remnants of gray ore and manganosiderite is still in progress and doubtless has been to a greater or less extent ever since oxidation began.

Calamine and locally aurichalcite and zinciferous clay were next formed. The calamine in part was formed at the expense of smithsonite, leaving relatively pure residual iron oxide; in part it was deposited in fractures and vugs in both smithsonite and dolomite (limestone). Aurichalcite, as shown in thin section, was deposited at the same time as calamine. The zinciferous clay in some places appears to have been formed instead of calamine in the presence of alumina, as it bears the same relations to all the minerals of earlier growth. Where calamine and the zinciferous clay are present together, the calamine in some places forms the margins and the clay the middle fillings of veinlets. In the Belgian mine the clay forms the margins of pockets and a parallel growth of calamine and clay the central fillings, whereas in one specimen the calamine forms networks of veinlets through the clay. These differences may be attributed to varying conditions of chemical equilibrium; a relative excess of zinc over alumina may have caused calamine to represent the beginning of deposition in the first case, and a corresponding excess of alumina may account for the marginal growth of clay in the second; the calamine veinlets in the clay may be a decomposition product of the clay, or a deposit from solutions of a later stage which reached the previously dried and cracked clay. The small size and scattered distribution of these occurrences prevent the drawing of a definite conclusion regarding the relations between calamine and zinciferous clay.

Silica, either in an amorphous or a minutely crystallized condition, was deposited with or just after calamine and, in most of the specimens studied, appeared to represent the excess of silica over zinc in solution. The presence of aurichalcite with calamine and silica is interesting in this connection, suggesting a rather delicate balance between carbon dioxide and silica that allowed the formation of aurichalcite instead of additional calamine and the copper silicate, chrysocolla. The replacement of smithsonite by calamine in several places and the occurrence of smithsonite in contact with a later growth of quartz in at least one place (specimens from the Chrysolite dump) raise another question as to the conditions under which zinc silicate may form.

Calcite was distinctly the latest of all the common minerals of the oxidized zinc deposits, except, of course, iron and manganese oxides, which may still be forming. Its period of growth may have slightly overlapped that of calamine, but it is for the most part distinctly later. The exact position of aragonite and nicholsonite in the paragenesis can not be stated. Both have formed in pockets in iron or iron and manganese oxides, but their relations to the different zinc minerals have not been ascertained.

VARIETIES OF ORE.

So far as appearance and differences in composition are concerned, four varieties of oxidized zinc ore may be distinguished, but these are so intimately associated that all may enter into a single carload. The four varieties are (1) gray carbonate ore, (2) reddish-brown to brown carbonate ore, compact or filled with calamine pockets, (3) brownish-black to black carbonate-oxide-silicate ore, and (4) white to brown dense silicate ore (zinciferous clay or "talc"). The brown varieties, Nos. 2 and 3, are by far the most abundant.

GRAY CARBONATE ORE.

OCCURRENCE.

Gray carbonate ore was noted at a few different places in the Maid of Erin mine and on the dump of the Chrysolite mine. At least two of the occurrences in the Maid of Erin were found immediately below pyritic sulphide ore. The others had not been developed, and their relations to other ores was not definitely known. An occurrence of grayish-brown to yellowish-brown ore on and below the Henriette fourth level, although not found immediately in contact with other ores, is doubtless below lead carbonate ore, as only lead carbonate ore has been found at so high a level in the vicinity. (See Pl. VII and section AA, Pl. VIII.) One of the deposits of gray ore contained an inclusion of manganosiderite, which had evidently escaped replacement. Further evidence of this replacement is given in the description of the microscopic features of the ore (pp. 37–38).

MEGASCOPIC FEATURES.

The ore is of medium to light gray color where quite free from oxidation, but some specimens show more or less yellowish-brown iron oxide stains in places, and by increase in the amount of staining the gray ore grades into the reddish-brown to brown variety. The texture of the gray ore is very fine grained to dense (microgranular) for the most part, but small cavities or vugs ranging from minute pores up to holes an inch or two in diameter are irregularly scattered through it. In places these cavities are small enough and regularly enough distributed to suggest shrinkage accompanying replacement of the original rock; in others they appear to be enlargements of fractures; and in still others they are clearly the result of the leaching out of the more permeable portions of the ore. Cavities of the first two kinds have rounded edges where the carbonate ore has developed microscopic drusy surfaces. Those of the last kind have rough, corroded surfaces. No minerals of megascopic size were seen in the fresh gray ore, except a few specks of pyrite, zinc blende, and possibly galena, which were noted in two specimens. These sulphides occur in minute veinlets and scattered grains, just as they do in the manganosiderite. In the brownish-gray partly oxidized ore from the Henriette workings the fine-grained carbonate aggregate is traversed by veinlets of calamine.

MICROSCOPIC FEATURES.

In thin section (Pl. II, *A*) the gray carbonate ore is composed mostly of a uniform aggregate of very fine carbonate grains of high relief, typically high birefringence, and cloudy appearance. This aggregate is cut by veinlets of smithsonite that are characterized by a somewhat coarser grain and freedom from cloudiness. Smithsonite, optically similar to that in the veinlets, also forms minute rhombohedrons lining small cavities. A few minute diverging aggregates and single grains of calamine were noted filling small cavities, but the total amount is negligible so far as the amount of zinc in the ore is concerned. Incipient oxidation is marked by faint brown and black stains of iron and probably manganese oxides. A veinlet of calcite, distinguished from smithsonite by distinctly lower index of refraction, was noted.

The ore incloses small veinlets and patches consisting of varying proportions of quartz, sericite, pyrite, and locally zinc blende and galena. It also incloses scattered single grains of the same minerals. Many of these inclosed veinlets have a marked "wriggling" shape. Some are distorted and even appear to have been pulled apart. Some are penetrated or cut by veinlets of smithsonite. Small aggregates of pyrite also appear to have been pried apart by smithsonite veinlets. The quartz-sericite-sulphide veinlets and aggregates have the same features, except for the distortions just described, as in the manganosiderite and are evidently all that is left of the manganosiderite body originally present.

Under high magnification the fine aggregate proves to be composed of countless anastomosing rows of clear, transparent granules inclosing small rounded bunches of clouded (more strongly absorptive?) granules. The anastomosing rows are so arranged as to indicate the outlines of former manganosiderite grains. In some thin sections the small clouded bunches have been removed by leaching and, perhaps, in part during grinding of the section, leaving a porous mass of anastomosing rows of smithsonite. These pores may also be in part due to removal of grains or minute aggregates of quartz, sericite, and pyrite, but removal of these minerals certainly can account for only a minor part of the entire pore space. As this finely porous texture has been noted in specimens as well as thin sections, there is no doubt that it has resulted mainly from leaching.

This anastomosing structure indicates that the zinc solutions permeated the manganosiderite (or dolomite in some places) along the boundaries of grains and replaced the grains from their margins inward. The replacement was not strictly pseudomorphous, as the texture of the ore is markedly finer than that of the manganosiderite, even including the clouded bunches of granules inclosed among the anastomosing grains. An attempt to prove the assumption that the clouded bunches have stronger absorption and are therefore probably higher in iron than the anastomosing portions was unsuccessful, owing to the extremely fine grain of the ore.

If manganosiderite corresponding to analysis 1 (p. 47) was completely replaced by gray zinc carbonate ore corresponding to analysis 2, the replacement should have been accompanied by about a 15 per cent shrinkage;[1] but evidence of shrinkage is obscured by different factors other than the effects of partial leaching of the ore. The recrystallization that accompanied replacement may have distributed the amount of shrinkage so as to render it inconspicuous, or it may have readjusted the material so that shrinkage was expressed by numerous small fractures. The fractures in the ore, whether due to shrinkage or to other causes, are now filled with the smithsonite veinlets, which may represent material recrystallized practically in place, or additional material introduced after the direct process of replacement had practically ceased. Furthermore, deposition of the smithsonite veinlets appears to have caused expansion in certain places. The conclusion that the theoretical amount of shrinkage took place rests on the assumption that the zinc was introduced as some salt, presumably sulphate, which could react with manganosiderite (or dolomite) and deposit an amount of zinc carbonate exactly equivalent to the amount of manganosiderite replaced. It is probable that the zinc was largely introduced as sulphate, but the veinlets of second-stage smithsonite show that a part of it was introduced as carbonate and that deposition was not entirely the result of simple molecular interchange. The amount of shrinkage can therefore not be determined from the porosity of the ore in its present state, nor can it be closely estimated from the texture and structure of the ore.

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[1] Specific gravities were not determined, as the zinc ore is much more porous than the manganosiderite. Porosity was not determined, as the pores and other cavities in the ore are obviously due in part to other causes than shrinkage. Published specific gravities of the several carbonates represented in the analyses vary according to impurities, and 15 per cent shrinkage is an approximate average based on these varying data. Theoretically the shrinkage may have amounted to as much as 17 or 18 per cent.

CHEMICAL COMPOSITION.

The chemical composition of the gray ore is shown by analysis 2 (p. 47), made by R. C. Wells, of the United States Geological Survey, from material collected in the narrow stope on the first intermediate level above the second in the Maid of Erin mine, about 100 feet south of the New Maid (Maid Combination) shaft. The ore lay beneath a sulphide body and contained small stringers of sulphides; but these were avoided in the material analyzed, as were portions showing brown or black stains.

The silica and alumina in this analysis represent quartz and sericite, which together amount to about 2 per cent. The total absence of ferric oxide (Fe_2O_3) is noteworthy when this analysis is compared with analyses 3 and 4, of brown zinc ores. The ferrous oxide, magnesia, lime, manganese oxide, and zinc oxide are present as carbonates, but the total of their molecular ratios is a little in excess of the total carbon dioxide. If the excess is placed wholly in the manganese oxide, there remains an excess of 0.2 per cent, which is decidedly high in view of the color and microscopic composition of the material analyzed. No trace of any mineral containing phosphorus was noted, and the phosphorus pentoxide (P_2O_5) can not be definitely accounted for. If it were combined with enough lime to form apatite, a corresponding reallotment of carbon dioxide (CO_2) would almost balance the excess of manganese oxide (MnO); but this arrangement would demand the presence of 0.67 per cent apatite, whereas none was found in thin section. The water driven off above 110° C. (H_2O+) is also in excess over the amounts necessary to enter into sericite and possible hydrous manganese oxide, and the excess is interpreted as being so intimately inclosed in the ore that it is not driven off until temperatures above 110° are reached. In this connection it is interesting to note that all the P_2O_5 and more than half the H_2O+ shown in the manganosiderite analysis are in similar excess. Their presence both before and after replacement implies that they, like the quartz and sericite, were not affected by the solutions that introduced the zinc.

The approximate mineral composition of the gray ore, based on microscopic study and the chemical analysis, is as follows:

Carbonates:		Sericite	0.8
$ZnCO_3$	76.5	Excess MnO	.2
$FeCO_3$	14.5	Excess P_2O_5	.3
$MnCO_3$	3.2	Excess H_2O+	.9
$MgCO_3$	1.0	Excess H_2O-	.5
$CaCO_3$	.5		
Quartz	1.1		99.5

If the carbonates are recalculated to 100 per cent, and the carbonates of the manganosiderite are similarly recalculated from analysis 1, the following comparative results are obtained:

Recalculated composition of manganosiderite and gray zinc ores.

	Manganosiderite.	Gray ore.	Difference (per cent).
$ZnCO_3$	....	79.88	+100.0
$FeCO_3$	51.49	15.14	− 70.6
$MnCO_3$	38.15	3.36	− 91.2
$MgCO_3$	10.12	1.06	− 89.5
$CaCO_3$	.24	.56	+ 57.1
	100.00	100.00	....

The percentage differences—that is, the gain or loss of the different constituents during the replacement process—are given in the third column, which shows that manganese and magnesia were very largely removed in nearly equal proportions, whereas iron was removed in less but still very considerable amount. The increase in calcium carbonate is attributed to the presence of a few microscopic veinlets in the gray zinc ore. The chemistry of replacement is considered further in the discussion of the genesis of the ores (pp. 68—85).

BROWN CARBONATE ORES.

MEGASCOPIC FEATURES.

The brown carbonate ores vary considerably in character. In some places they are hard and compact, without conspicuous vugs or with only very small vugs lined with fine druses of smithsonite (Pl. III, *A*); in others they are softer and may be filled with vugs of varying size lined or nearly filled with white calamine (Pl. IV, *A*). Their color ranges from chocolate-brown to dark brick-red. The only minerals of megascopic size are present in vugs and veinlets. As a rule, where the vugs are small and relatively scarce, they are lined with fine druses of second-stage smithsonite, which may alternate with films of hetaerolite or iron oxide. In the larger vugs similar linings of smithsonite are covered by typical growths of calamine, or in places by exceptionally large growths of hetaerolite or chalcophanite (Pl. I, *B*), which in turn may be covered by calamine. Aurichalcite may accompany the calamine, as in the Ibex mine. (See Pl. V, *B*.)

The compact body of the ore is not to be distinguished at first glance from much of the iron ore or iron-stained manganosiderite, dolomite, or limestone. It may be of uniform brown color or may be spotted with stains of black manganese oxide (hetaerolite?). In some places it preserves rather thin bedding planes and breaks into layers; in others it has a marked conchoidal fracture. It may be hard, or it may be soft and crumbly. Although compact brown zinc ore even of rather low grade may be readily distinguished from iron-stained dolomite or limestone by its higher specific gravity and finer grain, it can not be so distinguished from dense forms of iron ore. Again soft porous ore can not in some places be surely distinguished from either porous iron ore or decomposed wall rock, owing to the relatively light specific gravity of all three materials. Calamine growths in vugs are not an absolutely sure indication of good ore, as one of two samples of similar appearance may prove to be excellent ore and the other to be of too low grade to ship. The latter variety is due in part to a leaching of the brown carbonate to form the silicate, or to the deposition of calamine in cavities of stained and partly decomposed limestone. In one sample the soft brown material around the calamine pockets was found by Mr. Wells to contain only 14.1 per cent of zinc oxide (11.3 per cent of zinc), which on close inspection proved to be largely in the form of minute calamine crystals that had grown within the porous mass. Nearly all the zinc carbonate had been leached, and almost the entire zinc content of the material was contained in the calamine druses. In other specimens, where the carbonate ore was not leached and the calamine was introduced from elsewhere, the value of the ore, already of good grade, was increased.

Of the many specimens of compact ore collected, one, said to represent ore containing 22 per cent of zinc, proved on microscopic study to be composed almost entirely of iron oxide and silica. Another, which was said to contain 30 per cent of zinc but whose texture gave it a close resemblance to the altered manganosiderite that borders some of the ore bodies, was found by George Steiger to contain 50.69 per cent of zinc oxide (40.72 per cent of metallic zinc), 2.38 per cent of insoluble (probably quartz and sericite), only 0.63 per cent of magnesia, and no lime. The specimen had a rather high specific gravity, but that could easily have been attributed to iron originally in manganosiderite.

The brown ore may include small bodies, patches, or seams of the zinciferous clay colored by a small amount of iron oxide. This clay may be distinguished from the brown carbonate by its characteristic properties described on pages 24–28.

Where the original bedding is preserved, thin streaks or bunches of calamine are distributed along the bedding planes and also along short cross fractures that connect bedding planes, as shown in figure 2. This distribution of the calamine, which is well exhibited at several places in the Maid of Erin mine, is of interest in showing the courses followed by the zinc-bearing solutions, which evidently percolated along bedding planes, cross joints, and minor (microscopic) fractures and were thus able to react uniformly throughout a body of great horizontal and vertical extent. The process was evidently entirely metasomatic at first, and any resulting shrinkage may have served to widen the openings along bedding planes and fractures, and perhaps also to develop new contraction fractures, thus allowing percolation of additional solution through already replaced rock to lower levels and affording openings for the deposition of second-stage smithsonite and calamine. The gradation of linear fracture fillings of calamine into vugs, especially at junctions of fractures with one another or with bedding planes, points to the origin of the vuggy ore as the extreme development of the structure just described—crisscross fractures and bedding planes having enlarged into vugs, and the smithsonite having been more or less converted into calamine.

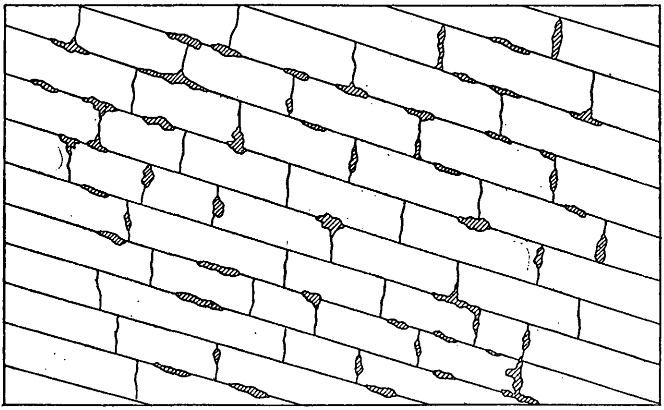

FIGURE 2.—Diagram showing distribution of calamine along bedding planes and cross fractures in brown zinc carbonate ores.

A few vugs have evidently resulted from replacement by smithsonite only along the immediate walls of fractures and the subsequent removal of the unreplaced rock, leaving a cellular ore which is usually of very good grade. Material of similar appearance, however, has been found to be composed chiefly of silica and iron oxide.

MICROSCOPIC FEATURES.

In thin section the brown carbonate ore consists of a very fine, even-grained aggregate of carbonate grains stained by iron oxide but with many microgeodes lined or filled with transparent carbonate grains. (See Pl. III, *B*.) The transparent grains under high magnification show characteristic acute rhombic terminations. Some of them appear pure, some of them have zonal inclusions (or alternating growths) of black manganese oxide (hetaerolite?), and others have similar inclusions of brown iron oxide. The last two occurrences indicate a breaking down of the ferruginous gray zinc carbonate of the first stage and its recrystallization as purer smithsonite of the second stage and iron or manganese oxides. Some of the vugs of second-stage smithsonite are surrounded by what appears to be pure iron or manganese oxide, a relation which also points to a breaking down of the impure zinc carbonate of the first stage, accompanied by segregation of the different products. Throughout the mass of the ore the iron and manganese oxides show this tendency to segregate, the iron oxide having a weak tendency to form a network of hairlike veinlets and the manganese mineral a much stronger tendency to gather into spots or to fill distinct fractures.

The relations of the calamine to the rest of the ore may be illustrated by two contrasted examples. In one a small group of diverging calamine crystals filling a vug was seen to be surrounded by iron oxide, which was opaque except along the edges of the vug, where it formed translucent pseudomorphs after acute smithsonite rhombs. Here the zinc in the calamine was evidently formed largely in place at the expense of smithsonite. In the other example a calamine veinlet cut through a black spot of manganese oxide, proving that it was formed after the breaking up of the impure first-stage carbonate ore was well advanced; but there was no uniform accumulation of iron or manganese oxides along the vein, and the margins of the vein were lined with clear smithsonite rhombs. Inclusions of brown carbonate ore in the vein showed no evidence of leaching. The calamine, therefore, must have been wholly deposited by infiltrating solutions.

One thin section of a specimen of brown ore, taken beneath a sulphide body and very near a mass of gray carbonate ore that contained an inclusion of manganosiderite, is of especial interest in showing the relation of the brown to the gray ore. This section contained within the typical fine-grained carbonate a relatively coarse grained remnant having a texture quite like that of the manganosiderite but showing a relatively weak absorption, presumably due to partial or complete oxidation of the iron. The same section contained quartz-sericite veinlets in both the gray ore and the manganosiderite, and there seems no occasion to doubt that the brown ore at this place is the oxidized product of the gray ore.

The great extent and uniformity of oxidation of the brown ore is a striking feature, as the few small bodies of gray ore appear to be the only remnants of the original zinc carbonate ore that have escaped oxidation. The ore as a whole must have been easily and uniformly permeable by oxygen, a character which indicates a very finely porous structure. It may be suggested that the porosity was developed during replacement of the original rock by gray zinc ore, but are already pointed out (p. 38) the factors influencing porosity in the present gray ore are too varied and opposite in their effects to permit a definite conclusion on this point, and the effects of oxidation add one more obstacle to its determination in the brown ore.

CHEMICAL COMPOSITION.

In the light of microscopic evidence chemical analyses of the brown ores are not difficult to interpret. In the table on page 47 analysis 3 represents the sample of high-grade ore from the Maid of Erin mine which contains the microscopic quartz-sericite veinlets above mentioned and is clearly an oxidized product of gray ore, and analysis 4 an ore of lower grade beneath a Gray porphyry sheet and between walls of dolomite (Blue limestone), from the first level of the New Dome No. 2 mine. Sample 3, in comparison to the gray zinc carbonate ore, represented by analysis 2, contains a larger amount of quartz and sericite. It also contains considerably more iron, and the iron is completely oxidized to the ferric state. Magnesia and lime are each a little higher, whereas zinc oxide and carbon dioxide are correspondingly lower. The absence of phosphoric acid is noteworthy, suggesting its removal in solution during the oxidation and breaking down of the gray carbonate ore. In the material for analyses 2 and 3 calamine druses were avoided. As the irregular distribution of calamine and of iron and manganese oxides renders strictly representative analyses out of the question, the determinations are only made to tenths of 1 per cent.

The calculated mineral composition of the ore represented by analysis 3 is as follows:

Carbonates:	
$ZnCO_3$	71.3
$FeCO_3$	0.0
$MnCO_3$	3.0
$MgCO_3$	1.3
$CaCO_3$	.7
Quartz	2.9
Sericite	2.5
Limonite	15.7
Excess MnO	1.1
Excess H_2O+	.1
Excess H_2O-	.9
	99.5

The excess MnO and H_2O+ are present as black oxide, which is probably hetaerolite, but as the formula of that mineral is in doubt (p. 23) no attempt is made here to estimate its small percentage. Comparison with the mineral composition of the gray ore (p. 39) shows that whereas all the iron has been oxidized, the manganese remains mostly as carbonate. The magnesia and lime carbonates also have remained unaffected during the process of oxidation.

Analysis 4 represents an ore of lower grade and one deposited under somewhat different conditions. The ores represented by analyses 2 and 3 were deposited directly beneath sulphides, by replacement of manganosiderite, but that represented by analysis 4 was deposited directly beneath Gray porphyry, by replacement of dolomite (Blue limestone). The ore is of dark-red color and is too soft to permit the grinding of a thin section, but it contained small vugs of drusy smithsonite and calamine, and so far as could be seen, the only essential difference between it and sample 3 was the presence of a small amount of light-brown zinciferous clay. The silica and alumina in the analysis are accounted for by calamine and zinciferous clay. The ferric oxide is much greater than in analysis 3 and indicates either that the waters which introduced the zinc carried a great excess of iron or that the ore was deposited by different solutions, one, carrying the zinc and some iron, migrating along the bedding planes of the Blue limestone, and another, carrying iron but little or no zinc, working downward through the overlying porphyry. (See fig. 5, p. 55.) The impossibility of learning the exact geologic conditions surrounding this deposit leaves the matter in doubt. The softness of the ore suggests that there has been a downward leaching of zinc, but hard ore directly below the soft contains no more than 30 per cent of zinc, and mere leaching of zinc is far from enough to account for the excess of iron. Another explanation is that after zinc carbonate ore had been formed ferric sulphate solutions, with excess of acid derived by decomposition of pyrite, could redissolve the zinc carbonate, and after they had become neutralized the ferric sulphate in them could become oxidized and be deposited as ferric oxide. The dissolved zinc carbonate could be transferred downward through the ore and replace the dolomite walls, thus extending the original lower limit of the ore body. This hypothesis could also be applied in explaining the layers of iron oxide that are commonly found between lead carbonate and zinc carbonate stopes.

The magnesia in analysis 4, though low, is about three times as high as in analyses 2 and 3, an excess corresponding approximately to the proportional difference between the magnesia in dolomite and in the manganosiderite represented by analysis 1. The lime, however, is quite as low as in analyses 2 and 3, although its difference in the two rocks replaced was decidedly greater than that of magnesia. Manganous oxide is somewhat greater than in analysis 3, but little significance can be attached to the difference, owing to the irregular distribution of manganese oxide stains. The zinc oxide, though much lower than in analyses 2 and 3, is in excess over the available carbon dioxide. The excess, as will be shown presently, in the calculated mineral composition, indicates the proportion of calamine and zinciferous clay present. The higher percentage of combined water (H_2O+) is insufficient to hydrate all the large amount of ferric oxide to the composition of limonite. The absence of phosphoric acid, in contrast to its presence in analysis 2, is again noteworthy.

The following calculation of the mineral composition of the ore is less satisfactory than those made from the other analyses, owing to the indefinite composition of the zinciferous clay and the uncertainty of the exact formula for hetaerolite:

Carbonates:		Kaolin	5.9
$ZnCO_3$	37.5	Calamine	5.0
$MgCO_3$	3.6	Excess ZnO	2.4
$CaCO_3$	.5	Excess MnO	3.3
		Limonite	15.3
		Hematite	24.2
		H_2O-	1.7
			99.4

The kaolin and calamine are of course arbitrarily separated. A little calamine is undoubtedly present, but how much of the calculated calamine is in reality present as zinciferous clay is not known. The excess zinc oxide is for the most part accounted for by the reasonable assumption that all the manganous oxide is present as hetaerolite, but there is a small excess (nearly 0.6 per cent) of zinc oxide over the $ZnO:Mn_2O_3$ ratio demanded by either of the proposed formulas for hetaerolite, and this excess may also be regarded as belonging to the zinciferous clay. The total absence of manganese carbonate can not be proved, but in view of the relatively low carbon dioxide any error in the assumption that all the manganese is oxidized is negligible. The iron oxide is figured so far as possible as limonite, for convenience in comparison with the other analyses, and the excess of iron oxide over water is recorded as hematite. The ratio of water to iron oxide is slightly in excess of that for turgite ($2Fe_2O_3.H_2O$). The red color indicates the presence of a considerable amount of either hematite or turgite.

BLACK ZINC ORE.

The black or brownish-black zinc ore is found only in small quantity and varies considerably in composition. In part it is essentially of the same character as the brown vuggy ore, except for its greater content of a black manganese oxide, which in some specimens has the crystalline structure of hetaerolite or chalcophanite. The vugs are commonly lined with calamine, and some cellular specimens may be found consisting almost entirely of calamine and hetaerolite or chalcophanite, accompanied by a small amount of iron oxide. This silicate-oxide variety of black ore is clearly derived from the carbonate ore. Other samples of black ore are composed chiefly of zinciferous clay stained black by a manganese oxide. The occurrences of this variety seen by the writer were all said to be of low grade. Specimens of the black ore, especially of the silicate-oxide variety, whether of high or low grade, are likely to have a surprisingly low specific gravity, owing to their vuggy or very porous character. No chemical analyses of the black ore were made, as they would serve only to show to what extent manganese and silica had been locally concentrated and carbon dioxide eliminated.

WHITE OR "TALCY" ZINC ORE.

The zinciferous clays, described on pages 24–28, may occur in masses large enough to be considered ore bodies. It is questionable whether they could be smelted at a profit.

ANALYSES.

In the following table are given chemical analyses of the more important varieties of zinc ore discussed above:

Analyses of zinc carbonate ores.[a]

	1	2	3	4
SiO_2	10.08	1.5	4.1	4.0
Al_2O_3	3.16	.3	1.0	2.3
Fe_2O_3	None.	....	13.4	36.9
FeO	26.80	9.0	....	....
MgO	4.04	.5	.6	1.7
CaO	.08	.3	.4	.3
MnO	19.71	2.2	3.0	3.3
ZnO	Undet.	49.6	46.2	30.2
PbO	Undet.	....	....	....
Ag	Undet.	....	....	....
CO_2	33.14	34.4	27.2	15.3
P_2O_5	.47	.3	....	....
SO_3	Undet.	....	....	....
Cl	Undet.	....	....	....
H_2O+	.89	1.0	2.5	3.8
H_2O-	.22	.5	.9	1.7
Na_2O	.57	Undet.	Undet.	Undet.
K_2O	.08	Undet.	Undet.	Undet.
BaO	Trace.	Undet.	Undet.	Undet.
TiO_2	Trace.	Undet.	Undet.	Undet.
FeS_2	.84	Undet.	Undet.	Undet.
	100.08	99.6	99.3	99.6
Metallic zinc	....	39.9	37.1	24.2

[a] U. S. Geol. Survey Bull. 591, p. 240, 1915.

1. Manganosiderite, seventh level Tucson mine (collected by J. D. Irving). J. G. Fairchild, analyst.
2. Gray zinc carbonate ore, Maid of Erin mine, first intermediate above second level. R. C. Wells, analyst.
3. Brown zinc carbonate ore, Maid of Erin mine, "high line" level. R. C. Wells, analyst.
4. Red zinc carbonate ore, New Dome mine, first level (at No. 2 shaft). R. C. Wells, analyst.

RANGE IN METAL CONTENT OF THE ORES.

ZINC CONTENT.

The zinc content of the ores varies greatly from place to place. In some stopes bodies running over 40 per cent of zinc have been mined, and many others, especially in the Carbonate Hill workings, have yielded much ore averaging 30 per cent of zinc. In fact, up to the end of 1913 the Western Mining Co.'s great shipments did not run below 28 per cent. These high-grade bodies, however, are bordered and separated by large quantities of lower-grade ore, averaging about 20 per cent of zinc, and these in turn may grade into iron ore or altered dolomite, in which the percentage of zinc drops to practically nothing. In some places the transition from pay ore into low-grade material is gradual; in others, pay ore is rather sharply bounded by unaltered rock, an altered zone a few inches or a foot or two in thickness separating the two.

In some places it is a rather easy matter to distinguish between ore and waste, but in others distinction is possible only after frequent and careful sampling. Two of the most influential factors causing this difficulty are the varying degree of porosity and the varying though usually considerable percentage of iron in the ore. Some high-grade ore closely resembles altered manganosiderite or dolomite in color and texture, but its microscopic porosity would lead to an underestimate of its zinc content. Another sample of similar appearance and approximately equal specific gravity may prove on analysis to contain a large amount of iron, either as ferrous carbonate or as ferric oxide. Some brown zinc ores of moderate to high grade may be practically identical in appearance with very low grade zinc ore, or even to iron and iron-manganese ores. High-grade brown vuggy ore with calamine druses may have the same appearance as leached brown earthy material with similar druses. Considerable experience may give the ability to detect inconspicuous though critical differences between ore and waste, but the principal result of experience tends rather to make one more cautious than ever, and to depend on frequent sampling and assaying as the only reliable means of distinguishing ore from waste.

This question of the grade of the ores was experimentally investigated by Butler,[1] who analyzed and determined the specific gravity of nearly 50 specimens and found that they all absorbed water slowly, but at varying rates, for many hours. In order to procure comparable data, he allowed particles weighing about 1 gram to soak 15 minutes before weighing, his determinations thus representing the specific gravity of the samples with their pores nearly filled with

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[1] Butler, G. M., Econ. Geology, vol. 8, pp. 14–15, 1913.

air. He states that in consequence of these and many other tests, it can be said that an ore with a specific gravity of less than 3.3 as determined in this way is in all probability of too low grade (under 27 per cent) to be mined profitably when the market price of zinc averages about 5 cents a pound, as it did during the greater part of 1913, when Butler's paper was written. The following table gives the results of Butler's determinations, together with calculated specific gravities of seven of the samples based on chemical analyses:

Data on oxidized zinc ore of various grades from Leadville.

Ore.	Per cent of zinc.	Observed specific gravity.	Calculated specific gravity.	Effervescence in dilute hydrochloric acid.
1. Light gray, granular, with cavities; considerable pyrite and other sulphides visible.	17.7	3.5	3.8	Very slight.
2. Reddish brown, earthy	20.9	2.7	3.6	Vigorous.
3. Reddish brown, earthy, with cavities	22.4	2.7	....	Do.
4. White, finely granular, compact to earthy	23.7	2.9	3.6	Considerable.
5. Brown, cryptocrystalline; many cavities lined with druses of smithsonite crystals, some of them underlaid with psilomelane.	30.4	3.8	....	Do.
6. Light gray, very finely granular, cavernous, a few druses of scalenohedral calcite.	31.4	3.9	....	None.
7. Dark brownish-red, cryptocrystalline; many cavities with druses of smithsonite crystals; some psilomelane and calamine.	31.5	3.9	....	Considerable.
8. White, with a brownish tint, very finely granular, with a spongy appearance; microscopic drusy cavities.	32.4	3.9	....	None.
9. Same as No. 7 but contains no calamine or psilomelane.	32.7	3.9	4.0	Considerable.
10. Same as No. 5	38.4	4.0	4.1	Very slight.
11. Yellowish brown, microscopically spongy to very finely granular and compact.	41.6	3.9	4.1	Considerable.
12. Brown and white, cryptocrystalline to earthy, with a cavernous appearance; cavities wholly or partly filled with calamine.	45.4	3.7	....	Do.
13. Same as No. 12 except that some hydrozincite is recognizable.	45.4	3.9	....	Do.
14. Yellowish brown, very cavernous, with thin, plane walls.	46.0	3.9	....	Very slight.
15. Light yellowish brown, finely granular, cavernous	46.4	4.0	4.2	Considerable.

Butler's analyses of seven of these samples are given in the following table:

Analyses of oxidized zinc ores from Leadville.

	1	2	4	9	10	11	15
Zinc	17.7	20.9	23.7	32.7	38.4	41.6	46.4
Lime	.8	.3	.6	.3	.4	.3	.9
Magnesia	.8	1.1	.7	2.2	2.0	.4	.5
Silica	4.0	22.4	33.6	3.3	3.8	8.7	.9
Iron	17.0	14.7	5.4	12.2	5.1	3.5	2.2
Sulphur	.6	.....	.....	.....	.....	.....	.....
Alumina	.4	2.2	2.8	.4	.2	.2	.2
Manganese	11.2	2.1	2.0	.....	6.0	2.8	.....
Insoluble	4.4	24.8	34.6	3.8	4.2	9.0	2.2

Sample 1 is evidently a partly replaced manganosiderite and has a specific gravity nearly as high as those of the high-grade samples. The other low-grade specimens show a much greater discrepancy between observed and calculated specific gravities than the high-grade ores and evidently possess a much higher degree of porosity. The relation between specific gravity and the zinc percentage in the high-grade samples, however, shows that specific gravity is not a closely accurate indication of the grade of ore.

The degree of effervescence of fragments in dilute hydrochloric acid (3 parts water to 1 of acid), as determined by Butler, is given in the first table on page 49 and, as he states, is not of much avail as an indication of the grade of ore. Similar tests by the present writer confirm those of Butler. Gray zinc carbonate ores, which contain considerable amounts of iron carbonate, and also the manganosiderite yield little or no effervescence, as shown by samples 1, 6, and 8. Even when partly stained by oxidation, they effervesce very slightly. In the more thoroughly oxidized samples, where fine drusy or second-stage smithsonite is abundant, effervescence is more pronounced.

Blowpipe tests by Butler on all grades of the material yielded similar results, regardless of the percentage of zinc, low as well as high grade ores giving the characteristic sublimate of zinc oxide.

In concluding his discussion of the grades of the ores, Butler outlined the following method for quick determination of the grade:[1]

> Probably the simplest method for quickly ascertaining the approximate grade of oxidized zinc ore is to place about a teaspoonful of the finely powdered material to be tested upon a piece of iron or steel barrel hoop, 1½ to 2 inches in width. This charge should be introduced into the incandescent coals of a blacksmith forge which has been blown until little black smoke is evident. The iron should be sunk into a depression in the glowing coals so that they stand a half inch or so above the sample on all sides. Then the draft should be increased until the iron is heated white hot. Oxidized zinc ore will take fire at this point, burning with a bluish flame and emitting white fumes of zinc oxide. The density of these fumes varies with the grade of the ore. Experience enables one to judge within 5 per cent of the zinc content by this method, which, although long known and practiced in some places, is unfamiliar to those in other localities. The scheme can be applied to ore of any grade, as material assaying 5 per cent zinc will yield visible fumes.

OTHER CONTENTS.

If the percentages of zinc oxide and carbon dioxide are subtracted from analyses 2, 3, and 4 on page 47, and the remainder recalculated to 100 per cent, the iron oxides will range from 50 to over 65 per cent. The residues, therefore, after extraction of the zinc become possible iron or manganiferous iron ores. The content of silver in each of the ores analyzed is less than 0.001 per cent. As 1 ounce per ton of 2,000 pounds equals 0.0034 per cent, it is doubtful whether the residues from ores corresponding to these analyses would contain enough

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[1] Op. cit., p. 17.

silver to pay for its extraction. Although these samples analyzed are believed to represent typical oxidized zinc ores of the district, there may be exceptions, for it has been stated that early shippers of rich silver ore appear to have purposely broken the zinc ore in some places.[1]

DISTRIBUTION AND MODE OF OCCURRENCE OF THE ORES.

GEOGRAPHIC DISTRIBUTION.

Oxidized zinc ores have been found in practically all the hills of the district, as far east as the Resurrection mine, near the head of Evans Gulch, and as far south as the Continental Chief mine, at Weston Pass, 9 miles south of Leadville. Thus far, however, although extensive low-grade bodies have been reported from several places, all the high-grade deposits in the other hills have proved very small in comparison with the immense bodies in Carbonate Hill.

DISTRIBUTION WITH RESPECT TO KINDS OF COUNTRY ROCK.

The oxidized zinc ore bodies thus far found are limited to the horizons of the two limestones. The small bunches of red siliceous zinc material found in fissures cutting a porphyry sill in the Belgian mine are the only deposits noted that were not within or along a contact of one of the limestones. Porphyry and quartzite in different places form rather sharply defined roofs or floors to ore bodies of considerable size.

RELATIONS TO THE DIFFERENT KINDS OF LEAD CARBONATE AND MIXED SULPHIDE ORE BODIES.

The ore bodies thus far worked are all closely associated with blanket bodies of lead carbonate ore. For the most part the zinc bodies underlie the lead bodies, but in some places they have replaced the same strata, either down the dip or even along the strike. Those in the Ibex No. 1 (Little Johnnie), although they are in the vicinity of lode fissures and magnetite-pyrite bodies, are immediately associated with old blanket stopes. The only apparent reason to account for this association is that the lode fissures and magnetite-pyrite bodies in this vicinity have not as a rule been subjected to oxidation, and their original zinc content accordingly has not been removed to form a body of oxidized ore. The Luema vein contains a considerable quantity of zinc blende, and as its upper part is oxidized, a corresponding quantity of oxidized zinc ore could be expected somewhere along the vein, below the level of oxidation. None, however, has been

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[1] Eng. and Min. Jour., Feb. 14, 1914, p. 396.

found, and the only apparent explanation is that the strong kaolin ("talc") selvages along the vein have prevented any considerable quantity of zinc solutions from penetrating into the limestone walls. It is also possible that the great amount of kaolin has absorbed the meager amount of zinc from the solutions, giving rise to zinciferous clay; but this point has not been tested.

One feature that is of great annoyance to miners and prospectors and is difficult to explain satisfactorily is the lack of uniformity in the relations between the oxidized zinc bodies and the associated blanket lead bodies. At the north end of Carbonate Hill large bodies of both have been mined, but in Fryer and Iron hills, where large blanket deposits of lead ore have been mined, only small bodies of zinc ore have thus far been found among a great amount of iron-stained "contact matter," and some of these bodies have not been of very high grade. In some places, although blanket lead stopes are of considerable size, associated zinc ore has been found only in small bunches from a few inches to 3 or 4 feet in diameter.

The causes of this variation are probably several and can be best discussed in connection with the genesis of the ores. (See pp. 68–85.) It may be stated here, however, that the size of a zinc body depends on the amount of zinc in the original ore body, the kind and distribution of openings through which the waters transferring the zinc had to pass, the composition and texture of the rocks through which the waters passed, and the materials that accompanied the zinc in solution. Consideration of these factors, in places where the zinc ores have been mined or searched for, may yield a satisfactory explanation; but without a knowledge of them it is impossible to make a definite prediction as to the size and position of oxidized zinc bodies that may be associated with old blanket bodies of lead carbonate.

As none of the old blanket stopes were accessible to the writer, predictions regarding the location and extent of undiscovered bodies are not warranted here. It may be said that the amounts of "vein matter" shown in the cross sections by Emmons[1] suggest the probable presence of good oxidized zinc bodies in the northern part of Carbonate Hill other than the bodies already worked and of good-sized bodies on other hills; but experience in Fryer and Iron hills proves that the thickness and extent of "vein matter" shown in Emmons's sections are far from being good indicators of the amount of zinc ore present.

In two places noted by the writer bodies of oxidized zinc ore of rather low grade are not closely associated with old lead-silver stopes. In the Cord Mining Co.'s workings (Page lease, 1913) a small body of red zinc carbonate ore has been mined, which is 150 to 200 feet away (down the dip) from the nearest known lead-silver stope of

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[1] U. S. Geol. Survey Mon. 12, atlas, 1886.

any considerable size. The ground in the immediate vicinity, up the dip, has not been prospected, and it can not be stated whether the zinc was carried in solution for an unusually long distance before being deposited, or whether there may be an undiscovered lead-silver body nearer the zinc carbonate body.

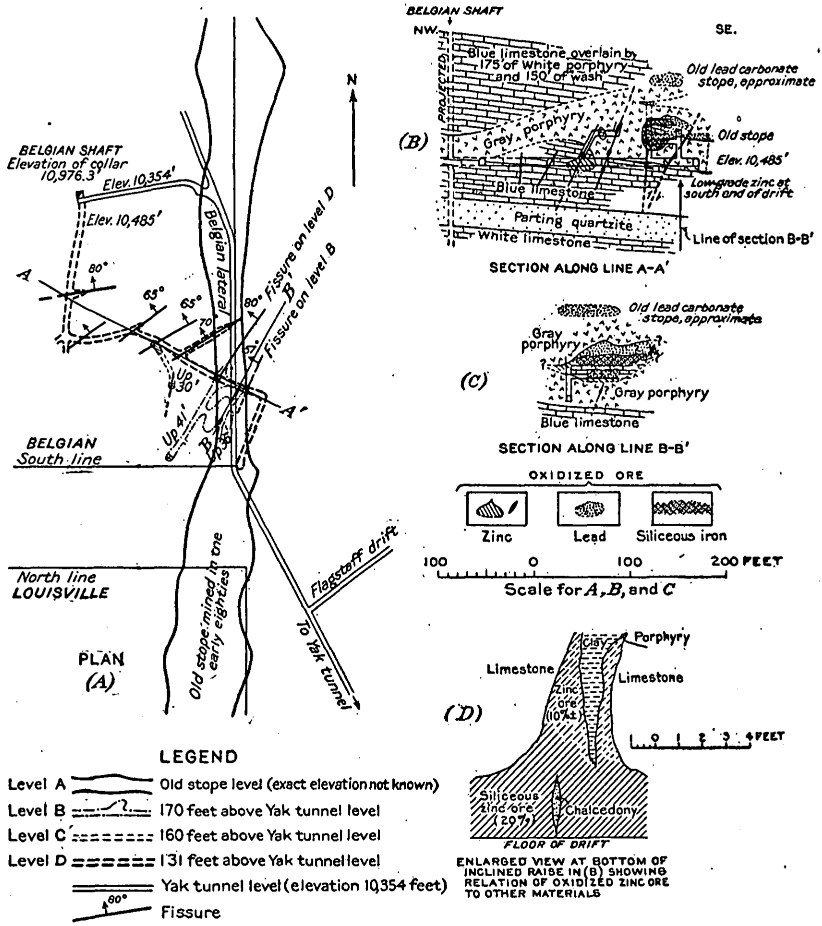

FIGURE 3.—Plan and sections of lead-silver stopes in Belgian mine. Oxidized zinc ore occurs chiefly along the three fissures nearest to these stopes. Section *A–A'*, shows relation of zinc ore to lead-silver stopes. Section *B–B'* shows siliceous iron oxide immediately below lead-silver stopes and small deposit of low-grade zinc material in the angle between converging bodies of Gray porphyry. Fissures in the lower body of porphyry contain small bunches of siliceous zinc material. The sketch (*D*) shows relations of siliceous zinc ore, clay, and chalcedony in fissure just below porphyry contact, 170 feet east-southeast of Belgian shaft.

In the Belgian mine (Fenton lease, 1913) small bodies of low-grade siliceous oxidized zinc ore were formed by the replacement of limestone at the base of a complex Gray porphyry sheet, which separated the zinc ore below from silver-lead bodies above, as shown in figure 3. Fissures containing small amounts of very low grade red siliceous zinc material pass through the porphyry, and some of them certainly connect zinc bodies with lead-silver bodies, although the largest of the zinc ore exposures appears to have the most remote connection. There seems, however, no reason to doubt that the zinc-bearing solutions were able to travel for considerable distances through unfavorable porphyry to a more favorable place before depositing any considerable quantity of zinc.

SHAPES AND SIZES OF ORE BODIES.

GENERAL FEATURES.

The ore bodies, as shown in the different plans and sections (figs. 3 to 7 and Pls. VII and VIII), are for the most part very irregular. Nevertheless, they show in several places structural features that go far toward indicating their origin. The simplest examples are represented in the sketches in figure 4, illustrating the mode of occurrence in the Oro La Plata mine. Figure 4, C, represents zinc carbonate ore of shipping grade forming borders or casings to a lead stope that had replaced the wall rock along a fissure. The zinc on oxidation of the primary (sulphide) ore evidently moved downward, at the same time permeating the limestone for a distance of 2 feet or more. Figure 4, *B*, illustrates a place where the zinc solutions, descending from a blanket sulphide body, found the easiest course along a fracture plane, replacing the fracture walls and infiltrating to some extent along the more open bedding planes. Occurrences in the Maid of Erin mine similar to these have been described by Philip Argall.[1] Figure 4, *A*, illustrates what is probably

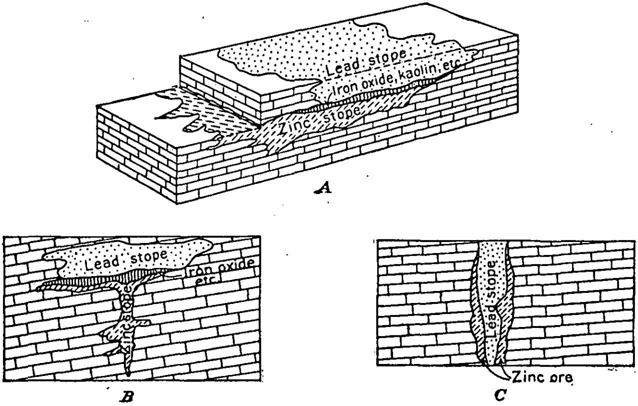

FIGURE 4.—Diagrams illustrating relations of oxidized zinc ore bodies to lead carbonate stopes in the Oro La Plata mine: *A*, Replacing beds beneath a blanket stope; *B*, replacing rock along fissure and beds beneath a blanket stope; *C*, replacing walls of a fissure stope.

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[1] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, p. 284, 1914.

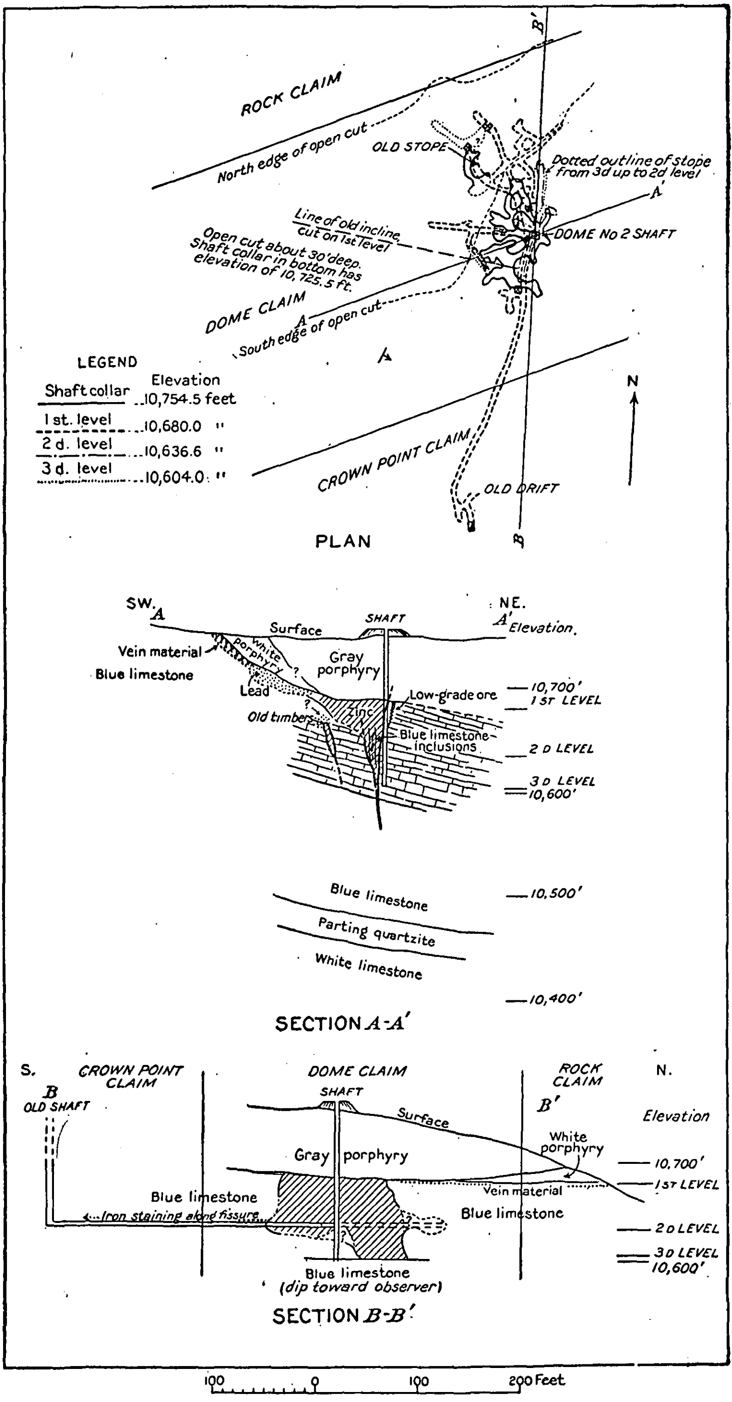


FIGURE 5.—Plan and sections showing relation of oxidized zinc ore body on the Dome claim to old lead carbonate stope. Section *A–A'*, an east-west section through the Dome No. 2 shaft, shows concentration of ore in shattered ground along fissures; section *B–B'* shows northward pitch of ore body.

the most common mode of deposition, in which the zinc solutions worked down into the beds just beneath a blanket stope and then tended to migrate downward along the dip. In one of the stopes in the Ibex mine the zinc solutions migrated outward and replaced the same strata as the original ore body, the silver-lead and the zinc stope lying side by side.

Other ore bodies represent some combination of the conditions just described. The New Dome deposit, represented by figure 5, illustrates the downward migration of the zinc solutions along bedding planes just beneath a Gray porphyry sill as far as a fissured zone, which then afforded the readiest channel. The shattering of the rock along the fissure zone permitted the replacement to extend over a rather great width in proportion to length and depth.

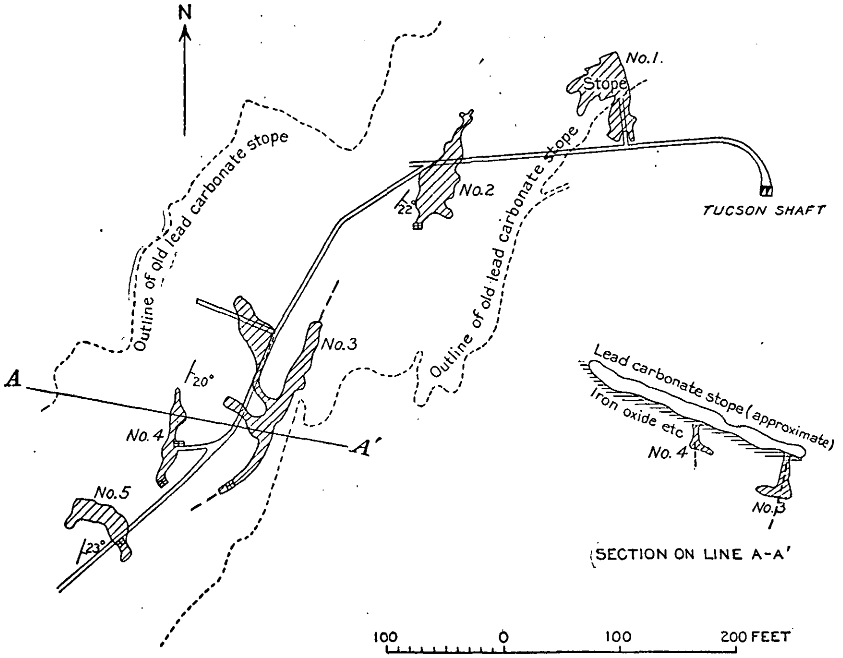


FIGURE 6.—Plan and section showing relations of oxidized zinc ore stopes (shaded) to old lead carbonate stopes, Tucson mine.

The plan and section of the Tucson first level (fig. 6) also illustrates the development of the oxidized zinc ore bodies along fissures, with local spreading along bedding planes and minor fractures. The scattered distribution of these small bodies beneath a large continuous old silver-lead stope is in marked contrast to the extensive bodies of the northern part of Carbonate Hill.

CARBONATE HILL ORE BODIES.

The enormous size and the details of outline of the Carbonate Hill bodies can be explained to some extent, but the surrounding ground is so thoroughly altered and soft and in large part so inaccessible that a complete explanation of all the details is out of the question. The plan of these ore bodies is shown in Plate VII and cross sections in Plate VIII. The outlines of stopes in the plan are not everywhere indications of the boundaries of the ore body. In several places the narrow stopes, which might be interpreted as branches of ore along fissures, merely represent beginnings of stopes or exploration drifts to block out ore. Other boundaries represent the limits of high-grade ore without giving any idea of the large amount

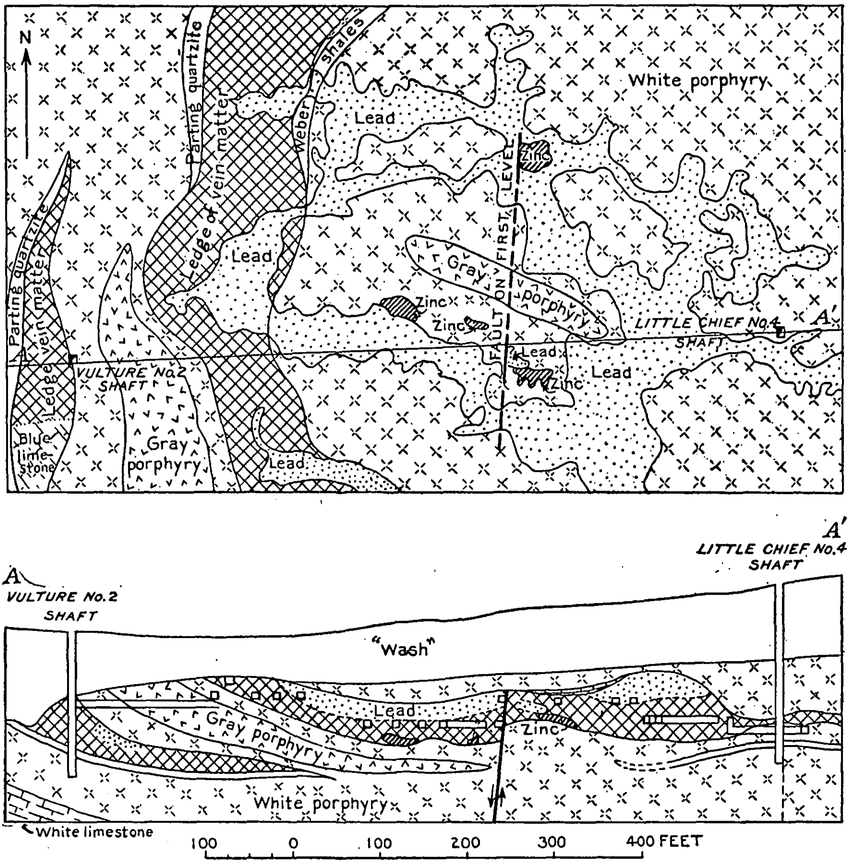
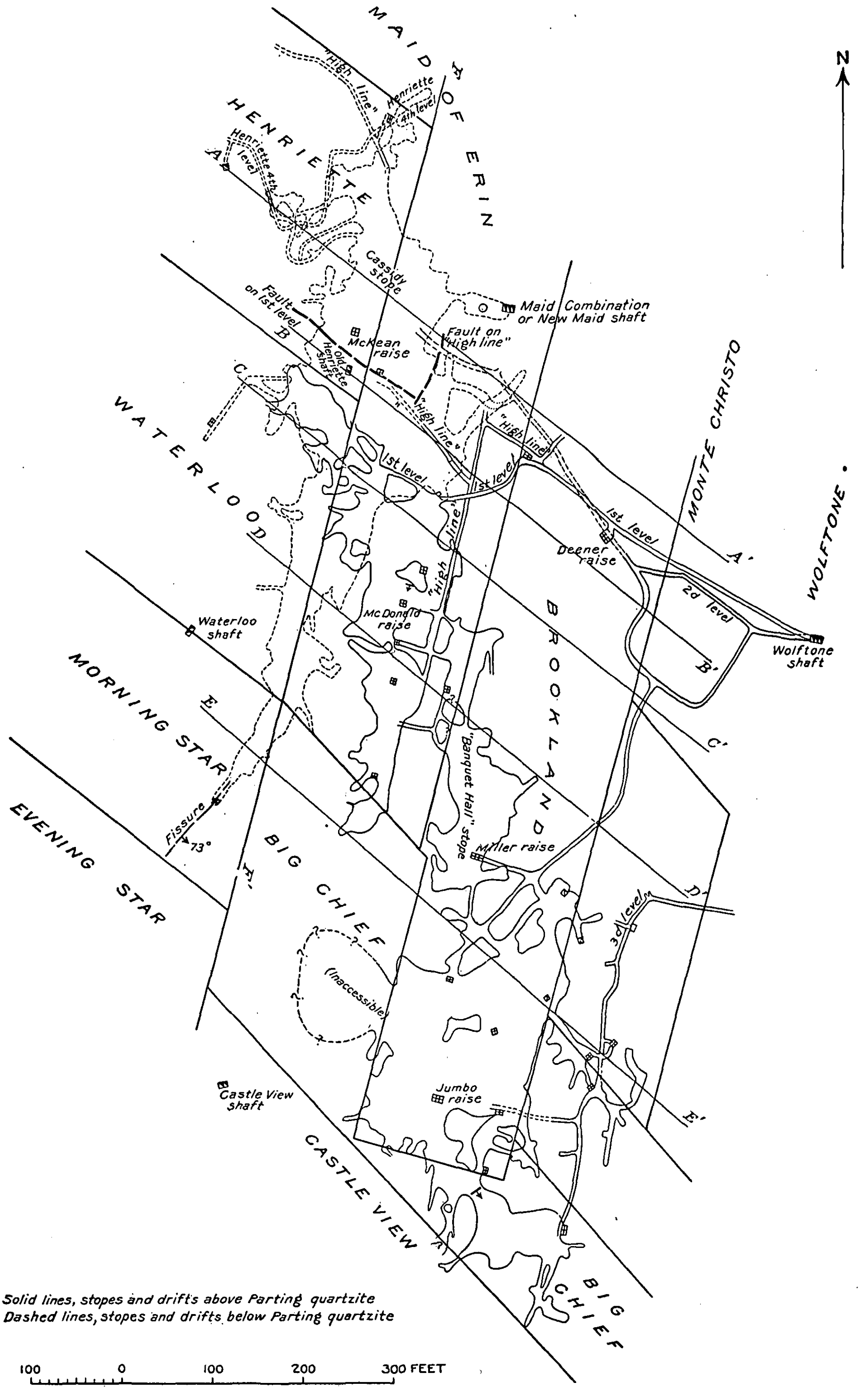


FIGURE 7.—Plan and section showing relations of oxidized zinc ore to old lead carbonate stopes in Chrysolite mine. Outlines of lead carbonate stopes copied from atlas sheet 31, U. S. Geol. Survey Mon. 12. Outlines of zinc stopes only approximate. Surface east of the outcrop of vein matter is all White porphyry except the dike of Gray porphyry in the central part of the area. Section adapted from section *B–B*, atlas sheet 32, U. S. Geol. Survey Mon. 12.

of adjacent low-grade ore (averaging near 20 per cent of zinc). The vertical sections throw more light on the dimensions of the ore bodies, but it must be remembered that the outlines of these sections are for the most part approximations, as the boundaries of the ore bodies in most places either had not been reached or were no longer accessible. The sections are somewhat generalized to include important features near but not exactly on the lines of the sections.

In sections A–A and F–F, Plate VIII, the maximum thickness, about 130 feet, of the ore body beneath the Parting quartzite is shown, the ore extending in places down to the Cambrian quartzite. Evidence pointing to the cause of this unusual thickness is very scanty but suggests a plausible explanation. Data on the size and distribution of associated old lead stopes, which have been exposed at a number of points, are scarce and indefinite. Such exposures beneath the Parting quartzite represent comparatively thin blanket bodies. A large stope has been exposed in a raise through the quartzite, but little is known of its extent and thickness. Comparison with the stope map of the monograph on the Leadville district of which this paper is to form a part will show that these old stopes lie close to the area of extreme metallization, but, although this fact indicates that there was an abundance of oxidized lead-silver ore in the immediate vicinity, there is no means of knowing whether the bulk of the zinc migrated vertically downward through the Parting quartzite, or down along the dip beneath the Parting quartzite. Both processes no doubt took place, but it can not be said which predominated.

Although the immediate sources of the zinc ore are very obscure, there is some evidence in the location of faults and open structure of the rocks to account for the great thickness of some of the ore bodies. The southeastward dip of the strata is interrupted by a fault of west-northwesterly trend (section F–F), with relative down-slip on its south side. This fault was exposed at only one place, on the first Wolftone level, and its length and exact course are not known. The amount of displacement where the fault is exposed must be at least 25 or 30 feet, according to the positions of exposures of the Parting quartzite on either side; but the Parting quartzite does not appear to have been displaced to the east, along the "high line" drifts connecting with the Deener raise, and it is therefore concluded that the fault stops against one of north-northeasterly trend, as suggested in Plate VII. A strong clay-filled fissure, corresponding in position to the suggested north-northeasterly fault, was exposed on the "high line" 90 feet east of the McKean raise. The ground on both sides of it consisted of ore or thoroughly altered carbonate rock, and no idea of the amount of displacement could be gained. It is significant, however, that ore of shipping grade was not being mined on the east side of this fissure.



PLAN OF ZINC CARBONATE ORE BODIES IN WORKINGS OF WESTERN MINING CO.

This fissure with its heavy clay filling evidently served as an effective barrier, at least locally, against the spreading of the zinc solutions. The Parting quartzite, as may be inferred from sections A–A and F–F, Plate VIII, could also have served in places along both faults as a barrier against circulation along the bedding, although in the planes of both sections it happens that blocks of unreplaced carbonate rock are exposed on the up-slip sides of the fault. Just what protected these masses from replacement can only be inferred from the evidence presented in the next paragraph. The distribution of the quartzite on both sides of the fault would tend to impound the solutions and to deflect them downward to some point where they could escape from the fault block.

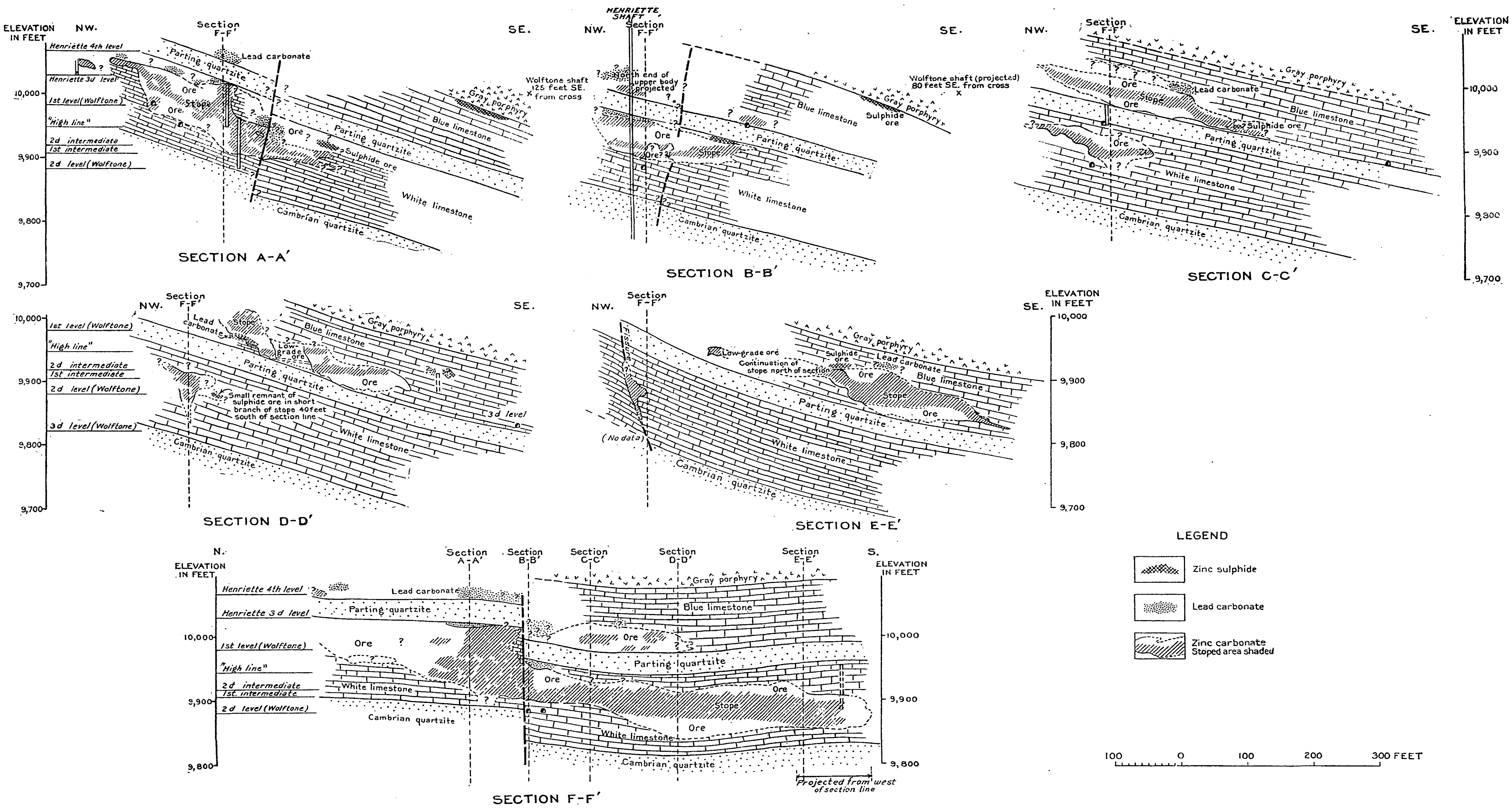
At several places in the stopes of this thick ore body the generally open structure of the replaced carbonate rock is well preserved, as illustrated in figure 2 (p. 42). The bedding planes are mostly open and connected by short cross fractures, thus allowing the impounded solutions to permeate the rock throughout a vertical range bounded only by the top and bottom of the White limestone. The inclusions and bordering masses of carbonate rock found here and there, including those represented in sections A–A and F–F, Plate VIII, owe their preservation, to judge from their small exposures, to the local absence of this characteristic open structure. Most of these inclusions and masses are now stained by oxidation, and no tests of their composition were made, but the inclusion represented in section A–A proved to be typical manganosiderite. A specimen of this inclusion proved to be surprisingly porous for a crystalline rock, a character which, if common to the rock as a whole, would afford more complete permeation when once the zinc solutions had gained access along the numerous bedding and fracture planes. The porosity alone, however, was evidently not sufficient to allow extensive permeation.

The great thickness of the ore body therefore appears to be due to a combination of three conditions—the distribution and local impounding influence of two faults, the distribution of the Parting quartzite, and the open structure of the carbonate rock in the block bounded by the faults. That the faults were not effective barriers at all points is shown in sections F–F and B–B, Plate VIII, which represent the ore body extending across the lines of faulting. So far as underground study is concerned the principal factor in determining the shape of the ore body as far south as the line of section C–C, Plate VIII, was the open structure of the rock. From this line southward the ore body gradually assumes a narrow elongate outline (sections D–D and E–E) and at its southern extremity is limited to a width of 5 feet or less, replacing the dolomite walls of a fissure. The relation of the preserved bedding planes on each side of this fissure indicate faulting but give no idea of the amount of displacement. The occurrence in the fissure of a small amount of dense white quartz inclosing microscopic grains of a decomposed ferruginous carbonate and perhaps also of pyrite indicates a presulphide age for this fissure. The zinc ore along this fissure, as along those in other mines already described, tends to spread for short distances along the bedding and in one place was found to inclose a small bedded layer of sulphide ore, consisting chiefly of galena with cavities partly filled with calamine to mark the probable former presence of zinc blende.

The narrow stope extending northeastward from the east side of the lower ore body between the lines of sections B–B and A–A, Plate VIII, has no apparent connection with a pronounced fissure and is not necessarily a close indication of the limits of the ore. It deserves special mention, however, because it has yielded gray zinc carbonate ore, clearly formed by the replacement of manganosiderite, directly underneath a mass of sulphides. The existence of this ore is evidently due to the migration of zinc solutions chiefly along bedding planes east of the line of the fissure described on page 59. The geology was too much obscured by timbering here to warrant a more definite statement.

The upper ore body of Carbonate Hill, above the Parting quartzite, extends obliquely down the dip from a point near the old Henriette or "Old Maid" shaft to the southwest boundary of the Big Chief claim, a distance of about 1,050 feet. Its boundaries, however, are sharply defined at only a few points, and the factors influencing its outline can only be inferred rather than determined. The branch stope that extends a little west of south, just crossing the Big Chief northeastern boundary, underlies old silver-lead stopes that have been exposed at different points. It has at one place on its west side a nearly vertical dolomite wall opposite a wall of low-grade (10 per cent) ore. No strong fissures were exposed in the ground accessible to the writer, but the trend of the higher-grade ore and the position of its walls strongly indicate replacement along a fractured zone. At one place just south of the Big Chief line the ore narrowed downward to a fissure filling only a few inches wide.

Northeast of this branch stope, about 50 feet south of the line of section C–C, Plate VIII, the zinc ore, with an inclusion of manganosiderite, was seen directly underlying a mass of pyritic sulphide ore. There was no indication of distinct fissuring in the ground accessible. The inclusion of manganosiderite, however, would, from analogy with the evidence obtained in the thick portion of the lower ore body, warrant the inference that the rock replaced by the ore was of open structure.



SECTIONS THROUGH ORE BODIES SHOWN IN PLATE VII

About 100 feet south of this point, in the Banquet Hall stope, the ore body attained a thickness said to be 50 feet, and still farther south, a short distance beyond the line of section E–E, it was as thick or thicker. The ore was worked out in the former place, but in the latter it was seen to preserve the open structure of the original rock. This thick body underlay old silver-lead stopes, but nothing is known of their dimensions. The body diminished rapidly in thickness eastward, and on the east side of the main third level drift, along the line of section E–E, had dwindled to a bedded replacement deposit only 2 or 3 feet thick.

The most reasonable inference to account for the shape of the upper ore body, based on the scanty evidence presented, is that the rock had become more or less shattered along certain zones characterized by anastomosing fractures rather than pronounced fissures. The zinc solutions, descending from the oxidizing blanket bodies (now the old silver-lead stopes), found the easiest courses along these zones, with the result that bodies of relatively great thickness in proportion to their width were formed by replacement of the carbonate rock. The width of the ore body was limited by the extent of the openings in the rock; the depth, as shown in sections D–D and E–E, was limited by the Parting quartzite, which in places has been exposed as the approximate floor of the stopes. Whether or not these zinc solutions found their way in any considerable amount downward along fractures through the Parting quartzite has not been demonstrated by mining. It seems doubtful, however, in view of the size of the ore body and its depth with respect to oxidation, if any considerable amount of zinc carbonate or silicate ore can be expected beneath it, on the under side of the Parting quartzite.

Comparison of the position of the Carbonate Hill bodies and the slopes on the surface fails to show a concordant relation. The depths of oxidation as recorded in Emmons's notes are likewise independent of the topography, and it is evident that the depth and circulation of ground water has been governed rather by the rock structure—that is, the trends of the open portions of fissures, minor fractures, and bedding planes.

CHARACTER OF BOUNDARIES OF THE ORE BODIES.

The character of the boundaries of the ore bodies, as has already been mentioned, varies in different places, and little additional description is necessary. It seems desirable, however, to summarize the variations and to check them with certain chemical data. The simplest case includes the rather sharply defined nearly vertical walls along nearly vertical fissure bodies. The west wall of the fissure stope near the south end of the lower Carbonate Hill body is sharply bounded by soft, sandy dolomite, a specimen of which was found by R. C. Wells to contain 1.28 per cent of zinc oxide, or 1.59 per cent of zinc carbonate. At the northwest end of the small fissure stope in the New Dome mine (fig. 5) similar but more rusted soft material bordering the stope was found by George Steiger to contain 19.22 per cent of insoluble matter, 0.36 per cent of magnesia, 0.53 per cent of lime, and 6.33 per cent of zinc oxide. The zinc here showed a stronger but still not great tendency to permeate the wall rock, which elsewhere in the mine is Blue limestone (dolomite). The insoluble material appears to be chiefly silica intimately associated with brown iron oxide and possibly combined with the zinc as zinciferous clay. This material, only a few inches thick, passed into unstained dolomite. Similar siliceous material was found along the main body of the New Dome mine on the first level. The occurrences in the Maid of Erin mine, described with assays by Argall,[1] are of similar character, though the transition from ore to country rock is more gradual.

Some of the bedded zinc carbonate bodies have rather clearly defined floors, though not nearly so sharply defined as the fissure walls just described. Two specimens taken from the floor of a small bed stope in the Ibex mine, one at the very contact of the stope and the other 5 inches below it, were found by Mr. Wells to contain respectively 27.4 and 14.9 per cent of zinc oxide, or 22 and 12 per cent of metallic zinc. These figures indicate a gradual change from ore into country rock within a zone between 1 and 2 feet thick. The bottom of the upper ore body of Carbonate Hill is in places abruptly bounded by the Parting quartzite, the top layers of which have been deeply stained by iron and manganese oxides, which may be accompanied by a little zinciferous clay. The lower ore body is said to be similarly floored by the Cambrian quartzite at a few places. At one place in the lower ore body, about 230 feet west-northwest of the Deener raise (Pl. VII), the high-grade ore passes downward into a decomposed low-grade material consisting chiefly of silica with minor amounts of iron oxide and clay, which appears to be the residue of a siliceous or silicified carbonate rock. In other places the ore passes downward into unaltered carbonate rock. Such variations evidently depend on the composition of the rock replaced and on the amount of leaching that has been possible since the deposition of the zinc ore.

The sides of the bedded bodies may be rather abruptly bounded, but much more commonly they are marked by a gradual decrease in zinc content so that the high-grade ores merge into large bodies of ore averaging near 20 per cent in zinc. How extensive such low-grade bodies are has not been definitely stated, but they are said to constitute large reserves in several different places.

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[1] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag. (London), vol. 10, p. 284, 1914.

The main factor determining the character of the boundary is evidently rock structure. Where permeable rock is abruptly limited, as along clear-cut fissures or impervious beds, either of quartzite, shale, or porphyry, the contact is also abrupt; where the rock bordering the main ore channels is of more open structure, there is likely to be a gradation from high-grade ore through a large extent of low-grade ore into barren rock. In the latter case the degree to which zinc is concentrated in the solution may be an important factor, solutions above a certain strength readily replacing the rock, whereas solutions below that strength but otherwise under similar conditions could react only slowly and to a small extent. No experimental data are at present available to throw light on this matter.

The upper contacts of the ore bodies are marked for the most part by layers of siliceous iron oxide and clay in varying amounts, which separate the zinc ore from overlying lead-silver bodies. These layers range in thickness from a few inches to 6 feet or more. They are characteristic of oxidized zinc deposits in several mining districts and are subject to more than one interpretation. They may represent the first substances deposited by the solutions that transferred material downward from the oxidizing sulphide bodies; they may represent the oxidized residue of a largely insoluble material which formed a casing to the original sulphide bodies; they may be the insoluble residue left by the leaching of the topmost part of the zinc carbonate body; or they may consist principally of material leached from the original ore bodies at a relatively late stage and deposited at the same time that the topmost part of the zinc carbonate was being leached. Partial evidence in different places suggests one or another of these processes, and it is possible that a combination of processes took place. It is also possible that one process may have been of relatively great influence in one district and of relatively slight influence in another, owing to differences in chemical conditions. The chemical conditions are considered in the discussion of ore genesis (pp. 68–85).

Where the oxidized zinc bodies have been seen immediately underlying porphyry or shale, their upper contacts are marked by a layer of zinciferous clay that may be 2 or 3 feet in thickness. The presence of the clay is evidently due to the alumina and silica leached from or residual after the porphyry or shale. In some places it seems that the alumina must have been precipitated with the zinc; in others it seems probable that the clay, already present, has adsorbed zinc from solutions which have come into contact with it.

At a few places bodies of oxidized zinc ore have been found in contact with bodies of iron or manganiferous iron ore. These contacts are considered in the following paragraph.

RELATIONS TO OXIDIZED IRON AND MANGANIFEROUS IRON ORES.

The oxidized zinc ores have been found beside and beneath oxidized iron and manganiferous iron ores and have also been reported to occur above them. The evidence obtained by the writer, while affording some explanation of these variations in distribution and occurrence, does not point to any systematic association. The lack of systematic association may be appreciated when it is realized that the iron ores may have originated from the complete oxidation of either pyrite or manganosiderite masses, and that the zinc ore may have been deposited directly either beneath or beside masses of either of these materials; also that the primary shoots of zinc blende from which the oxidized zinc ores were derived were irregularly scattered through the sulphide bodies or were in places underlain by manganosiderite. The evidence as a whole indicates that if either an oxidized iron or zinc ore body is present a body of the other may be present close by; but the relative position of the two bodies can not be predicted. In view of the relative abundance and distribution of the primary minerals, pyrite, manganosiderite, and zinc blende, it is evident that the presence of the iron ore is not a certain indication of the presence of the zinc ore, for large bodies of almost pure pyrite bordered by manganosiderite are known to exist with no noteworthy amount of zinc blende in the immediate vicinity. Oxidation of such a body would yield a large deposit of iron and manganiferous iron ore, with no associated body of zinc ore.

VERTICAL DISTRIBUTION AND RELATION TO DEPTHS OF OXIDATION AND GROUND-WATER LEVEL.

Oxidized zinc ores have been found in a few places close to and even at the surface and at varying depths down to 750 feet. The depths at different places depend as a rule on the depths of the contact of the White porphyry and Blue limestone, as most of the zinc bodies have been found in association with the "first contact" ore bodies of this horizon. The deepest deposit in the northern part of the Maid of Erin mine is associated with a series of ore bodies including "second contact" bodies (below Gray porphyry) and with bodies just above and just below the Parting quartzite. It is in the White limestone, extending in places from the base of the Parting quartzite even down to the top of the Cambrian quartzite. This is the thickest and one of the largest two oxidized zinc ore bodies thus far worked in the Leadville district. It is associated with the thickest as well as one of the most continuous bodies, or series of bodies, of lead-silver ore in the district, and general conditions appear to have been favorable to concentration rather than dispersion of the zinc.

All the zinc carbonate and silicate thus far mined have been found in the zone of complete oxidation, except the lowest parts of the great Carbonate Hill bodies. These, as indicated in sections A–A to F–F, Plate VIII, in places underlie sulphide ore. In some of these places the zinc ore is practically in immediate contact with the sulphides and may even inclose small amounts of them and of associated manganosiderite. Here the zinc ore has been deposited below the local depths of oxidation.

These exposures of sulphides over or within the zinc ore have been made at depths of about 640 to 700 feet and more below the collar of the Wolftone shaft. Old lead carbonate stopes were noted as far down as about 650 to 660 feet below the shaft collar. These figures, based on observations at several places in the Western Mining Co.'s ground, place the average local depth of complete oxidation about 640 to 650 feet below the collar of the Wolftone shaft, or at an elevation of about 9,950 feet. They correspond closely with figures in Emmons's notes, for he found the depths of oxidation to be at an elevation of 9,936 feet (660 feet below the surface) in the Wolftone mine, 9,941 feet (639 feet below the surface) in the Brookland, and 9,981 feet (667 feet below the surface) in the Upper Henriette. Emmons's notes, however, show that the depth of oxidation fluctuates considerably in the northern part of Carbonate Hill.

The relation of the oxidized zinc ores to ground-water level can not be definitely shown, because the original water levels in different places have been greatly disturbed by underground operations. All the ore bodies studied, except those in the northern part of Carbonate Hill, are well above the original ground-water level, so far as can be learned from available data. It is stated that in northern Carbonate Hill water to-day would rise to a level about 300 feet below the surface in the Wolftone shaft were pumping operations to cease. This is over 300 feet above the average depth of complete oxidation and well above all the oxidized zinc bodies thus far mined. It can not, therefore, be considered as any indication of the original ground-water level. Neither can the average depth of complete oxidation be considered a close indication of the original ground-water level, as oxidation is known to extend somewhat below that level in some places and considerably below it in excessively fractured zones. On the other hand, sulphide bodies of small to considerable size are found, in more protected ground, above ground-water level. The depths at which the zinc carbonate and silicate are found are also unreliable indications, for the reason that they may be deposited by the replacement of limestone below as well as above ground-water level. The composition of the zinc carbonate ores is such as to indicate that they were deposited in the absence of free oxygen, a condition that may exist in the lower part of the ground above the water level as well as below it.

The zinc carbonate ores also show that they themselves have certainly, to a large extent, undergone considerable oxidation and leaching, a fact which proves the downward migration of the oxidized zone since the bulk of the carbonate ores were deposited. The ground-water level also doubtless migrated downward, keeping pace with surface erosion. It is obvious, therefore, that no exact relations can be determined between the distribution of the oxidized zinc ores and the ground-water level. The evidence as a whole, however, indicates that the zinc carbonate ores were deposited close to if not in part below the water level that then existed, and it is possible that their lower portions were still below the natural water level that existed just prior to the disturbances caused by mining.

LACK OF ASSOCIATION WITH SECONDARY SULPHIDES.

No evidence of secondary sulphides of any kind was found in connection with the oxidized zinc ores, and no positive evidence of secondary zinc sulphide was noted anywhere in the district. The sulphide ore exposed in contact with the zinc carbonate ores had all the characteristics of primary ore. Even small grains of pyrite, zinc blende, and galena found inclosed in the ore proved under the microscope to be intimately associated with veinlets and patches of quartz and sericite, the typical gangue minerals of primary sulphide ore. The three sulphides, as well as the quartz and sericite, were evidently unaffected by the zinc-bearing solutions that replaced the carbonate rock.

The sulphide masses adjacent to the zinc carbonate ore are all composed largely, if not entirely, of pyrite, but no sign of zinc sulphide, either sphalerite or wurtzite, upon pyrite was found. This is a point of some significance in view of the conclusions expressed by Blow and Emmons (see p. 10) that the zinc removed from the oxidized zone had been precipitated just below water level and had thus migrated downward at equal pace with the limits of oxidation. The only available agents for the precipitation of zinc as a sulphide, on the assumption that the zinc was in solution as sulphate, were a very small quantity of organic matter and a large quantity of pyrite.

It has been assumed by some writers that pyrite or marcasite has precipitated secondary zinc sulphide, especially in deposits of the

Mississippi Valley; but experiments with the two minerals have not confirmed this assumption, at least in a convincing way. The experiments of Schuermann[1] and Weigel[2] lead to the conclusions that under certain conditions zinc has a slightly stronger affinity for sulphur than iron has—in other words, that zinc sulphide is slightly more insoluble than iron sulphide—but that the two metals are so very nearly equal in solubility that any precipitation of zinc sulphide at the expense of an iron sulphide would not be nearly so marked as a precipitation of silver or copper sulphide by the same agent. The conditions of these experiments by no means duplicate the conditions governing the secondary deposition of zinc minerals at Leadville. So far as they go, they may suggest that if pyrite can precipitate zinc sulphide from the ground waters in question, it does so very slowly and can hardly precipitate large quantities of zinc blende just below the zone of oxidation.

The only experiment, to the writer's knowledge, in which zinc sulphide has been precipitated by pyrite or marcasite is one by Stokes[3] who treated pyrite and marcasite each with an excess of zinc carbonate and potassium bicarbonate in sealed tubes filled with carbon dioxide for 24 hours at 180° C. Other experiments under similar conditions, also by Stokes, on the action of alkaline solutions alone on pyrite and marcasite show that the alkaline solutions, including potassium bicarbonate, decompose pyrite and marcasite. It therefore seems probable that the potassium bicarbonate was the influential factor in making the precipitation of zinc sulphide possible. In the Leadville deposits the secondary zinc solutions, whether sulphates or carbonates, evidently found the surrounding carbonate rock to be more readily replaceable than the pyrite. After the zinc carbonate had been thus precipitated the conditions, including low temperature as well perhaps as absence of a sufficient amount of alkali in solution, were not right to convert it to secondary sulphide at the expense of pyrite.

Experimental evidence is thus negative, and local field evidence shows that conditions were not favorable for the precipitation of secondary zinc sulphide. Local evidence furthermore accords with general evidence, which has been discussed by W. H. Emmons,[4] who says:

> It has frequently been stated that zinc sulphide has been precipitated at the expense of iron sulphide and that zinc has driven iron out of its sulphide com-

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[1] Schuermann, Ernest, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, p. 326, 1888.

[2] Weigel, Oskar, Die Löslichkeit von Schwermetallsulphide im reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, pp. 293–300, 1907.

[3] Stokes, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, p. 17, 1907.

[4] Emmons, W. H., The enrichment of sulphide ores; U. S. Geol. Survey Bull. 529, p. 86, 1913.

bination, but no examples of the pseudomorphous replacement of pyrite or marcasite by zinc blende are available. On the other hand, Hintze[1] notes a pseudomorph of marcasite after zinc blende.

Lindgren[2] states that "zinc is not, as a rule, deposited as a secondary sulphide, and no authentic case has been recorded where it replaces pyrite, as chalcocite so often does." In his discussion of Bain's conclusion that secondary zinc and other sulphides have been deposited at Joplin, Mo., below the zone of oxidation, he states[3] that "possibly this has taken place on a small scale, but most of the ore immediately below the oxidized zone appears to be of primary origin."

In a few places, the most recently discovered of which has been described by B. S. Butler,[4] wurtzite, the hexagonal form of zinc sulphide, occurs as a probable secondary mineral. Butler, while suggesting that the replacement of pyrite by zinc sulphide may be possible, remarks that—

> in none of the ore examined can the zinc sulphide be seen replacing the iron, but there are abundant specimens that show wurtzite surrounding sphalerite, apparently as a later growth on it. This suggests that the precipitation has been effected by agents other than the pyrite, and that the attraction of the sphalerite had caused the secondary sulphide to be added to it. * * * E. T. Allen and J. L. Crenshaw have suggested that acid solutions containing zinc sulphate and hydrogen sulphide in solution on having their acidity reduced would precipitate zinc sulphide. That such solutions are formed in the zone of oxidation there can be little doubt, and as they pass to lower levels their acidity may be reduced either by solutions from the adjacent limestone or by reaction with alkali silicates that form a part of the gangue of the ore.

From this evidence it would seem possible that wurtzite could be found crystallized upon zinc blende in some of the Leadville deposits at or below the downward limit of oxidation, but no such occurrence, to the writer's knowledge, has been reported. So far as positive evidence is concerned, no bodies of secondary zinc sulphide have been formed. The bodies of zinc blende just below the zone of oxidation, referred to by Blow and Emmons, can doubtless be interpreted as primary and can be shown to differ in no essential way from other segregated deposits of zinc blende found well below the zone of oxidation, such as have been found in the Cord mine below the level of the Yak tunnel.

GENESIS.

That the oxidized zinc ores of the Leadville district are believed to have been derived through oxidation of zinc blende in the original

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[1] Hintze, Carl, Handbuch der Mineralogie, vol. 1, p. 481.

[2] Lindgren, Waldemar, Mineral deposits, p. 811, 1913.

[3] Idem, p. 834.

[4] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 154, 1913.

sulphide ore must be apparent to all who have read the foregoing pages. Below are considered the chemical processes involved in the derivation. Some of the evidence afforded by study of the specimens and underground workings may not accord perfectly with all the experimental data available, and such discordances necessarily leave some doubt as to the exact conditions of chemical equilibrium which existed and which exerted a greater or less influence on the reactions that took place. The genesis of the ores may be conveniently considered in three stages.

FIRST STAGE.

DERIVATION OF MATERIALS.

The original ore bodies consisted essentially of the ore minerals pyrite, zinc blende, and galena, with small amounts of chalcopyrite in places and of the gangue minerals manganosiderite, quartz, and sericite, the gangue minerals for the most part forming a casing around the ore bodies. The zinc blende was the ferruginous variety, marmatite, composed of about 3 parts zinc sulphide and 1 part iron sulphide, as shown by the following analyses:

Analyses of zinc ore from Leadville district.[a]

[A. W. Warwick, analyst.]

	Adams.	Colonel Sellers.	Yak.
Zinc [b]	52.8	47.6	45.1
Sulphur	34.7	35.7	36.4
Iron [c]	12.1	14.8	17.8
Silica	.2	.4	.2
	99.8	98.5	99.5

[a] Bain, H. F., U. S. Geol. Survey Mineral Resources, 1905, p. 384, 1906.
[b] Includes cadmium, which varied from 0.1 to 0.35 per cent.
[c] Includes manganese, which varied from 1.3 to 3.7 per cent.

Study of the sulphide ores in the Leadville district and of similar ores in other districts shows that the zinc blende is the first of the ore minerals to be removed by oxidation and may be nearly or quite all removed before the other sulphides are attacked to any considerable extent. The rapidity and thoroughness of removal would obviously depend on the degree to which oxidizing solutions could permeate the ore of the three sulphides. Galena is the most protected from oxidation, owing to the insolubility of the sulphate which forms around it. The writer has seen very little chalcopyrite in place at Leadville and has no definite data at hand regarding its position in the order of oxidation. His observations of ores in other districts would lead him to favor the view that chalcopyrite underwent oxidation before the pyrite and after the zinc blende—a view which accords with the occurrence of copper in the oxidized zinc ores at Leadville and with the interpretation of their genesis but which does not harmonize with certain experimental data.[1] The conditions of these experiments, however, do not approach very closely the natural conditions under which the Leadville ores were oxidized.

These experimental data have been summarized and discussed by W. H. Emmons, who makes the following concluding statement: "All these experiments and observations seem to indicate that in the zone of oxidation in many deposits the sulphides are dissolved in the following order: Sphalerite (?), chalcocite, pyrrhotite, chalcopyrite, pyrite, galena, enargite." The positions of sphalerite, chalcopyrite, pyrite, and galena in this order accord with the writer's observations.

The ore bodies are covered by a greater or less thickness of porphyry, through which the oxidizing waters must have descended. Those bodies which are exposed at the present surface were once covered by porphyry, or in some places by the Parting quartzite and porphyry, and oxidation in all probability began before these overlying rocks were removed. Possible exceptions may have existed locally where sulphide bodies unusually well protected from preglacial oxidation were exposed by glacial scouring and were later oxidized by waters that had not previously passed through porphyry; but study of the geologic sections in the atlas accompanying Monograph 12 shows convincingly that in practically all the places where oxidized zinc ore bodies have been found the oxidizing waters must have descended for considerable distances along major and minor fractures through porphyry.

The porphyries which the writer has studied, both White and Gray, are extensively altered to aggregates of pyrite, quartz, and sericite, and it is most probable that alteration of this type extended for a considerable distance above the "first contact" bodies. The descending waters, therefore, already containing oxygen and carbon dioxide from the air, attacked and decomposed the pyrite, taking ferric and ferrous sulphates and sulphuric acid into solution. In the earliest stages of oxidation the supplies of oxygen as well as of free sulphuric acid and ferric sulphate may have become exhausted through further reactions before reaching the ore bodies, but as the erosion surface and the limits of complete oxidation were gradually lowered these active reagents persisted until the ore bodies were reached. The waters at this stage probably contained in solution considerable quantities of alkalies, alkaline earths, carbon dioxide, and oxygen, but larger quantities of the two iron sulphates and sulphuric acid.

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[1] Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull, 529, pp. 76–78, 1913.

The presence of alkalies and alkaline earths may have exerted some influence in accelerating the processes of solution and deposition, as suggested by Nishihara.[1] Minor quantities of alumina and silica also were doubtless present in solution, as indicated by the composition of many mine waters that have percolated through pyritized siliceous rocks.[2]

Of these constituents sulphuric acid, ferric sulphate, and oxygen had the most influence on oxidation and the removal of the sulphides. It is doubtful if carbon dioxide could have exerted much solvent action on zinc blende, so long as these three constituents were present in excess, owing to the much higher degree of solubility of zinc sulphate than that of zinc carbonate. This statement is supported by the fact that where descending waters have locally evaporated in the Leadville mines, desposits of goslarite, the zinc sulphate, have been found, but none of a zinc carbonate. Experiments by Gottschalk and Buehler[3] have shown that although zinc blende alone when leached by water is oxidized very slowly, the process is hastened if the water has first descended through pyrite or marcasite—that is, if it has first become charged with sulphuric acid and ferric sulphate. They have shown also that oxidation is much more rapid if the blende is in contact with galena or especially with pyrite, the oxidation being accelerated by electrolytic action. The water used in these experiments is not strictly analogous in composition to the ground waters that had descended through the pyritized porphyries of Leadville, but the results of the experiments accord with those of the natural process. Whatever the exact reactions were, the zinc blende was oxidized before the other two sulphides, and there is little doubt that the zinc and iron of the zinc blende were removed as sulphate.

The supply of free oxygen in these solutions probably became exhausted at an early stage of the process, and it may be that more or less sulphuric acid and ferric sulphate were still available for further reactions. Experiments by R. C. Wells[4] have shown that sulphuric acid, out of contact with air, dissolves zinc blende more readily than it dissolves either galena, pyrite, or chalcopyrite, converting the zinc to sulphate and setting free hydrogen sulphide. The hydrogen sulphide, if free to escape upward, could finally reach the zone of free oxygen, oxidize, and thus tend to renew the supply of sulphuric acid; if not free to escape it could, after the sulphuric acid had become exhausted, possibly succeed in reprecipitating some of the zinc as the hexagonal sulphide, wurtzite, but no evidence has been found to

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[1] Nishihara, G. S., Geology and ore deposits of the Tetiuxe district, Russia: Econ. Geology, vol. 12, pp. 277–278, 1917.

[2] Analyses of 37 such waters are tabulated and discussed by W. H. Emmons (U. S. Geol. Survey Bull. 529, pp. 60–74, 1913).

[3] Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides: Econ. Geology, vol. 5, pp. 28–36, 1910; vol. 7, pp. 15–34, 1912.

[4] Emmons, W. H., op. cit., pp. 59, 76.

show that this reaction has taken place in the Leadville deposits. Ferric sulphate, out of contact with air, could also convert the zinc and iron in zinc blende to sulphates, setting free sulphur and itself changing to ferrous sulphate. The disposition of the free sulphur under these conditions is questionable, but there is nothing to indicate that it played a conspicuous part in the genesis of the oxidized zinc ores. The results of these reactions which may have taken place after the free oxygen in the descending waters had become exhausted served to supplement those of the reactions which had taken place before—in other words, to increase the amount of zinc sulphate, and also of ferrous sulphate, already in solution.

After the reactions that produced zinc and iron sulphates in solution had been completed, the carbon dioxide in solution may have aided to a minor extent in the further decomposition of zinc blende by uniting with some of the zinc in solution as bicarbonate, leaving a corresponding amount of sulphuric acid to continue attack on the sulphide. The original amount of carbon dioxide in solution may have been considerably increased if the descending waters passed through any carbonate rock, either manganosiderite or dolomite, before their supplies of sulphuric acid and ferric sulphate had become exhausted.

The reactions outlined above are believed to include all that appear to have been important in the decomposition of zinc blende and the provision of a supply of zinc available for deposition as oxidized ore. The materials that were taken into solution, or left in solution, as a result of such reactions are principally zinc sulphate, ferrous sulphate, and more or less zinc and iron carbonate, with corresponding amounts of lime, magnesia, and manganese sulphate.

DEPOSITION OF MATERIALS FROM SOLUTION.

Deposition in the oxidized zone may take place by processes of hydration and oxidation of the solutions, desiccation or evaporation, reaction or metasomatic interchange with the wall rock, and reaction between different solutions. The first two of these processes have resulted in deposition of some iron sulphate, goslarite (the hydrous zinc sulphate), hetaerolite, hydrozincite, some smithsonite, and calamine. Reaction between different solutions may have caused deposition of some of the zinciferous clays, waters descending through porphyry with alumina and silica in solution reacting with zinc-bearing waters that percolated along the lower contact of the porphyry and depositing the layers of zinciferous clay along the bottom of the porphyry. Metasomatic interchange with the wall rock, however, has been the chief agent in producing the deposits of commercial grade, although these deposits have been more or less reworked by one or more of the other processes.

The disposition of the materials can most conveniently be discussed by following the different courses which the water may have followed after its leaching of the zinc from the sulphide bodies. Where the water, after taking zinc sulphate into solution, became locally supersaturated through desiccation, while still in the sulphide body or in a porphyry sill beneath the sulphide body, goslarite was formed (and is being formed), lining fractures and other openings. The only occurrence of goslarite seen by the writer in his study of the Leadville sulphide ores was a coating on pyritic sulphide ore along a drift on the sixth level of the Tucson mine. The mineral here formed white, soft, fine, hairlike crystals associated with relatively thick prisms of epsomite, a hydrated sulphate of magnesia, the two minerals forming a parallel fibrous growth. Such deposits are only temporary, being redissolved sooner or later by unsaturated waters which reach them.

Where the waters pass through the sulphide bodies into underlying rocks two sets of conditions may be considered, according to the kind of rock (porphyry or carbonate rock). Each of these sets of conditions may be subdivided into two phases—one in which the free sulphuric acid and ferric sulphate have not been exhausted and the other in which they have been exhausted. If the underlying rock is sericitized porphyry, and sulphuric acid and ferric sulphate are present, either or both of these reagents will tend to decompose the sericite and any unaltered feldspar in the porphyry, taking into solution silica and sulphates of alumina and alkalies. The alumina and silica will tend to be precipitated again, perhaps without having traveled for any considerable distance, as kaolin, or material of similar composition and appearance. This process will also cause the deposition of an indefinite amount of zinc and result in zinciferous clay. Whether the zinc is deposited simultaneously with the other materials as a primary constituent of the clay or through the replacement of aluminum in clay previously deposited is an open question. Where the percentage of zinc in such clay is very high it could be regarded as a primary constituent; where the percentage of zinc is low it could be regarded either as the result of replacement or as a primary constituent of clay deposited from a solution poor in zinc. The origin of the iron and manganese oxides locally present in these clays is obscured by their segregation, since their deposition, into red, brown, and black patches and streaks. They, like the zinc, may have been original or secondary (adsorbed) constituents of the clay. Under all these suppositions the precipitation of aluminum and zinc compounds from solution may imply the liberation of a corresponding amount of sulphate radicle and the renewal of sulphuric acid capable of dissolving new portions of the rock and tending to repeat the process until the water itself should become exhausted or should reach ground-water level.

Where the entire process has taken place within the porphyry mass, the zinciferous clays are scattered along fissures and minor fractures in the porphyry; where the waters containing the constituents of the clay in solution passed through the porphyry into carbonate rock, the clay was deposited through metasomatic replacement, the size and shape of the deposit depending on the relative openness of fractures and bedding planes and on the amount of clay material introduced. The chemical reactions involved in this replacement are not simple, but the replacement of carbonate rocks by masses of kaolin is not an uncommon occurrence.

It is believed that the process outlined above goes far toward explaining the occurrence of low-grade siliceous and argillaceous zinc ore like that at the base of a porphyry sill in the Belgian mine. (See fig. 4, p. 54.) This ore contains veinlets and vugs lined or filled with calamine, which was deposited with and just after the clay and appears to represent the excess of zinc over that which could be contained by the clay. The opal and chalcedony closely associated with the calamine represent a further excess of silica. The presence of calamine appears also to indicate that sulphuric acid and ferric sulphate had become exhausted, and that zinc sulphate in the neutralized solution, concentrated by depletion of the water, could not remain in solution in the presence of an excess of silica. The absence of any conspicuous amount of smithsonite in this deposit is noteworthy as an indication that carbon dioxide was a very minor constituent of the solution which introduced the zinc. The presence of a few miscroscopic needles of aurichalcite associated with the calamine and chalcedony also points to the scarcity of carbon dioxide, as it is probable that the basic carbonates of zinc are deposited when there is no excess of carbon dioxide.

It is known that sodium carbonate produces a basic carbonate of zinc, when added to zinc sulphate; on the other hand, sodium bicarbonate yields a normal carbonate. Raikow[1] showed that an excess of carbon dioxide transforms the hydroxide of zinc into the normal carbonate.

If the descending waters on passing from the sulphide body into underlying porphyry have been depleted of their free sulphuric acid and ferric sulphate, it is doubtful if any considerable replacement of the wall rock can occur, at least until the waters become concentrated through depletion or adsorption by wall rock material. It seems unlikely that the difficultly soluble minerals of the porphyry can be readily replaced by interchange with the easily soluble sul-

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[1] Raikow, P. N., Weitere Untersuchungen über die Einwirkung der Kohlensäure auf die Hydrate der Metalle: Chem. Zeitung, vol. 31, p. 55, 1907.

phate of zinc, and no indication of such a process has been noted. It seems probable, on the other hand, that such a solution will pass through the porphyry until ground-water level is reached, or until concentration by the above-mentioned factors causes the deposition of goslarite, or of calamine in the presence of sufficient silica, or of zinciferous clay in the presence of alumina and silica. The alumina and silica would presumably have been derived chiefly from gangue material within the sulphide body and from porphyry above the ore body. Workable deposits of calamine with more or less zinciferous clay could be formed in this way where excessive fracturing of the porphyry would afford an opportunity. It is possible also that in such places some replacement of the shattered porphyry by these minerals could be effected if the solutions were sufficiently concentrated, but no such deposits in porphyry have been noted at Leadville.

If the solution with a high content of zinc should pass through the porphyry into carbonate rock, deposition of the zinc as carbonate by replacement would be possible, and the process would be analogous to that described below.

None of the Leadville deposits can be attributed chiefly to this set of conditions, although the occurrence of zinc carbonate bodies separated from parent sulphide bodies by a sheet of porphyry is a possibility. If the solution were low in zinc and in consequence relatively high in silica and alumina, calamine and zinciferous clay could be expected, as the conditions would be similar to those illustrated by the occurrence in the Belgian mine.

Where the solution passed directly from the sulphide body into carbonate rock, either manganosiderite or dolomite, and contained an excess of sulphuric acid and ferric sulphate, the sulphuric acid would at once be neutralized by reaction with the carbonates. If free oxygen were also present in solution, a corresponding amount of ferrous sulphate formed by the reaction would be oxidized to ferric sulphate, and this together with ferric sulphate already in solution would react further with the carbonate rock and be precipitated as ferric hydrate, according to the following equation:[1]

$$Fe_2\ (SO_4)_3+3(Fe,\ Mn,\ Mg,\ Ca)CO_3+3H_2O=2Fe(OH_3)+3(Fe,\ Mn,\ Mg,\ Ca)SO_4+3CO_2.$$

The ferric hydrate thus formed would, by gradual loss of a part of its water, be gradually transformed into one of the hydrous oxides and thus account for a part of the iron oxide in the layers that separate the lead-silver stopes above from the zinc carbonate stopes

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[1] The action of sulphuric acid and ferric sulphate on limestone has been studied by W. Meigen (Beiträge zur Kenntnis des Kohlensauren Kalkes: Naturforsch. Gesell. Freiburg im Breisgau Ber., vol., 13, p. 76, 1903). The equation given above is adapted from one given by Meigen, in which $CaCO_3$ is the only carbonate represented.

below. The carbon dioxide formed by this reaction would augment the small amount already present in solution.

If aluminum sulphate were present in considerable amount it may have reacted in the same manner as the ferric sulphate and have been precipitated in the presence of sufficient silica to form kaolin. The greatest argument for this reaction is the intimate association of kaolin with iron oxide in the layers just mentioned. There is also evidence that small amounts of alumina, now present as pockets of zinciferous clay in zinc carbonate ore, were formed at a later stage. The precipitation of the silica in the kaolin may be attributed to the mutual absorptive tendencies of colloidal silica and ferric and aluminum hydroxides. More or less zinc may have been removed from solution by the same influence at this time. The solution, after being depleted of free sulphuric acid and ferric sulphate, would meet the same conditions as those considered in the next paragraph.

Where the solutions had become depleted of free sulphuric acid and ferric sulphate before reaching the carbonate rock, no layer of ferric oxide and kaolin would be formed at first, but replacement of the carbonate rock by zinc carbonate would occur. This reaction has usually been explained by the simple equation

$$ZnSO_4+CaCO_3=ZnCO_3+CaSO_4,$$

zinc carbonate being precipitated as smithsonite and calcium sulphate passing off in solution. This reaction, however, although it plays an important part in the process, is not sufficient to explain the entire metasomatic process involved in the deposition of the Leadville zinc carbonate ores. Direct replacement of calcium, magnesium, and manganese carbonates by zinc carbonate involves a high percentage of shrinkage; similar replacement of iron carbonate involves less but still considerable shrinkage. Some of the Leadville zinc carbonate ore of the first stage, as shown on page 38, presents some indications of shrinkage, but the amount is so much obscured by later processes of leaching and cavity filling that it can not be even approximately measured. Other specimens of the gray ore which show little or no evidence of leaching contain no pore spaces large enough to be detected with the high powers of the microscope, and the only evidence of shrinkage is the presence of microscopic fractures containing veinlets of smithsonite. The metasomatic process in this material, as shown on page 38, evidently proceeded by infiltration of the solution along the boundaries of the original carbonate grains and replacement of them from the boundaries inward, leaving a very small amount of indeterminable material (unreplaced carbonate?) in the center of each grain. The only conclusion warranted by such inconsistent evidence is that some shrinkage may have been developed during replacement but did not develop everywhere in an amount sufficient to correspond to the effects of a direct molecular replacement of dolomite or manganosiderite by the gray zinc carbonate ore.

This problem in metasomatism has been discussed by Lindgren,[1] who states:

> Replacements of limestone by smithsonite within the rigid rocks are quite common, and in this case the mineral often reproduces exactly the texture of the original rock, even to the most minute details; the resulting secondary zinc mineral is compact and at least not more porous than the original limestone. If this replacement were effected according to a chemical equation, be it by substitution of zinc for calcium in carbonate or by interchange of zinc sulphate and calcium carbonate, a reduction in volume should necessarily be expected. It does not take place provided the metasomatic action goes on within the mass of the rock itself.

It is therefore necessary to look to the mineralogic evidence in the ores for suggestions as to the metasomatic processes that took place. This evidence, presented in the ore descriptions, shows that both manganosiderite and dolomite were replaced by the gray zinc ore, also that after replacement of manganosiderite by ferruginous smithsonite had ceased fractures and other openings were partly or completely filled by smithsonite relatively free from iron.

The descending zinc solutions, depleted of free sulphuric acid and ferric sulphate and most or all of their alumina, contained principally zinc and ferrous iron, with minor amounts of manganese, alkalies, and alkaline earths, chiefly as sulphates and to a minor extent as bicarbonates. Silica was also present. The conditions of chemical equilibrium that exist when so complex a solution attacks the complex carbonate rock manganosiderite can be only roughly inferred from experimental data on relatively simple solutions and compounds. Lack of solubility is the predominating factor in determining the order of separation of the products of such a reaction.[2] The composition of the gray ore is proof that under the conditions here discussed zinc carbonate was the least soluble product. It is therefore concluded that the zinc in solution as sulphate replaced the bases of the manganosiderite, and that the zinc in solution as carbonate was also precipitated. Precipitation of zinc as smithsonite thus proceeded either until the manganosiderite was completely replaced or until the total zinc in solution became exhausted.

Any shrinkage due to replacement by reaction between zinc sulphate and manganosiderite is believed to have been compensated by simultaneous precipitation of the zinc carbonate from solution, as long as the supply of zinc and the carbonate radicle remained. If the supply was insufficient to compensate fully for shrinkage, a corresponding amount of shrinkage space in the gray ore must have

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[1] Lindgren, Waldemar, The nature of replacement: Econ. Geology, vol. 7, p. 530, 1912.

[2] Johnston, John, and Niggli, Paul. The general principles underlying metamorphic processes: Jour. Geology, vol. 21, p. 506, 1913.

resulted. This space may later have been filled by precipitation from a new supply of solution, or modified, if not obliterated, by the effects of oxidation.

The constituents removed from the manganosiderite by this process, thus became, with the sulphate radicle, the principal constituents in solution and were presumably removed from the manganosiderite zone. Whether or not they could have reacted with and replaced dolomite is a question on which the writer has no definite evidence. The manganese and magnesium in the manganosiderite were evidently more soluble, or replaceable, than the iron, as shown by comparison of the analyses on page 47.

The replacement of iron carbonate by zinc carbonate is not in accordance with certain experimental data. Knopf,[1] in his description of zinc carbonate deposits at Cerro Gordo, in the Inyo Mountains of California, cites experiments by R. C. Wells that showed ferrous carbonate to be less soluble than zinc carbonate; but more recent experiments by Mr. Wells[2] have shown that the relative solubility or precipitability of the two carbonates differs according to the precipitant used. Thus if sodium carbonate is used in a sulphate solution of the two metals, zinc (carbonate) is precipitated before iron (carbonate); if sodium bicarbonate is used, the order is reversed. The precipitants, or replaced compounds, of the Leadville zinc ores were carbonates, not bicarbonates, and this fact in the light of Wells's experiments may be of some significance.

That both zinc and iron and possibly manganese are similarly precipitated by magnesium and calcium carbonates is shown by the composition of the zinc carbonate ores which have replaced dolomite.[3] In this case zinc, iron, and manganese carbonates were precipitated together, in varying proportions, which depended no doubt on their proportions in the solution.

This isomorphous character of the carbonate ore is of interest. The fact that the gray carbonate ore, although free from visible microscopic inclusions of manganosiderite, contains about 14 per cent of ferrous carbonate and smaller amounts of manganese, magnesium, and lime carbonates suggests that replacement of these carbonates by zinc carbonates can extend up to a certain limit but not to their complete elimination. The same feature may have been shown by the ore that replaced dolomite or limestone, but oxidation has obscured the evidence. The ratio of calcium carbonate to other carbonates in

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[1] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 107, 1914.

[2] Personal communication.

[3] No unoxidized carbonate ore replacing dolomite was seen by the writer at Leadville, but the ferric and manganese oxides in the brown ore are mostly or wholly the result of oxidation in place of gray (ferrous) zinc carbonate. In the Tintic district, Utah, the writer found gray zinc-iron carbonate ore replacing practically pure limestone (Econ. Geology, vol. 9, pp. 2–3, 1914).

these ores is misleading, owing to the presence of calcite fillings of fractures and vugs of later origin than the replacement ore.

The progress and behavior of the solutions after deposition of the zinc carbonate could not be adequately studied underground, as the mine workings do not generally follow watercourses beyond the limits of ore bodies. The few such watercourses seen were stained by iron and manganese oxides, but these could hardly have been deposited directly from the waters that deposited the gray zinc ore. The waters after the replacement of manganosiderite must have been sulphate waters containing principally iron and manganese, with some magnesium and small amounts of several other elements. It seems quite possible that they could cause a replacement of dolomite by manganosiderite, but no such replacement is known, and it is doubtful if such a secondary manganosiderite could be distinguished without microscopic study from the primary manganosiderite, which is clearly an intimate associate of the sulphide ores. It is doubtful if the neutral sulphate waters could cause any other chemical action. They would presumably pass on to ground-water level, if they had not already reached it, enriching the ground water in sulphates.

The relation of ore deposition to ground-water level is discussed on pages 64–66, where it is concluded that the gray zinc carbonate ore was deposited close to if not below water level. In this connection the following statement by Lindgren[1] is of interest:

> Replacement by equal volume demands the nicest balance between solution and precipitation and takes place when the rock is permeated by stagnant or slowly moving solutions.

These conditions are satisfied below ground-water level and probably in the zone just above it. In arid regions similar replacement deposits are found well above the present ground-water level and are to be attributed either to the existence of a higher water level when replacement occurred, to local impounding of water above an impervious stratum, or to gradual exhaustion of the descending waters by permeation of the rock, with resulting slow movement and supersaturation, thus producing conditions of chemical equilibrium essentially the same as those already considered. The abundant precipitation at Leadville and the presence of sulphide bodies above gray zinc carbonate ore favor the conclusion that deposition of the zinc carbonate bodies on Carbonate Hill below the surface of ground water was quite possible. The ground-water level in fact may have aided the geologic structure in the concentration of these great bodies. In other places—for example, in Iron and Rock hills—deposition took place above the water level, the concentration and the size of the ore bodies being determined by the amount of zinc and other ele-

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[1] Lindgren, Waldemar, The nature of replacement: Econ. Geology, vol. 7, p. 531, 1912.

ments in solution and by the rock structure, which influenced the slow or rapid movement of the descending solutions and the degree to which they could permeate the rock.

SECOND STAGE.

It is not to be supposed that the processes of solution, transfer, and deposition already described were sharply separated in all respects from those that remain to be considered. The oxidation of zinc blende was accompanied by simultaneous oxidation of some pyrite and a little galena, and the greater the amount of pyrite oxidized the greater the amounts of iron sulphates that took part in the different reactions; but the much greater susceptibility of zinc blende to oxidation caused its practically complete removal while large amounts of the other two sulphides remained. The first stage, marked by transfer and redeposition of the zinc, is thus distinct from the second stage, which was characterized by oxidation of the remaining pyrite and galena and by a working over of the newly formed zinc carbonate bodies.

The oxidation of the remaining pyrite, as before, caused generation of sulphuric acid and ferric sulphate; the oxidation of galena to sulphate and finally to carbonate generated additional sulphuric acid. The presence of considerable amounts of jarosite and plumbojarosite, however, gives proof that a part of the iron sulphates were deposited without further reactions of present significance and that not all the galena was finally changed to carbonate. The amount of sulphuric acid and ferric sulphate which succeeded in reaching the zinc carbonate bodies therefore represented only a part of the quantity of pyrite and galena oxidized.

The sulphuric acid, on attacking the ferruginous zinc carbonate decomposed it, taking zinc and iron sulphates into solution. The iron sulphate, if free oxygen were present, oxidized to ferric sulphate, which, with the ferric sulphate already in solution, in turn attacked and replaced more of the zinc carbonate and was deposited itself as hydrate or hydrous oxide, thus forming or adding to the layer of iron oxide and kaolin at the top of the ore body. The zinc thus removed was carried in solution until it could again attack and replace manganosiderite or dolomite.

The principal work of the second stage, therefore, was a slight downward migration of the zinc carbonate bodies, material removed from their upper parts being added to their lower parts. The extent of migration obviously depended on the amounts of pyrite and galena oxidized.

THIRD STAGE.

The third stage includes the operation of those processes which have been active since the decomposition of the original sulphides. The principal agents were oxygen and carbon dioxide, which, as lowering of the surface by erosion progressed, became more and more abundant.

Oxygen on reaching the gray carbonate ore oxidized the iron and manganese, causing the formation of red or brown ferric oxide and the zinc-manganese oxide, hetaerolite, the zinc carbonate recrystallizing in a relatively pure state. The iron oxide, to judge from the many specimens of brown ore studied, tended to remain in place, while the new smithsonite and hetaerolite migrated short distances to fractures and other openings to form druses or complete fillings.

This process shows that the smithsonite and hetaerolite were to some extent soluble in the solutions, and that although they were for the most part quickly redeposited, small amounts of them may have been carried for considerable distances. The free carbon dioxide in the water also had a tendency to dissolve the carbonate ore and carry the zinc as bicarbonate, the iron and manganese separating out as oxides. The combined effect of the oxygen and carbon dioxide was to induce a slow downward migration of the zinc carbonate bodies and a corresponding thickening of the layers of iron oxide and clay at their tops.

After the exhaustion of carbon dioxide to a certain degree silica became the active acid radicle, uniting with zinc to form calamine, the latest of the more abundant zinc minerals. The character of different calamine aggregates shows that the zinc and silica were for the most part carried in solution and the calamine was deposited in openings as a result of supersaturation; on the other hand, replacement of smithsonite by calamine shows that a part of the zinc was derived in place and the silica introduced in solution. The source of the silica is to be referred especially to the porphyry overlying the original sulphide bodies. Small amounts of silica may also have been derived from the gangue of these ore bodies and from the original carbonate rocks.

The conditions of equilibrium governing the deposition of calamine are not well understood.[1] It is evident from paragenetic study that calamine can not form until smithsonite (the late drusy form) has finished crystallizing; on the other hand, it is also evident that

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[1] Since this paragraph was written experiments to throw light on the conditions affecting the deposition of calamine have been made by Y. T. Wang (The formation of the oxidized ores of zinc from the sulphide: Am. Inst. Min. Eng. Bull., September, 1915, pp. 1988–1991). He found that calamine is soluble in water containing carbon dioxide and even more soluble in water containing bicarbonate of zinc as well. These results agree with the fact that calamine at Leadville is deposited after smithsonite.

calamine can, under certain conditions, replace smithsonite. Why smithsonite is the less soluble in one case and the more soluble in the other is not clear. There is no reason for supposing that silica was not present while the smithsonite was being deposited. A reasonable inference is that crystallization of smithsonite, once started, continued for a time after the equilibrium point was passed, and that the smithsonite was later redissolved by the now more stable calamine. Another conjecture is that, as the solution, through prolonged permeation, became more concentrated, silica superseded carbon dioxide as the stronger acid radicle—in other words, whereas smithsonite was the more insoluble mineral in the dilute solution, calamine was the more insoluble in the concentrated solution.

The occurrence of small amounts of zinciferous clay closely associated with calamine shows that the two were deposited at about the same time. These small amounts of clay may be attributed to alumina, which is commonly present with silica in mine waters of the oxidized zone and was derived from the same sources; but in this case the occurrence of the clay as one of the latest minerals is rather surprising, especially as the waters that deposited it appear to have been practically free from sulphates. Some of the clay however, has evidently resulted from chemical precipitation and suggests that aluminum can be held in solution until the waters become concentrated by depletion, when, in the presence of silica and zinc, it is precipitated as zinciferous clay.

Another interpretation is that the clay was in reality precipitated at an earlier stage and carried in suspension for indefinite distances until finally it was deposited in openings where the waters became stagnant, the zinc content being due to replacement of the aluminum in the clay. This suggestion could be applied to the clay fillings in fractures and fissures. Such fillings may have been formed during the first two (sulphate water) stages, and if they were the chemistry of deposition could be regarded as generally similar to the processes outlined in the preceding pages.

Failure to find any conspicuous occurrences of hydrozincite prevents an adequate discussion of its place and significance in the genesis of the Leadville deposits. The writer, in his study of the Tintic zinc ores,[1] found that hydrozincite as a rule followed the drusy smithsonite and therefore belonged to the same period of crystallization as calamine. This paragenetic relation is in accord with experimental evidence,[2] which shows that when carbon dioxide

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[1] Econ. Geology, vol. 9, pp. 3, 7, 1914. Where hydrozincite in the Tintic district alternated with drusy smithsonite, the later smithsonite was evidently deposited from a new supply of solution, and this was in turn followed by renewed deposition of hydrozincite.

[2] Raikow, P. N., Weitere Untersuchungen über die Einwirkung der Kohlensäure auf die Hydrate der Metalle: Chem. Zeitung, vol. 31, p. 55, 1907.

is present in the solution in excess the carbonate of zinc, smithsonite, will crystallize, but that when carbon dioxide is not in excess the basic carbonate, hydrozincite, will crystallize. This principle applied to the waters at Leadville would imply that as the solutions diminished in volume, owing to their spreading along fractures or to permeation through the ore bodies, they lost their excess of carbon dioxide. Smithsonite therefore would cease to form, and the remainder of the zinc carbonate would crystallize as hydrozincite. According to this principle, hydrozincite should be found coating druses of smithsonite and lining fractures below the limits of smithsonite deposition, also as a local alteration product where water containing no free carbon dioxide succeeded in causing recrystallization of smithsonite.[1]

The aurichalcite in the Ibex mine accords with this interpretation. The aurichalcite was deposited at the same time as calamine, and both were formed later than drusy smithsonite. Evidently the solution, locally impounded in cavities in the ore, lost its excess of carbon dioxide. The copper and a corresponding amount of zinc then crystallized as the basic carbonate, aurichalcite, and the rest of the zinc went to form calamine. Any excess of silica over that required to form calamine was deposited as opal, chalcedony, or quartz coating or inclosing the calamine crystals.

After the waters had become depleted of zinc carbonate and silicate calcite was deposited in small amount, though only in a few places, as the final product of the third stage. As nicholsonite and aragonite were not found within the ore, they can not be assigned to a definite place in the sequence. Both minerals crystallized in openings in limonite, and from their mode of occurrence would appear to belong to the later part of the third stage of deposition—that is, to the calamine-calcite period—but their relations to calamine, hydrozincite, aurichalcite, and calcite are not known.

The third stage of transfer and redeposition is still in progress. Remnants of gray carbonate ore are undergoing oxidation, and the other zinc minerals are doubtless slowly forming at their expense. These minerals also are being subjected to further leaching and redeposition, and even calamine, the latest of the abundant zinc minerals, may be found in places with corroded surfaces, which signify that slow leaching and continued downward migration are still going on.

SUMMARY.

The detailed discussion of genesis may be briefly summarized as follows:

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[1] Since this statement was written Philip Argall (Min. Mag., vol. 10, fig. 4, p. 285, 1914) has published an illustration of a specimen taken from a fissure cutting the lower beds of White limestone in the Maid of Erin mine. The specimen consisted of fibrous (drusy) smithsonite covered by a coating of hydrozincite an eighth of an inch thick.

In the first stage ferruginous zinc blende (marmatite) was decomposed by sulphate waters, which also contained carbon dioxide. Where the solutions containing zinc and iron sulphates and smaller quantities of other salts passed through porphyry any free sulphuric acid and ferric sulphate decomposed sericite and feldspar and later deposited the alumina, silica, and zinc as zinciferous clay, either along fissures in the porphyry or by replacing limestone just beneath the porphyry. Where the zinc solutions passed from the sulphide body into limestone any free sulphuric acid at once became neutralized and ferric sulphate was precipitated as ferric hydrate, which replaced the limestone and formed part or all of the characteristic layers that separate the zinc from the lead-silver stopes. If no free sulphuric acid or ferric sulphate was present, no such layer was formed at this time. The neutral solution then caused replacement of carbonate rock, both manganosiderite and dolomite, by gray smithsonite. In the manganosiderite greater proportions of magnesia and manganese than of iron carbonates were replaced. Deposition of the smithsonite took place, at least in part, not so much by direct reaction between the carbonates and a molecularly equivalent amount of zinc sulphate as by a volume for volume interchange. In the replacement of dolomite the magnesia and lime appear to have been replaced simultaneously by zinc and iron carbonates. The replacement of the carbonate rocks was effected by stagnant or slowly moving solutions, which in the northern part of Carbonate Hill may have been close to or even below the level of ground water. Elsewhere the replacement occurred well above the water level.

The second stage was characterized by decomposition of the pyrite and galena that survived the first stage. The resulting sulphuric acid and ferric sulphate that reached the newly formed zinc carbonate bodies tended to leach and replace their upper portions, with a corresponding thickening of the iron oxide layers at their tops, and to remove the dissolved materials to the lower ends of the ore bodies, where additional replacement of carbonate rock could occur. The final result of processes active during the second stage was a greater or less downward migration of the zinc carbonate bodies, the extent of migration depending on the amount of sulphuric acid and ferric sulphate available at any particular place.

The third stage includes the changes that took place after the sources and supplies of sulphuric acid and ferric sulphate had become practically exhausted, leaving carbon dioxide and oxygen as the principal active agents. These attacked the gray zinc carbonate ore, oxidizing its iron to red or brown ferric oxide and its manganese and some zinc to hetaerolite and recrystallizing a part of the remaining zinc carbonate into drusy smithsonite. Although these changes were mostly brought about with very little transfer of material, there was probably a slight tendency to downward migration of the ore bodies and corresponding thickening of the overlying iron oxide layers. After the work of oxygen and carbon dioxide had been mostly accomplished and the excess of carbon dioxide had escaped, small amounts of aurichalcite and hydrozincite were formed. At about the same time silica succeeded carbon dioxide as the dominant acid radicle and caused the deposition of calamine, mostly as cavity fillings but to a minor extent replacing smithsonite. Where aluminum was locally an abundant constituent of the solutions at this period small amounts of zinciferous clay were deposited in cavities along with or in place of calamine. If silica was present in excess, small amounts of opal, chalcedony, or quartz were deposited after the calamine. Calcite and probably also aragonite and nicholsonite were deposited later than the calamine, representing the latest of the succession of minerals in the oxidized zinc ore bodies. Oxidation of the third stage, however, is still in progress.

PROSPECTING FOR BODIES OF OXIDIZED ZINC ORE.

The more consideration one gives to the factors chiefly concerned in the genesis and distribution of the oxidized zinc ore bodies, the more hesitant is he likely to become in any attempt to predict the location of undiscovered bodies. It is obvious that the zinc bodies are intimately associated with the old lead-silver stopes, but their exact positions, shapes, and sizes depend upon too many variable factors to be determined without actual prospecting. In the first place, the distribution of zinc blende in the original sulphide bodies was very irregular, as it is in the sulphide bodies now being mined.

In some ore bodies zinc blende although abundant, may have been accompanied by even more abundant pyrite, as in most of the present sulphide bodies. In such deposits the effects of the first and second stages of oxidation may have removed the bulk of the zinc a considerable distance from the corresponding lead-silver body, the intervening space being occupied by iron oxide or "contact matter." Whether such prolonged transfer would result in greater concentration or dispersion of the zinc would depend upon local structures. Local concentrations may be represented by some of the Chrysolite bodies (fig. 7, p. 57) found a considerable distance below the stopes shown in Emmons's sections and just above the upper contacts of porphyry sills.[1]

In other ore bodies a shoot of zinc blende may have existed side by side with one of pyrite, and oxidation with downward migration may have resulted in the formation of zinc carbonate and iron oxide

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[1] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, atlas sheets 31 and 32, 1886.

bodies side by side. Oxidation of manganosiderite beside or even beneath the zinc carbonate bodies may also have yielded iron oxide or manganese-iron oxide bodies, but oxidation beneath the zinc ores was doubtless of relatively infrequent occurrence and small extent.

At some places the rock underlying original sulphide bodies may have contained much siliceous matter and correspondingly little carbonate material. In such places the smithsonite, deposited by replacement of the carbonate content, may have formed low-grade ore bodies of considerable extent or local shoots where fissuring or shattering permitted thorough permeation of the elsewhere relatively impervious rock. Descending solutions from siliceous ore bodies may have been unusually rich in silica and alumina and deposited them in some form along with the zinc, thus giving ore of low grade. Such conditions may account for the characteristics of the ore bodies in the Tucson mine and of some ore bodies in the Chrysolite mine.

The influence of local structure has been illustrated on pages 54–56, and only summarized statements need be made here. Faults and strong fissures, if filled with impervious material or if bringing impervious or nonreplaceable beds opposite replaceable beds, may serve to impound the solutions and develop an ore body of unusual thickness; faults and fissures of similar magnitude, if open and very pervious, may serve to concentrate the flow of solutions along them and give rise to deposits of general veinlike form. If solutions traveling along open fissures pass beyond the limits of the carbonate rocks before effecting much replacement, it is probable that no workable deposits will be formed by them. Impervious rock layers, such as the quartzites and porphyries, may confine replacement to the limestone above them; but the same rocks, if fractured, may allow the solutions to pass into or through them. Where solutions penetrate Cambrian quartzite or thick masses of porphyry in this manner their zinc contents are not likely to be concentrated into workable deposits. If solutions find their way into a large body of rock which is chemically replaceable but only slightly permeable and which is not immediately underlain by some impervious bed, the solutions are likely to become dispersed and to yield an extensive body of low-grade ore or a series of shoots too small for profitable mining.

These many and varying conditions should convince operators that the more they know of the significance of structural details of their ground the more intelligently can they prospect for zinc ores. They should realize that large bodies of high-grade ore are to be found only where the original supply of zinc, local structural conditions, and the composition of the country rock have all been favorable. The area covered by the numerous and extensive oxidized lead-silver stopes in the district, extending from the western edge of the Downtown section eastward to Ball Mountain and from Fryer Hill southward to Rock Hill, is legitimate prospecting ground for oxidized zinc ores, but it remains for those most familiar with the details of individual mines or claims to formulate the best methods of prospecting. Furthermore, especially where ground has been abandoned for a long time and detailed knowledge of it is slight, prospectors should be ever on the lookout for new and unexpected evidence and should modify their methods accordingly.

INDEX.

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