OBSERVATIONS ON THE RICH SILVER ORES OF ASPEN, COLORADO.

By Edson S. Bastin.

INTRODUCTION.

In September, 1913, the writer paid a brief visit to the famous old silver camp of Aspen, in Pitkin County, southwestern Colorado, to obtain samples of the rich silver ores for microscopic study. Systematic studies of the distribution of the rich silver ores in the mines and of many other factors that have a bearing on their origin were not practicable in the time available, but some incidental observations on the depth of oxidation and downward enrichment and on the quality of mine waters are here recorded. Two analyses of mine waters were made by Chase Palmer, then with the United States Geological Survey. For more detailed accounts of the general geologic features of the district the reader is referred to the well-known reports of J. E. Spurr. ¹

The writer's observations are offered as a brief contribution to the problem of the origin of the rich silver ores of Aspen, with full recognition of the desirability of amplifying them and of supporting them by other lines of field evidence. As the writer will be unable personally to undertake such studies the data are here placed at the disposal of other observers.

GENERAL GEOLOGIC FEATURES.

According to Spurr ² sedimentary rocks exposed at Aspen include formations of Cambrian, Silurian [Ordovician], Devonian, Carboniferous, Triassic, Jurassic, and Cretaceous age, which rest upon pre-Cambrian granite. These rocks were intruded in late Cretaceous or early Tertiary time by rhyolite and diorite porphyries, of which the former are the more abundant.

The intrusions in the main assumed the form of sills or sheets forced in between the sedimentary beds and parallel to them. The largest is a sheet of rhyolite porphyry 250 to 450 feet thick intruded

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² Spurr, J. E., op. cit. (1909).
at the base of the Weber (?) shale (Carboniferous), which formed a yielding roof above the intrusion. Crosscutting dikes of rhyolite porphyry are probably offshoots from this sheet.

During the intrusion of the porphyries and subsequently the sedimentary rocks were folded and greatly faulted, and some of this deformation, according to Spurr, was a direct effect of the intrusion. Some of the faulting took place along bedding planes between formations; the fault of this type that is most significant in connection with ore deposition is the Silver fault, at the base of the Weber (?) shale.

Ore deposition followed closely upon the intrusion of the porphyries and took place along steeply inclined faults and along bedding-plane faults near their contacts with steeper faults. Mineralization occurred in all the formations from the pre-Cambrian granite to the Tertiary (?) intrusive rocks. That in the pre-Cambrian is economically negligible. Some ore occurs in Ordovician dolomite, and much in lower Carboniferous (Mississippian) and Devonian (?) dolomite and limestone. The chief ore horizon is the Silver fault, at the base of the Weber (?) shale (Pennsylvanian).

According to Spurr primary ore deposition was limited to a single period, which was brief as contrasted with the duration of faulting. Within this period he recognized three stages characterized by dominance of different minerals but showing transitions.

The first stage recognized is the deposition of barite in regular veins, usually parallel to the stratification. Some of these veins barren of sulphides represent the beginnings of mineralization in the district.

The second stage involved the deposition of tetrahedrite, tennantite, polybasite (?) [probably mostly pearceite.—E. S. B.], and argentite. In places these minerals occur intercrystallized with barite and apparently about contemporaneous with it, but elsewhere they occupy fractures in barite and are therefore slightly though probably not greatly younger. The rich ore shoots that made the Smuggler Union and Mollie Gibson mines famous were mainly formed at this stage along the Silver fault, and many of the rich specimens that form the special subject of this report came from these ore shoots. These rich silver ores were largely worked out many years ago, and representative specimens could be obtained only from private collections and from jewelers at Aspen.

The third stage in the mineralization involved the deposition of finely crystalline galena and subordinate sphalerite, mainly by the replacement of dolomite and limestone and in some places after breccia-
tion of the rich silver ores. The mineralization of this stage was more extensive than the rich silver mineralization. It is the ore of this stage that constitutes the "milling ore" which is now the main industrial resource of the district.

Finally, the modifying action of descending waters of surface origin is recognized by Spurr as the agency that caused the deposition of native silver from very shallow depths down to vertical depths of about 1,000 feet. Some of this silver, he states, was clearly deposited hundreds of feet below the original ground-water level. No other secondary (supergene) silver minerals were recognized by Spurr, and he calls attention particularly to the absence of ruby silver (proustite). He appears to hold that primary mineralization rather than secondary deposition was the main cause of the rich bonanzas of the early days of mining.

MINERALOGY OF THE ORES.

The microscopic studies recorded in this paper were made mainly on specimens of very rich silver ores obtained from private collections in Aspen. Ores of comparable richness have not been mined in noteworthy amounts in recent years. Unfortunately the exact localities in the mines from which some of these specimens were taken many years ago could not be learned. Most of the ores studied came from the Mollie Gibson and Smuggler mines.

Ore minerals noted by the writer in the ores studied are as follows:

A. Early primary (hypogene): Barite, tennantite, pyrite (rare), quartz (rare).

B. Later primary (hypogene): Galena, sphalerite, chalcopyrite, bornite, peacockite, argentite.

Groups A and B are not separable in all the ores.

C. Secondary (supergene): A possible lead-silver sulphide, peacockite, native silver (abundant), argentite(?), chalcocite (rare), covellite (rare).

To these should be added, according to Spurr, tetrahedrite, polybasite, pyrargyrite, several carbonates, and numerous oxidation products.

The "brittle silver" of the Aspen miners is commonly an aggregate of peacockite with some tennantite, galena, sphalerite, and other minerals, but when pure it has the appearance and physical properties of polybasite and was so denominated by the earlier observers. In 1892, however, Penfield analyzed specimens forwarded to him by Richard Pearce, of Denver, and found that the mineral was arsenical rather than antimonial, its composition corresponding closely to the formula $9\text{Ag}_2\text{S}_2\text{As}_2\text{S}_3$. Subsequently, in 1896, Pen-
field assigned to this “arsenical polybasite” the name pearceite. Penfield appears also to have been the first to identify the “gray copper” of the Aspen ores as tennantite.

PRIMARY LEAD ORES.

Galena-rich ores of the type now being worked were studied at typical exposures in stopes following the so-called contact between the eleventh and thirteenth levels of the Smuggler Hill workings (blocks 30-33). This “contact” is the Silver fault, a zone of movement and intense brecciation between Leadville dolomite and the overlying Weber (?) shales. On passing from the footwall to the hanging wall of this bedding fault there are transitions from massive dark-gray dolomite into dolomite breccia with crushed dolomite matrix, thence into a breccia of dolomite fragments in a black shale matrix, and finally into black slickensided shale much resembling coal. Throughout thicknesses in places as great as 20 to 25 feet the breccia has been partly replaced by ore minerals, and small stringers of these minerals penetrate the shale of the roof. In one place (stope 33) there was noted a streak 3 to 6 inches wide of nearly pure galena traversing brecciated dolomite, and gradations could be traced from this into breccia in which replacement affected only the matrix, and finally into unmineralized breccia. Ores of this type, when examined under the microscope, are found to be mainly dolomite and galena with a few minute crystals of quartz and a very little sphalerite. The dolomite in places shows smooth, straight contacts next to galena that represent crystal or cleavage planes of the dolomite, but elsewhere the contacts are exceedingly ragged, clearly indicating replacement of the dolomite by galena.

PRIMARY SILVER ORES.

In some places in these stopes the galena ores described above give way, apparently by transition, to ores in which fine-grained tennantite is the dominant metallic mineral, and this change is usually accompanied by a notable increase in the silver content. One such ore body above the eleventh level (block 98, south of the Mollie Gibson shaft) carried very little visible galena but abundant tennantite. This ore averaged 20 ounces in silver to the ton, and single assays ran up to 125 ounces. A specimen of ore of this type from block 30, on the thirteenth level of the workings under Smuggler Hill, shows pink barite in aggregates of radiating blades inclosed by a fine-grained sulphide aggregate which is mainly tennantite, all replacing black shale of the Weber (?) formation. Some of the

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barite may have been deposited before the sulphides, but some is intercrystallized irregularly with them and is clearly contemporaneous with them. The microscope shows in this ore a mineral composition and texture that is essentially identical with that noted in the specimen next to be described, which is shown in Figures 13 and 14.

A specimen of tennantite-rich ore said to run about 4,000 ounces to the ton in silver, from a stope just above the thirteenth level of the Smuggler Hill workings, block 30, was obtained through the courtesy of Mr. Charles E. Anderson. To the unaided eye it is a finely granular gray aggregate composed mainly of metallic minerals. This aggregate is bordered by and has apparently replaced black shale of the Weber (?) formation. Under the microscope
polished specimens of this ore presented the appearance shown in Figures 13 and 14. The microscope shows barite and tennantite intergrown apparently contemporaneously as in general the oldest of the ore minerals.

The tennantite is traversed in the fashion shown in Figures 13 and 14 by replacement veinlets of galena, sphalerite, bornite, chalcopyrite, pearceite, and calcite. In other parts of the specimen similar replacement veinlets follow the contacts of tennantite with bladelike crystals of barite. That this group of minerals is not greatly younger than the tennantite and barite is indicated by such relations as are shown at A, in Figure 13, where these minerals are irregularly intergrown with tennantite, and by such relations as are shown in Figure 15, where tennantite, argentite, and pearceite are in irregular contemporary intergrowth.

Figure 14.—Tennantite traversed by late primary replacement veinlets of pearceite, base-metal sulphides, and calcite. The textural relations suggest that some calcite and base-metal sulphides crystallized contemporaneously with the tennantite, but where they form veinlets they are clearly slightly younger. Smuggler Hill workings, block 30, Aspen, Colo., thirteenth level. Camera lucida drawing from polished specimen.
In the specimen from which Figures 13 and 14 were sketched the pearceite occurs in the replacement veinlets side by side with sphalerite, calcite, bornite, and galena; it does not follow contacts between these minerals and tennantite, nor does it follow galena cleavages or other planes of weakness. It is believed to have been deposited at the same time as galena, sphalerite, bornite, and calcite and like them to be late primary (hypogene). This forms an ex-

![Diagram](image-url)

**Figure 15.** Argentite, pearceite, and tennantite in irregular and apparently primary intergrowth. Aspen, Colo., precise location uncertain. Camera lucida drawing from polished specimen.

ample of the tendency emphasized by the writer in a previous paper for the simultaneous replacement of ore mineral by a group of several minerals, common in hypogene replacement but rare in supergene replacement.

A specimen of rich baritic silver ore from Aspen, purchased from a jeweler, presents to the unaided eye a mottled appearance due to the scattering of dark aggregates of metallic minerals 1 to 5

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millimeters across through a pinkish matrix of small bladed crystals of barite. Under the microscope the patches of metallic minerals are found to be mainly an aggregate of tennantite, pearceite, and argentite, the characteristic appearance of which is shown in Figure 15. The boundaries between these minerals are in general irregular, with a few suggestions of crystal boundaries. Contacts between tennantite and argentite are in some places smoothly curved and in others straight or subangular. The subangular contacts suggest that tennantite slightly preceded argentite in crystallization. The tennantite in a few places exhibits its characteristic tetrahedral outlines against the pearceite, but most of the boundaries between these two minerals are irregular and tend to interlock. Argentite boundaries against pearceite are in general smooth but give no strong indication
RICH BARITIC SILVER ORE FROM SMUGGLER MINE, ASPEN, COLO.

About 500 feet below surface. Typical of many of the richer ores. About seven-eighths natural size.
of crystal faces. The cuspatẹ boundaries and embayments in the upper right quarter of the figure suggest a tendency for argentite to replace pearceite; but there is no tendency for argentite to follow contacts between pearceite and tennantite, and it is regarded as chiefly or entirely a primary mineral. The argentite is distributed fairly evenly throughout the patches of metallic minerals; there is no tendency for it to develop most abundantly about the peripheries of these areas, such as was noted in the native silver and is described later. Therefore, although there is a little indication that tennantite slightly preceded and argentite slightly followed pearceite, the three minerals together with barite are interpreted as all primary (hypogene) and nearly contemporaneous.

Other specimens of the rich silver ores generally carried the same primary minerals that were noted in the tennantite-rich ores already described, although barite was in general more abundant and in larger crystals. A specimen from the Smuggler mine in the collections at the statehouse in Denver showed pearceite distinctly occupying cracks in pink barite, but this association grades into what appears to be a contemporaneous intergrowth of the two minerals in nearly equal amounts.

In some specimens of the very rich ores a division of the primary minerals into earlier and later groups is not feasible, all appearing to be intercrystallized essentially contemporaneously. Individual white, gray, or pink barite blades are not uncommonly a quarter to half an inch in length. The sulphides commonly form irregularly elongate patches between the blades of barite, as shown in Figure 17. A typical specimen of rich barite silver ore is shown in Plate III.

SECONDARY (SUPERGENE) ORE MINERALS.

Spurr has interpreted the native silver of the Aspen ores as a deposit from descending solutions—a product of downward enrichment. This interpretation is confirmed by the writer's studies, and several examples of silver developed by the replacement of primary minerals are described below.

Compounds of silver of supergene origin were not noted by Spurr and certainly are not conspicuous, native silver being the principal supergene mineral. In one specimen, however, such compounds were noted in abundance. This specimen came from the collection of Mr. Charles E. Anderson at Aspen and was taken from the Mollie Gibson mine, though the exact locality is now uncertain. The dominant mineral of this ore is pink barite, but with it are irregularly intergrown as primary and apparently contemporary minerals abundant galena and small amounts of quartz. By replacement of the galena and subordinately of the barite, silver minerals have been
developed in this ore in such abundance as to convert it into a rich silver ore, in the fashion shown in Figure 16. Galena has first been replaced along its contacts with barite and along contacts between different galena crystals by a galena-like mineral, probably the same that was previously noted by the writer in the ores of Tonopah, Nev., distinguishable from the galena under the microscope only when the galena is tarnished with hydrogen peroxide. The galena-like replacing mineral is probably a lead-silver sulphide, but it is present in too small amounts to be isolated for testing. As replacement proceeded the galena-like mineral was replaced by pearceite, as at A and A' in Figure 16. Finally, as at the top of Figure 16, native silver was formed, usually as a replacement of pearceite. These replacements are interpreted as the result of downward enrichment. In contrast to the ore shown in Figures 13 and 14 a primary mineral

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Figure 17.—Replacement of sphalerite stringers in barite by native silver. Smuggler mine, Aspen, Colo., from depth of 140 feet in shaft. Camera lucida drawing from polished specimen.

has been replaced by three minerals, not simultaneously but in definite succession. This succession involves progressive enrichment in silver, because pearceite, which contains about 57 per cent of silver, is probably more argentiferous than the galena-like mineral and is itself later replaced by native silver. In parts of this specimen some argentite, which contains 87 per cent of silver, is associated with the pearceite, but the mutual age relations are not clear.

A specimen from the second level of the Smuggler mine at the shaft and about 140 feet vertically below the surface showed the relations sketched in Figures 17 and 18. Late primary replacement veinlets of sphalerite, galena, bornite, and calcite, traversing barite, exhibit peripheral replacement of the sphalerite by native silver, as clearly indicated in Figure 17. Although the replacement began with sphalerite, as the more susceptible mineral, it later extended to the barite, as shown in Figure 18, drawn on a larger scale from

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**Figure 18.** Replacement of barite by native silver. Smuggler mine, Aspen, Colo., from depth of 140 feet in shaft. Process began with replacement of narrow areas of sphalerite between bladelike crystals of sphalerite and spread to the bordering barite. Camera lucida drawing from polished specimen.
the same specimen. In the silver veinlet of this figure there are replacement remnants of both sphalerite and barite. The hand specimens of this ore show irregular patches of metallic minerals scattered through a matrix of bladed barite. The native silver was developed mainly near the peripheries of these areas of metallic minerals, the portions most accessible to the enriching solutions.

Eventually, as is well shown by a specimen from the Mollie Gibson mine obtained from the D. R. C. Brown collections, the replacement of barite proceeded to a stage where only ragged remnants of barite remained in a matrix of silver, as is clearly shown in Figure 19. In the hand specimen this ore appears to be nearly pure silver. In parts of this specimen remnants of pearceite remain and are related to the silver in a fashion shown in Figure 21, sketched from ore from another locality.

In another specimen from the Smuggler mine (exact locality uncertain), obtained from the D. R. C. Brown collection, irregularly
tabular masses of metallic minerals occur between coarse crystals of barite. The metallic minerals include tennantite and some chalcopyrite. Partly replacing these is an aggregate of sphalerite, galena, bornite, and pearceite. Finally these primary minerals have been replaced by native silver, in the fashion shown in Figure 20. Small replacement remnants of tennantite, not shown in the figure, are scattered sparsely through some of the silver.

One specimen of very rich Aspen ore (exact locality uncertain) is of mottled appearance to the naked eye, black patches, as much as 5 millimeters across, of metallic minerals being scattered through a matrix of pink barite. The interiors of the patches of metallic minerals consist of tennantite, argentite, and pearceite in irregular primary intergrowth, as shown in Figure 15. About the peripheries of many of the patches of metallic minerals native silver is present. Its relations to pearceite are typically shown in Figure 21.
The convex outlines of the silver against pearceite and similarly in a few places against argentite indicate a growth of the silver radially or concentrically from numerous centers. The pearceite may be interpreted either as a later filling between the masses of silver or as remnants of larger pearceite areas now mainly replaced by silver. The fact that the silver is in general restricted to the vicinity of the borders of the sulphide patches against barite favors the replacement hypothesis. The silver is interpreted as a deposit from descending supergene solutions.

In the same specimen from which Figure 16 was sketched pearceite, argentite, and native silver have all been developed by replacement, presumably through the agency of descending solutions. A common replacement sequence is (1) lead-silver sulphide (?) after galena; (2) pearceite after lead-silver sulphide (?); (3) argentite after pearceite; and (4) native silver after argentite. In places, however, the silver directly replaced pearceite in a fashion similar
to that shown in Figure 21 or even directly replaced galena with contacts that under high power are found to be very irregular.

Some observations on the mode of occurrence of native silver made underground and on specimens in collections should also be recorded. Spurr states that native silver is found at depths of at least 900 to 1,000 feet below the surface. In the workings under Smuggler Mountain native silver was noted by the writer in the ore of the "contact" or Silver fault at vertical depths approaching 1,200 feet. Specimens said to have come from vertical depths of about 1,100 feet in the Durant tunnel workings under Aspen Mountain carried small plates of native silver along fractures. A short distance south of the Mollie Gibson shaft (block 98 south, near eleventh level) ore rich in tennantite carried scattered flakes and wires of native silver in vugs and fractures. This was about 1,000 feet vertically below the surface. In the workings under Aspen Mountain ore from the "contact" not far above the level of the Durant tunnel and about 900 feet vertically below the surface carried an abundance of native silver.

A specimen in the D. R. C. Brown collection at Aspen (exact locality uncertain) showed tapering and curling "teeth" of native silver implanted on "brittle silver" (probably pearceite) and clearly an alteration product thereof. Some of these teeth were half an inch in length. Another specimen in the same collection shows similar silver "teeth" implanted on a surface of black shale; these also may be alteration products of some silver compound, although no traces of such a compound remain.

A specimen in the Brown collection said to have come from a depth of about 700 feet in the Millinee mine, in Aspen Mountain, showed native silver in a slablike mass 5 by 6 inches across and half to three-quarters of an inch thick. This slab was not solid silver but was made up of a matt of silver wires, hairs, and teeth, in places loosely aggregated but elsewhere crowded closely together. This silver was deposited along a fracture in dark-gray shale, remnants of which are still attached to the silver. Isolated fragments of shale are inclosed by the silver. The silver-shale contacts are perfectly sharp, and it is clear that the silver (or some earlier mineral that it has replaced) has been deposited on the shale and not as a replacement of it. No silver compounds are associated with this native silver.

The Brown collection also contained a specimen of brecciated black dolomite from a depth of about 500 feet in the Aspen mine. Between the fragments of this breccia wires and plates of native silver have been deposited. It is noteworthy that some calcite is irregularly intergrown with the silver.
A specimen in the statehouse collection at Denver from the Millinee mine, in Aspen Mountain, shows native silver forming a veritable matrix between fragments of brecciated blue-gray dolomite.

To summarize the occurrence of native silver at Aspen, this mineral has been observed to vertical depths of around 1,200 feet. These depths are not greatly in excess of those to which local oxidation was observed. The microscope shows that some of the native silver was formed by a replacement of other minerals. Silver compounds such as argentite and pearceite seem to have been the first to yield to such replacement, and in general native silver appears to have been developed most abundantly in connection with ores rich in these silver compounds. Later the replacement by silver spread to base-metal sulphides, and finally even barite gangue was extensively replaced. The specimens of native silver in dolomite or black shale seen by the writer showed no evidence of the replacement of these rocks by silver, but it would be unsafe to conclude that such replacement nowhere occurred.

DEPTH OF OXIDATION.

No comprehensive study of ground-water conditions could be attempted in the brief time available, but enough was seen to make it clear that voluminous flows of ground water were present comparatively near the surface, far above the lower limits of oxidation. Most of these flows came from open watercourses. At the time of the writer's visit an open watercourse in Leadville dolomite below the "contact" had recently been tapped on the fifteenth level of the workings under Smuggler Mountain, in block 27, about 2,700 feet northeast of the Mollie Gibson shaft. This water was apparently draining from ground between the thirteenth and fifteenth levels. Similar heavy flows were obtained when the eleventh level was driven, from open watercourses that can still be seen but have long since dried up. Oxidation is pronounced on the fifteenth level below the "contact" or Silver fault, at slightly greater depths than the water flow above described. This was the deepest oxidation noted by the writer and was about 1,000 feet vertically below the surface. This oxidation is much too pronounced to have taken place since the mines were first opened.

More than half a mile farther southwest pronounced oxidation of Leadville dolomite below the "contact" or Silver fault was noted in block 98, to the south of the Mollie Gibson shaft, near the eleventh level. The material of the contact itself showed spotty oxidation at this locality. Small amounts of native silver were noted. This was at a vertical depth of around 1,000 feet.
In the workings still farther southwest under Aspen Mountain the "contact" was well oxidized in places, even when first broken into near the level of the Durant tunnel, at a vertical depth below the surface of nearly 900 feet. Extensive oxidation was noted at other localities underground at lesser vertical depths, ranging from 600 to 900 feet.

As indicative of the spotty distribution of oxidation it may be noted that specimens of lead ore from a depth of only 30 feet in the Smuggler shaft were almost wholly unoxidized.

**DESCENDING MINE WATERS.**

Mine waters, all clear and cool and descending, were tested at several places in the workings, and two samples were analyzed. (See fig. 22.)

![Composition diagrams of cool descending mine waters of Aspen, Colo.](image)

Cool, clear water dripping from the roof of stope No. 4 in the Durant tunnel workings under Aspen Mountain, at a vertical depth of about 900 feet, was not acid toward methyl orange but on the contrary gave a faint pink coloration with phenolphthalein, indicating faint alkalinity due to the presence of normal carbonates in solution. There were no stopes for considerable distances above this point. The analysis of this water is given on page 58. Water that was being pumped from the Smuggler mine gave similar reactions.

Water dripping through the "contact" on the first level of the Aspen mine, Aspen Mountain, at a depth of about 150 feet vertically below the surface, was neutral. There were no stopes above the point where this water was tested. Water dripping from the roof of the Hooper stope, on the third level of the Aspen mine, was also neutral.

A water sample for analysis was collected from the fifteenth level of the workings under Smuggler Hill in block 27, about 2,700 feet northeast of the Mollie Gibson shaft and about 1,000 feet
vertically below the surface. The water was flowing in a voluminous stream from a watercourse in dolomite and was probably draining from ground between the fifteenth and thirteenth levels. It was clear and of ordinary temperature. Its analysis is given below, and its quality has been calculated in accordance with the Palmer method.  

**Analyses of cool descending mine waters from Aspen, Colo.**  
*Durant tunnel.*  
[Analyst, Chase Palmer, U. S. Geol. Survey.]

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<thead>
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<th>Parts per million.</th>
<th>Reacting value.</th>
<th>Adjusted reacting value (per cent).</th>
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<td>By weight.</td>
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<td>.0001</td>
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<sup>a</sup> Assumed as ferrous.

Alkalies balanced by strong acids…………………….. per cent. 16.8
Earths balanced by strong acids……………………… do 55.0
Earths balanced by weak acids………………………… do 27.8
Metals balanced by weak acids………………………. do 44

**Fifteenth level, Smuggler Hill workings.**  
[Analyst, Chase Palmer, U. S. Geol. Survey.]

<table>
<thead>
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<th>Parts per million.</th>
<th>Reacting value.</th>
<th>Adjusted reacting value (per cent).</th>
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</table>

<sup>a</sup> Assumed as ferrous.

Alkalies balanced by strong acids…………………….. per cent. 13.8
Earths balanced by strong acids……………………… do 5.6
Earths balanced by weak acids………………………… do 80.2
Metals balanced by weak acids………………………. do 4

100.0

These waters resemble each other in their low content of alkalies and metals and their high content of earths. Both are low in chlorine. They contrast principally in the larger percentage of \( \text{SO}_4 \) radicle in the Durant tunnel sample. Both are dominantly calcium and magnesium bicarbonate and sulphate waters. Their composition is such as might be expected in waters of surface origin that have descended through a sedimentary series including limestone and dolomite. Their quality is neutral or slightly alkaline.

It is probable that the descending mine waters that deposited most of the native silver of the Aspen ores were similar in general composition to those analyzed.

As indicating that at least some of the native silver was deposited from calcium bicarbonate waters, the presence of calcite intergrown with native silver along fractures in dolomite at a depth of about 500 feet in the Aspen mine is noteworthy. The following statement by Spurr\(^9\) is also of significance in this connection.

In the concentrating works at Aspen, where ore is crushed and separated by means of ordinary cold water, certain iron parts of the apparatus become coated with native silver precipitated from the water that flows over them. This shows that ordinary surface waters have power to dissolve and carry away silver, which they deposit under favorable circumstances.

It is clear as a result of the microscopic studies that the waters which deposited native silver in many places simultaneously dissolved barite. In view of the extremely low solubility of barite under most natural conditions this observation warrants some discussion. The deposition of barite from natural waters, some of them of deep-seated and some of surface origin, has been repeatedly observed, but most of these waters are dominantly chloride solutions and so show no analogies to the Aspen mine waters.

Barium sulphate is soluble in pure water at 18° C. to the extent of about 24 milligrams per liter. The presence of free sulphuric acid in mine waters would not facilitate the solution of barite, for the solubility of barium sulphate in sulphuric acid solutions is actually diminished or even destroyed if the concentration of the acid is higher than 0.3 normal; with lower concentrations the solubility is almost the same as in pure water. The supposition that the enriching solutions carried free sulphuric acid does not, therefore, aid in explaining the unusual replacement of barite. Furthermore, the association of much of the silver with limestone and dolomite and the apparent deposition in one place of calcite with the silver are opposed to the conception that the enriching solutions were acid at the time that they deposited silver and dissolved barite.

It has been shown by Z. Karaglanow\(^{10}\) that through the influence of various electrolytes the solubility of BaSO\(_4\) in water may be increased or diminished. It is diminished if the electrolyte contains ions in common with BaSO\(_4\); it is increased if the electrolyte possesses the property of removing barium or sulphate ions from the solution. He concludes that

the solubility of BaSO\(_4\) in different electrolytes is determined by two factors, the anion and the cation. The anion SO\(_4^2-\) diminishes the solubility, NO\(_3^-\) increases it, and Cl is indifferent. Of the cations, Ba diminishes the solubility of BaSO\(_4\), while Ca is indifferent, and K, Na, Sr, Pb, Fe, and H increase it.

The influence of the carbonate or bicarbonate radicle on the solubility was not studied by Karaglanow, but some observations by P. Carles\(^{11}\) have a bearing on this point. In order to account for the simultaneous presence of barium and alkali sulphates in the mineral waters of Néris-les-Bains, France, the following experiment was made. A specimen of barytes from the district was boiled with twice its weight of sodium carbonate until partly converted into barium carbonate. The still alkaline paste was then supersaturated with carbon dioxide under pressure and filtered after 12 hours. The perfectly clear filtrate, which contained sodium sulphate, deposited barium carbonate when the excess of carbon dioxide was expelled by heating.

It is evident that alkali hydrogen carbonates in the presence of an excess of carbon dioxide are capable of holding barium hydrogen carbonate in solution in the presence of soluble sulphates.

From these experiments it would appear that the presence of alkali bicarbonates in a solution may appreciably facilitate the solution of barite. It is not unreasonable to suppose, therefore, that the waters that dissolved barite and deposited native silver at Aspen were of a quality similar to the present mine waters. It is well known that silver may be readily transported in mine waters in balance with either the sulphate or the bicarbonate radicle.

**SUMMARY.**

1. The lead ores of concentrating grade that constitute the present main economic resource of the Aspen district pass in places, apparently gradationally, into ores consisting dominantly of tennantite or of tennantite and barite but also rich in silver minerals. Some of these ores that carry silver only as primary pearceite and argentite are very rich.

2. In some places in the rich silver ores tennantite and barite are the oldest primary minerals and are traversed by replacement vein-

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lets of later primary galena, sphalerite, bornite, chalcopyrite, pearceite, and calcite, as shown in Figures 13 and 14. Elsewhere a division into two groups can not be made, all the primary minerals having apparently been deposited essentially contemporaneously, as suggested by the relations shown at A, Figure 13. Texture characteristic of a common type among the rich silver ores is shown in Plate III. In one specimen tennantite, pearceite, and argentite occur intimately intergrown and all apparently primary. (See fig. 15.) No evidence was found of more than one general period of primary mineralization.

3. Downward enrichment in silver has been most effective in those ores in which primary silver minerals were abundant. The principal secondary silver mineral deposited by the waters working down through the ore bodies from the surface was native silver, but in some places secondary pearceite and argentite were also deposited, as shown in Figure 16.

4. Native silver plays out with depth and is clearly a product of downward enrichment. It was noted to vertical depths of around 1,200 feet.

5. Most of the native silver has been deposited through the replacement of older minerals. Silver compounds are commonly the first minerals to yield to such replacement, but the replacement eventually involves base-metal sulphides and finally barite. (See figs. 17 to 21.)

6. Some tapering and curling "teeth" and wires of native silver have grown outward from their point of attachment into the open spaces of vugs and fractures. Many of them are attached to a base of pearceite and have clearly formed at the expense of this silver compound. Some wires, teeth, and plates of silver in vugs and fractures are not now associated with any silver compounds, but it can not be demonstrated that such compounds were absent at the time the silver was deposited.

7. Notable oxidation was observed in or adjacent to the ore bodies to a depth of around 1,000 feet.

8. Mine waters were tested at several points. All were cool descending waters, neutral or very faintly alkaline in reaction. Two samples were analyzed, and their quality is shown diagrammatically in Figure 22. They are dominantly calcium and magnesium sulphate and bicarbonate solutions, though alkalies are also present.

9. It seems probable that the waters instrumental in the deposition of the native silver were similar in quality to those analyzed. It is known that silver can be effectively transported in solution in balance with either the sulphide or bicarbonate radicle. The abundance of limestone and dolomite in association with some of the native
silver and the presence at one place of secondary calcite intergrown with the silver indicate that the silver-depositing waters were not acid.

10. Chemical data are cited to show that this interpretation of the quality of the enriching solutions is consistent with the observed solution of barite simultaneously with the deposition of native silver.