

# PRIMARY NATIVE-SILVER ORES NEAR WICKENBURG, ARIZONA, AND THEIR BEARING ON THE GENESIS OF THE SILVER ORES OF COBALT, ONTARIO.

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## INTRODUCTION.

The silver ores of the Monte Cristo mine, near Wickenburg, Ariz., are of peculiar interest to economic geologists because their principal silver mineral—native silver—is primary, whereas most occurrences of native silver are unquestionably secondary—the products of downward enrichment. Of interest also is the association of the native silver with nickel arsenides, in which respect the Wickenburg ores resemble the famous silver ores of Cobalt, Ontario, though they differ markedly from the Cobalt ores in another respect, for at Cobalt the native silver has commonly replaced calcite or arsenides or antimonides of nickel or cobalt, whereas at the Monte Cristo mine the native silver crystallized nearly or quite contemporaneously with the nickel arsenides, and there is no evidence that it has replaced any other minerals.

The field work on which this report is based was done in 1913 in the course of a study of silver enrichment undertaken by the United States Geological Survey in many mining camps of the western United States. The work of preparing the results for publication has been delayed by the war and other causes.

The Monte Cristo mine is about 12½ miles by wagon road northeast of Wickenburg, half a mile southwest of Constellation post office, and 65 miles northwest of Phoenix. No topographic maps of the district are available. In 1913 the mine was owned by Mr. Ezra Thayer, of Phoenix, to whom the writer is indebted for many specimens of high-grade ore and for numerous data concerning the mine.

## BEDROCK FORMATIONS.

The prevailing country rock in the immediate vicinity of the Monte Cristo mine is a granite gneiss whose well-marked banding in the area west and south of the mine shows steep dips and strikes ranging from N. 60° E. to N. 80° E. This gneiss is gray where

unaltered and is composed dominantly of white quartz, white feldspar, and biotite. The foliation is the result of parallel arrangement of the plates of biotite and their segregation in particular abundance in certain layers. Interlayered with the granite gneiss are bands and lenses of a hornblende diorite gneiss that in places carries distorted crystals or "augen" of feldspar. This rock has the appearance of a sheared diorite porphyry.

So far as the writer is aware no systematic geologic studies have been made of the area that includes the Monte Cristo mine, but the southern border of the Bradshaw Mountains quadrangle<sup>1</sup> lies only a few miles to the north. The granite and diorite gneisses probably belong to the series of supposedly pre-Cambrian igneous rocks described in the Bradshaw Mountains folio.

The granite and diorite gneisses in the vicinity of the mine are intruded, commonly parallel to their foliation, by dikes of granite pegmatite that carry pink potash feldspar, quartz, biotite, and black tourmaline.

All these rocks are cut by dikes of fine-grained diabase, which is in places amygdaloidal.

#### PRIMARY MINERALIZATION.

*Structural features of the veins.*—The workings of the Monte Cristo mine develop two veins—a west vein and an east vein, known locally as the main vein and the shaft or footwall vein. The first mining was done by Mexicans on the east vein and on a small vein still farther east, and the greatest depth they attained was about 80 feet. In 1909 the west vein, which is the mainstay of the mine, was discovered. It strikes in general slightly west of north and dips 45°–55° W. In 1913 it was developed by an inclined shaft connecting with nine levels spaced approximately at 100-foot intervals. The drifts in general follow the footwall of the west vein, and the longest (fifth level) in 1913 had been extended 580 feet north of the shaft. Although the relations of the two veins are not everywhere perfectly clear the east vein strikes in general similarly to the west vein but has a steeper dip, so that the two veins diverge downward. On the second level, for example, they follow opposite sides of a 4-foot diabase dike, but in a crosscut on the seventh level they are about 60 feet apart. Except possibly close to the surface the east vein has not proved productive, and practically all the drifts and raises are on the west vein, to which the following discussion is confined. The wall rock throughout most of the workings is granite gneiss with a few dikes of pegmatite. On the second level a dike

<sup>1</sup> Jaggard, T. A., jr., and Palache, Charles, U. S. Geol. Survey Geol. Atlas, Bradshaw Mountains folio (No. 126), 1905.

of diabase was encountered, and in a raise above the ninth level there is a little hornblende diorite gneiss.

In general the west vein is a zone from 1 to 15 feet wide of fractured, softened, and mineralized granite gneiss in which there are from one to half a dozen gouge-lined planes of slipping, all nearly parallel to the general trend of the vein. The ore minerals appear to have been in the main deposited by replacement of the fractured gneiss; evidences of deposition in large open spaces are lacking, crustification was not noted, vugs are commonly very small, and the ore texture is very irregularly massive. In general the metallic minerals are abundant only in bands or lenses a few inches wide, the intervening vein material carrying them only as sparsely disseminated grains.

*Chalcopyrite type of ore.*—The commonest type of ore throughout the mine and the only type noted in most places carries chalcopyrite as its dominant metallic mineral, in a gangue consisting mainly of quartz. Pyrite is invariably present in minor amounts, and in some localities tennantite, siderite, and calcite were noted. The tennantite is not appreciably argentiferous. Ore of this type was noted on all levels from the second to the ninth.

Assays of two samples of the chalcopyrite ore from the eighth level near the shaft showed 17.75 and 18 per cent of copper, 29 and 44 ounces of silver to the ton, and \$3.60 and \$3.68 in gold to the ton. In a raise from the ninth level ore of this type showed 30 ounces of silver and \$2 in gold to the ton. Some assays show small amounts of nickel and cobalt.

Ore of this type was expected to form the main product of the mine in operations on any considerable scale.

*Ore with magnetite and hematite.*—What appears to be an unusual variant of the chalcopyrite type of ore was noted at one place on the fifth level. Here the ore carries abundant hematite and magnetite intercrystallized irregularly with chalcopyrite, siderite, calcite, and a little quartz and pyrite. All these minerals are perfectly fresh and are unquestionably contemporary and primary.

*Distribution of rich silver ores.*—The rich silver ores of the mine, many of which carry niccolite, are largely restricted to a somewhat ill-defined shoot that intersects the shaft at the first level and appears to pitch about 45° S. South drifts on the fourth, fifth, and sixth levels have tapped this ore body, but in 1913 the seventh, eighth, and ninth levels had not been extended far enough to reach it. The rich ore may occur well within the main vein of relatively lean ore of the chalcopyrite type or in its hanging wall or foot-wall, and within the rich shoot the total width of vein may thus be considerably increased. A crosscut into the hanging wall within

this shoot on the fourth level exposes a width of about 30 feet of ore. In 1913 the rich ores were best exposed on the fourth level, on which, at a point about 160 feet south of the shaft, for example, a band of rich ore about  $1\frac{1}{2}$  feet wide occurs in the footwall of the vein, with a few smaller bands and lenses for a foot above it. This ore belongs to the niccolite-bearing type described below. A crosscut into the hanging wall 210 feet south of the shaft on this level reveals another band of rich ore about 6 inches wide that is of a different type, being composed of argentite, barite, and calcite. Above this band in the hanging wall occurs fully 12 feet of granite gneiss carrying replacement bunches and veinlets of chalcopyrite and pyrite. This rich band is short, for a parallel crosscut 20 feet farther south failed to encounter it.

Although native silver is in the main confined to the ore shoot described above, it occurs sporadically elsewhere. In 1913 the deepest point in the mine at which it had been found was on the eighth level near the shaft.

Ores carrying ruby silver have been found in small quantities within the main ore shoot at several points between the fourth and sixth levels.

*Niccolite-bearing silver ores.*—Ores carrying niccolite in scattered grains as much as 2 millimeters in diameter were noted on the fourth level at the point mentioned above and between the fourth and fifth levels. The minerals present in these ores are native silver, niccolite, chloanthite, chalcopyrite, tennantite, quartz, and barite; in a few places they contain also pyrite, enargite, calcite, siderite, and argentite. One specimen carried all these minerals except native silver and argentite. Characteristic relations between niccolite, chloanthite, and the gangue minerals are shown in figure 33. Although these minerals belong to a single period of mineralization it is evident, from this figure, that the general order of crystallization was (1) niccolite, (2) chloanthite, (3) quartz and barite, with doubtless some overlap. The chloanthite characteristically envelops the niccolite and more rarely traverses it as a sharp-walled veinlets (not shown in fig 33). Quartz and barite serve as matrix for the nickel arsenides and may also traverse them as veinlets, as at A, or embed fragments of them, as at B.

In other parts of the same specimen that is shown in figure 33 native silver is abundant, and its relations are illustrated in figure 34. Much of the silver is partly or completely inclosed by niccolite. Some of the silver within niccolite shows branching crystal forms characteristic of silver, and most of it shows straight crystal boundaries against the niccolite. As niccolite is an effective precipitant of metallic silver from silver solutions, we may inquire whether the

silver in this specimen has replaced niccolite. The regular crystalline outlines shown by the silver are not valid evidence against replacement, for it is well known that pyrite, for example, may assume its characteristic cubical form while replacing the minerals of rocks, and in this particular specimen if silver has not replaced niccolite

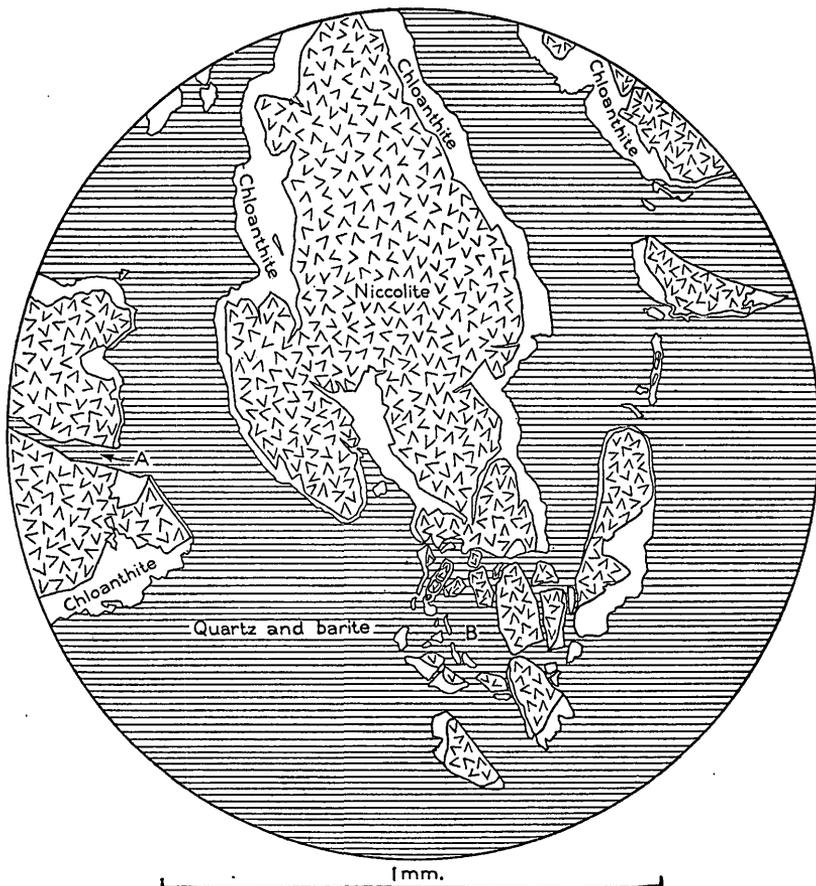


FIGURE 33.—Characteristic relations of niccolite, chloanthite, and calcite, Monte Cristo mine, near Wickenburg, Ariz. The chloanthite envelops the niccolite. Quartz and barite in turn envelop both; here and there veinlets of quartz and barite cut niccolite and chloanthite, as at A, or these minerals may embed fragments of niccolite and chloanthite, as shown at B. Camera lucida drawing from polished surface.

it has certainly replaced rock minerals. Yet where native silver has clearly replaced niccolite and similar minerals, as in the ores of Cobalt, Ontario, its form and distribution are plainly controlled by fractures and by the contacts between different minerals. Furthermore, where the replacement has been nearly complete rounded remnants of the replaced mineral are common within the silver. No such relations exist in the Monte Cristo ores. Areas of pure silver

enveloped in chloanthite and of pure niccolite enveloped in chloanthite may occur side by side, or the nucleus in the chloanthite envelope may be part silver and part niccolite separated by a single even, sharp contact. Such relations would be extraordinary if the silver had replaced the niccolite. The textural relations between silver and niccolite illustrated in figure 34 can be adequately ex-

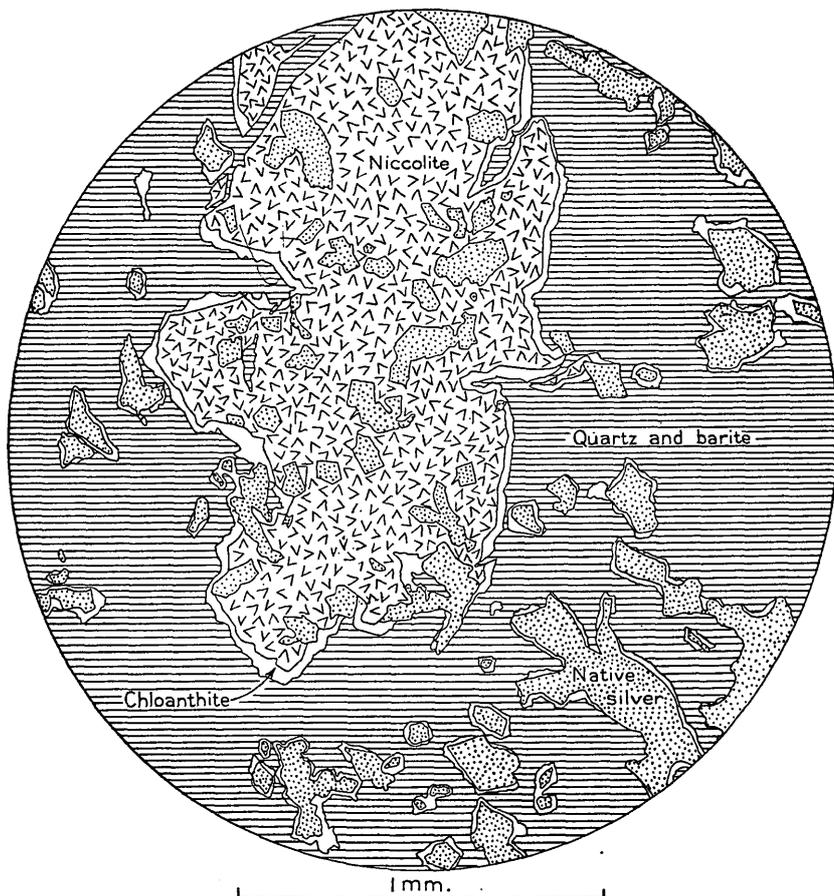


FIGURE 34.—Primary intergrowth of niccolite, native silver, and chloanthite, Monte Cristo mine, near Wickenburg, Ariz. Note the crystal forms assumed by much of the silver and the absence of any evidences that the silver has replaced other ore minerals. Camera lucida drawing from polished specimen.

plained on the hypothesis that both minerals are primary but that the silver began to crystallize about numerous centers slightly earlier than the niccolite. This interpretation is supported by other textural features to be described below. The contrasts between the mineral relations at Cobalt and at the Monte Cristo mine are discussed further on pages 147-150. Chalcopyrite, tennantite, and the rare enargite in general lie outside the chloanthite envelopes and appear

commonly to be slightly younger, but in places they are irregularly intercrystallized with chloanthite. Most of the silver is slightly older than the chloanthite, but minor amounts of it are in places intercrystallized with the chloanthite in very fine intergrowths. The order of crystallization appears to be roughly that in which the



FIGURE 35.—Primary native silver forming branching crystals enveloped by chloanthite, Monte Cristo mine, near Wickenburg, Ariz. Camera lucida drawing from polished specimen.

minerals are listed on page 154, but the periods of deposition of some of the minerals overlap. All, with the possible exception of calcite and argentite, belong to a single period of primary mineralization.

The small amounts of argentite noted in the niccolite ores are mentioned in the section on argentite ores (p. 141).

*Chloanthite-bearing silver ores.*—The niccolite-bearing ores described above grade into other ores that differ mainly in the absence of niccolite and the greater abundance of chloanthite. The general order of crystallization is the same as for the niccolite-bearing ores. Specimens from depths ranging from 80 to 400 feet were studied.

In some of these ores native silver forms groups of crystals enveloped in chloanthite, which in turn is inclosed by an association of quartz and barite. Figure 35 shows the appearance of a specimen of such ore, which came from a depth of only 80 feet below the surface, near the first level. The silver shows branching crystal forms that are characteristic of that metal and is generally inclosed in an envelope of chloanthite, although such envelopes may be very thin and are in a few places entirely absent, the crystals of silver being

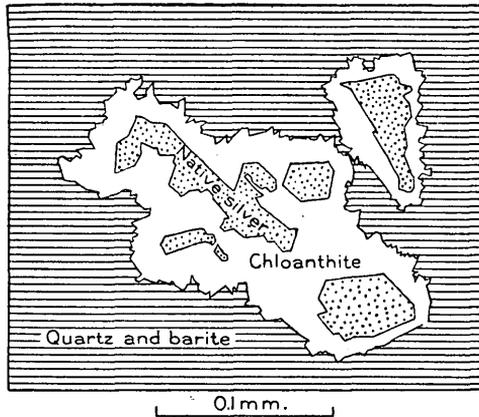


FIGURE 36.—Drawing on a larger scale of a portion of the specimen shown in figure 35. Note the straight crystal outlines of the silver. Chloanthite also shows crystal outlines against quartz and barite, though on a smaller scale.

directly inclosed by barite and quartz. The silver is nearly everywhere bounded by straight crystal faces, as shown in figure 35 and still more clearly in figure 36, a larger-scale drawing from a part of the same specimen. In other parts of the same specimen minute inclusions of silver are dusted abundantly through considerable masses of chloanthite. Under high power some of these inclusions are seen to be branching crystalline masses, miniatures of those shown in figure 35, but most of them are highly and fantastically irregular. In places they form a veritable sponge of silver within the chloanthite. They bear no relation in distribution to the borders or the crystallographic directions of the chloanthite crystals, and there are no indications that they have been formed by replacement. In other parts of the specimen shown in figures 35 and 36 silver, chloanthite, and quartz are intergrown in the intimate and irregular

fashion shown in figure 37; the silver of these intergrowths appears to be of approximately the same age as the other minerals. In a few places silver, chalcopryrite, and tennantite are irregularly intergrown without any chloanthite.

*Ores carrying ruby silver.*—At several places on the fourth to sixth levels in the main ore shoot ores rich in ruby silver (proustite) occur. In these ores the minerals are distinctly of two generations, both of which appear, however, to be primary. The minerals of the

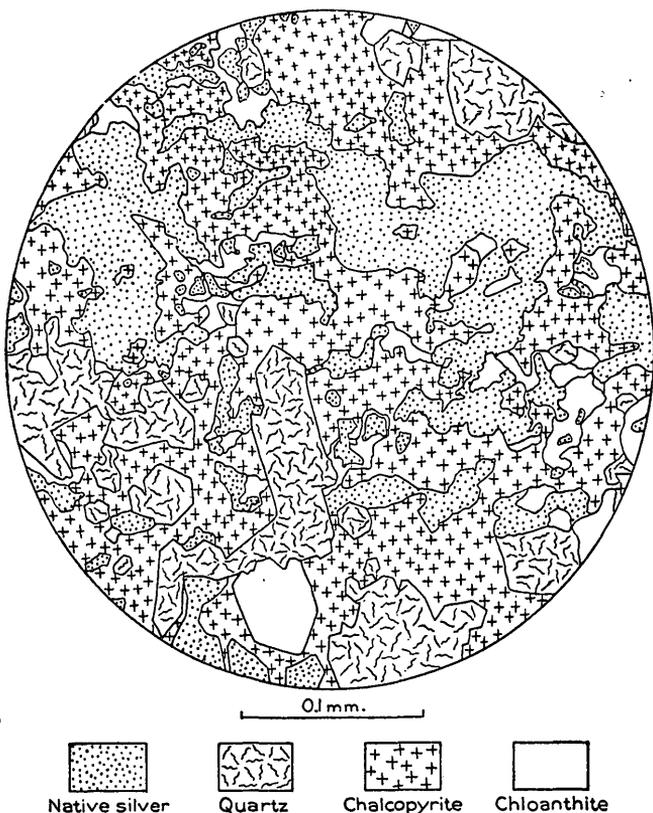


FIGURE 37.—Irregular primary intergrowths of native silver, chalcopryrite, chloanthite, and quartz, Monte Cristo mine, near Wickenburg, Ariz. Note that there are no indications that the silver has replaced other ore minerals. Camera lucida drawing from polished specimen.

first generation include arsenopyrite, pyrite, chalcopryrite, and quartz, with a little sphalerite and siderite. Those of the second generation are proustite, tennantite, and calcite, with minor amounts of chalcopryrite, gersdorffite ( $\text{NiAsS}$ ), argentite, pearceite, and quartz.

In a specimen from the 600-foot level minute sharp-walled veinlets of pearceite and calcite traverse the minerals of the first generation. In parts of this specimen coarser portions of the ore composed of an irregular intergrowth of calcite, chalcopryrite, and proustite

appear to grade into the finer portions characterized by the minerals of the first generation. Elsewhere, however, small veinlets composed of intergrown calcite, chalcopryrite, argentite, and proustite traverse the older minerals.

A specimen obtained between the fourth and fifth levels shows ore composed of the minerals of the first generation in places fractured

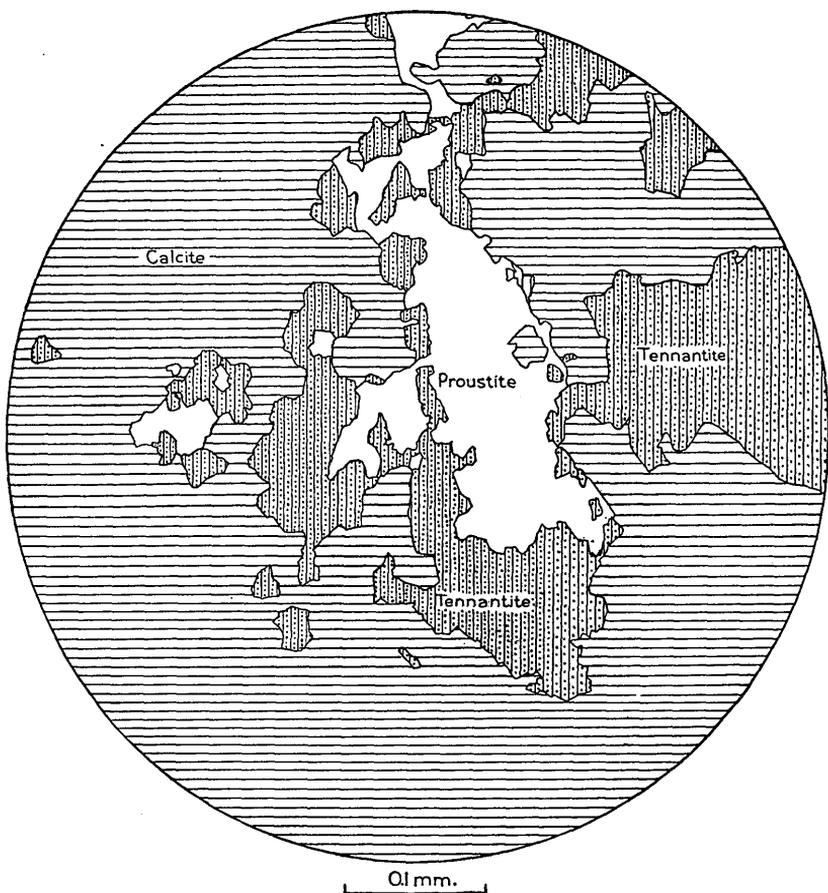


FIGURE 38.—Irregular primary intergrowth of proustite, tennantite, and calcite, between 400 and 500 foot levels, Monte Cristo mine, near Wickenburg, Ariz. Camera lucida drawing from polished specimen.

and traversed by veinlets of proustite, chalcopryrite, gersdorffite, tennantite, quartz, and calcite. The gersdorffite commonly occurs in radiating form along the walls of these veinlets. Tennantite and proustite are irregularly intergrown, as shown in figures 38, 39, and 40, all drawn from parts of the same specimen. As shown by these figures there is no evidence that the proustite has replaced tennantite. Either mineral may inclose the other; the boundary between them is usually characterized by crystal faces. The two

stages in the primary mineralization may be perceived in the hand specimens as well as microscopically.

*Argentite-bearing ores.*—Argentite was noted in the niccolite, chloanthite, and proustite bearing types of ore that have already been described. In these ores it is usually a very minor com-

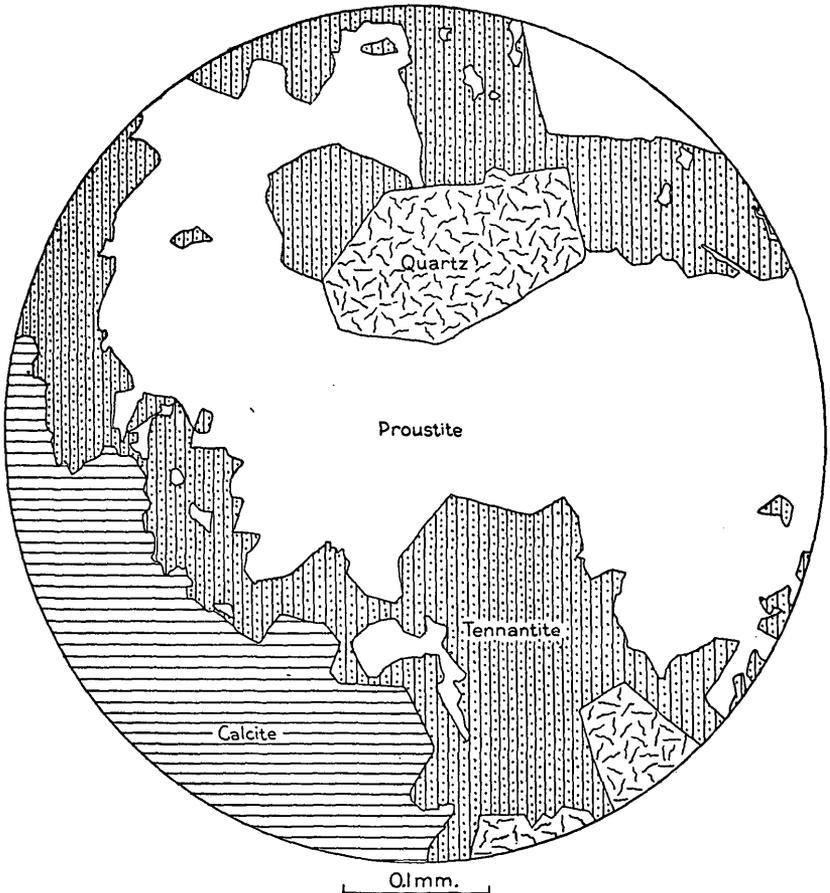


FIGURE 39.—Primary association of proustite, tennantite, calcite, and quartz, between 400 and 500 foot levels, Monte Cristo mine, near Wickenburg, Ariz. Note the nearly straight crystal faces common between proustite and tennantite; these indicate that neither mineral has replaced the other. Camera lucida drawing from polished specimen.

ponent and was among the last minerals to be deposited. Figure 41 illustrates its textural relations in ore containing niccolite and native silver. Argentite, calcite, and quartz form veinlets traversing both niccolite and chloanthite, and these veinlets are continuous with the calcite and quartz matrix that envelops the nickel arsenides. Evidently in such ores the argentite is one of the latest of the primary minerals.

In the proustite-bearing ores small amounts of argentite are intimately intergrown with proustite and tennantite and, like them, represent a late primary crystallization.

In some places argentite occurs in considerable abundance. On the 400-foot level, for example, it is associated with barite and calcite in parts of a 6-inch streak of rich ore. It forms well-defined crystals intercrystallized with calcite in vugs in this ore and also forms nar-

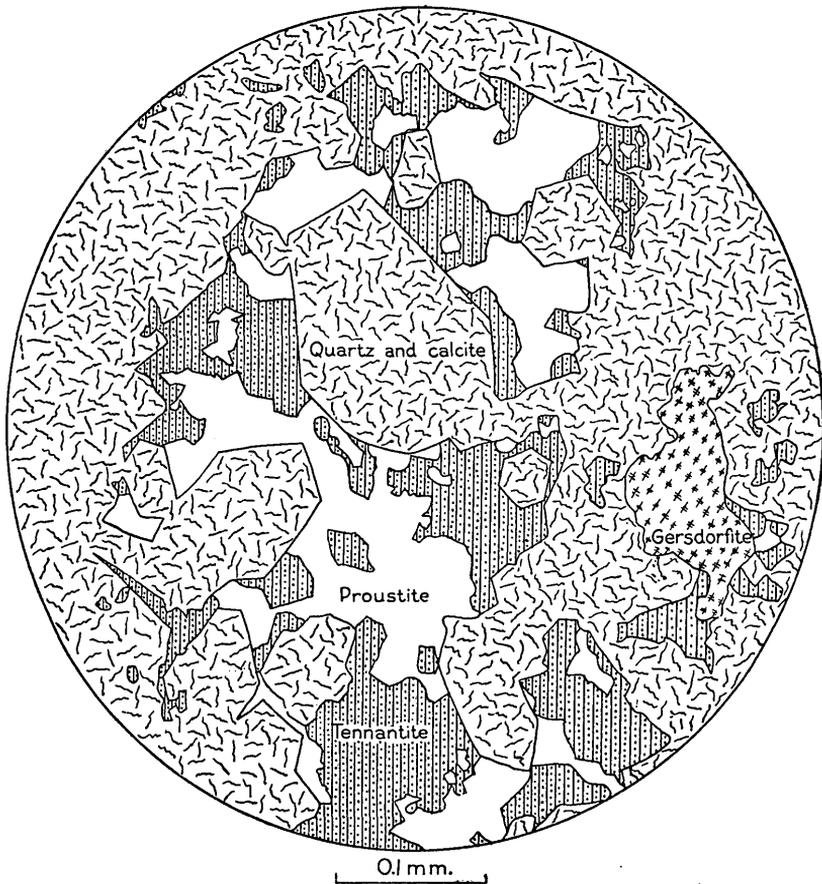


FIGURE 40.—Primary intergrowth of proustite, tennantite, quartz, and gersdorffite, Monte Cristo mine, near Wickenburg, Ariz. Camera lucida drawing from polished specimen.

row veinlets, 0.5 millimeter or less in width, cutting barite and calcite. These relations, though indicating that the argentite was deposited late in the epoch of mineralization, do not show whether it is primary (hypogene) or secondary (supergene). However, the rich argentite ore is associated in the same 6-inch band with ore showing native silver and chloanthite in branching intergrowths resembling those illustrated in figure 35, and in this ore some of the native

silver cores within chloanthite have clearly been replaced peripherally by argentite or by an intimate intergrowth of argentite and calcite. This is the only instance of replacement of one metallic mineral by another noted in the mine. The boundaries between silver and argentite or the argentite-calcite intergrowth are of the utmost irregularity, even when viewed under high power. The specimen

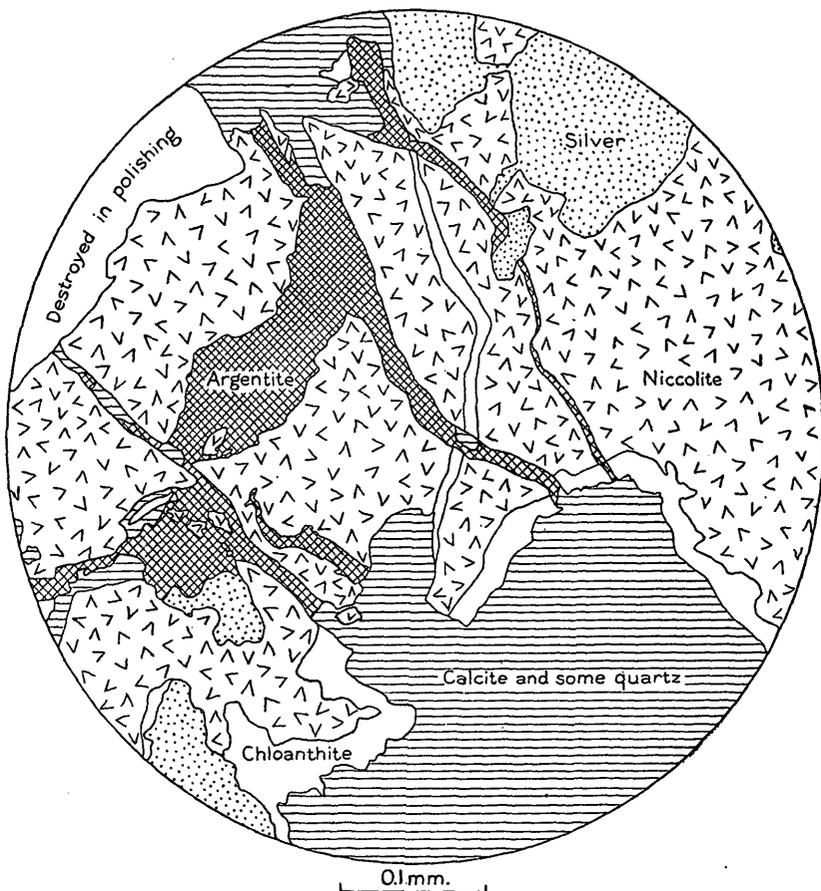
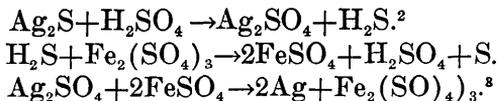


FIGURE 41.—Association of niccolite, chloanthite, and native silver which has been fractured and argentite and calcite have been deposited in the fractures, probably as late primary minerals, 400-foot level, Monte Cristo mine, near Wickenburg, Ariz. Camera lucida drawing from polished specimen.

was not suitable for the preparation of a large sketch, but the irregular nature of the silver-argentite boundaries at two places is shown by figure 42. The replacement of silver by argentite is the reverse of the characteristic replacement of argentite by silver so commonly noted in the downward enrichment of silver ores. The latter is usually attributed either to direct oxidation of the combined

sulphur by atmospheric oxygen or to its less direct oxidation through the united agency of sulphuric acid and iron sulphates in accordance with some such equations as



Such explanations, though not in all respects satisfactory, have the merit of invoking only reagents that are abundant and characteristic in the oxidized zones of sulphide ore bodies.

The replacement of native silver by argentite noted in the Monte Cristo ores can not be so readily explained as the work of reagents characteristic of the zones of oxidation or sulphide enrichment. It is

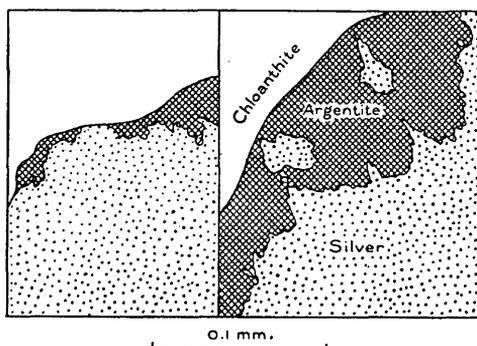


FIGURE 42.—Replacement of native silver by argentite, Monte Cristo mine, near Wickenburg, Ariz. Note ragged replacement boundaries between silver and argentite and the silver replacement remnants in argentite. Camera lucida drawing from polished specimen.

possible to regard the replacement of silver by argentite in these specimens as involving no chemical interchange and as therefore analogous to the well-known replacement of limestone by pyrite or of silicified wood by chalcocite. This interpretation is of improbable validity, however, because the argentite in the Monte Cristo ores replaces only native silver, a fact which strongly suggests that the silver content of the argentite was derived mainly if not wholly from the native silver. If this is true what was the agent that accomplished the oxidation? Hydrogen sulphide or alkaline sulphides, as is well known, may effect such transformations. It would appear also from experiments by H. C. Cook<sup>4</sup> that finely divided sulphur may also combine with silver even at ordinary temperatures and pressures to form silver sulphide. Hydrogen sulphide may be de-

<sup>2</sup> Cook, H. C., The secondary enrichment of silver ores: Jour. Geology, vol. 21, p. 25, 1913.

<sup>3</sup> Stokes, H. N., Experiments in the solution, transportation, and deposition of copper, silver, and gold: Econ. Geology, vol. 1, p. 649, 1905-6.

<sup>4</sup> Op. cit., p. 25.

veloped during downward enrichment by the action of sulphuric acid on certain sulphides, but such sulphides are absent from the Monte Cristo mine, and the prevalence of calcite shows that descending acid waters were not abundant. On the other hand, the presence of either hydrogen sulphide, alkaline sulphides, or sulphur would accord with our knowledge of the character of ascending waters of deep-seated origin.

In ore between the fifth and sixth levels argentite is found in fine-grained intergrowth with barite, bands half an inch across being about half argentite. Under the microscope it is found that the barite nearly everywhere shows its characteristic crystal faces next to the argentite. The argentite has clearly not replaced barite; if it had, the crystalline outlines of the barite would, in places at least, have been destroyed. What to the unaided eye appears to be veinlets of argentite traversing barite are shown by the microscope to be simply narrow masses of argentite lying between the flat faces of large parallel crystals of barite. In a few places small inclusions of chalcopyrite are inclosed by the argentite, but there is no evidence that argentite has replaced chalcopyrite. The argentite of this specimen is interpreted as probably of the same age as the barite. Barite, as is well known, may be deposited from descending solutions, but in this mine it is one of the principal primary gangue minerals.

Because argentite is in places intergrown contemporaneously with quartz, barite, and calcite, the common primary gangue minerals, and because in replacing silver it reverses the relation usual in downward enrichment, it is considered probable that much of the argentite is a late primary mineral.

*Gold ores.*—No gold minerals were noted in any of the ores collected, but assays show high gold content in a few places. The richest gold ores are reported to have been found south of the shaft on the sixth level, for a length of about 150 feet along the drift. The richest ore ran 25 ounces in gold to the ton, and the average gold content is said to have been about  $2\frac{1}{2}$  ounces.

#### OXIDATION.

The original ground-water level is reported to have stood about 300 feet below the surface. The first level was not accessible in 1913, but on the second and all deeper levels oxidation was notably slight. Limonite stains were noted along fractures in the vein as far down as the seventh level, but some of these stains may have been deposited since mining began. Ore said to have come from a depth of only 60 feet showed no evidence either of oxidation or of enrichment. Figures 35 to 37, sketched from this ore, show entirely unaltered primary ore.

Sparse and interrupted coatings of the hydrous arsenates cobalt bloom (erythrite) and nickel bloom (annabergite) were noted on a slickensided surface in ore from the second level that in other respects showed no alteration. These arsenates are in general of rare and meager occurrence, even in the shallow ores.

A little staining with malachite was noted along fractures in chalcopyrite ore on the third level. No halogen salts of silver were seen.

In general, therefore, with the possible exception of a few feet of vein material close to the surface in parts of the mine that were not accessible, there is no thoroughly oxidized zone. Oxidation products are found only in small amounts along a few fractures. Ores that are perfectly fresh were found at depths of only 60 feet and probably extend much nearer to the surface.

#### MINE WATERS.

The mine workings are comparatively dry. No water was noted above the fourth level. Numerous tests with litmus paper and methyl-red solution of waters dripping through the vein on the fifth and lower levels showed that they were all neutral.

#### DOWNWARD SULPHIDE ENRICHMENT.

Sulphide enrichment in copper was essentially negligible, being restricted to the development of peacock tarnishes on chalcopyrite, noted even on the deepest or ninth level. No recognizable chalcocite was seen.

Argentite that is probably of late primary origin has been described above, but in a few other occurrences the argentite may possibly be secondary (supergene). A specimen from the third level, for example, shows primary ore traversed by veinlets as much as 0.5 millimeter in width that consist mainly of argentite, although crystals of calcite and barite project into the argentite from the walls.

On the sixth level the granite gneiss of the hanging wall, carrying disseminated grains of pyrite, is traversed by numerous fractures, along some of which sheetlike masses of argentite less than 0.3 millimeter in thickness have been deposited. Minute crystals of calcite occur in close association with the argentite, and in one place sphalerite was apparently intimately intergrown with the argentite. Sphalerite where observed elsewhere in the mine is clearly primary.

Criteria seem to be lacking to determine the primary (hypogene) or secondary (supergene) origin of this argentite. If it is secondary it was not deposited from acid solutions, as is shown by its association with calcite. Even if this argentite is secondary, enrichment phenomena have at best played but a very minor part in the geologic history of the Monte Cristo mine.

**THE MONTE CRISTO ORES COMPARED WITH THOSE OF COBALT, ONTARIO.**

Native silver has long been recognized as a characteristic associate of cobalt and nickel arsenides and antimonides, and the type examples of this association in the Erzgebirge, Germany, and at Cobalt, Ontario, form the subject of a considerable literature. The minerals present in these deposits have been carefully identified, but the age of the native silver with respect to the other ore minerals has not been demonstrated for the Erzgebirge deposits and has been only partly demonstrated for the Cobalt deposits.

Because native silver in most sulphide ore deposits is clearly a product of downward enrichment many economic geologists have been inclined to regard the silver of the cobalt-nickel veins as also a product of enrichment. The apparent playing out of the silver in depth in certain of the veins at Cobalt lent support to this hypothesis, as did also the demonstration that cobalt and nickel arsenides and antimonides were effective precipitants of metallic silver from sulphate solutions.<sup>5</sup> On the other hand, those geologists who have had the most intimate first-hand knowledge of the geology of the Cobalt district have consistently held that the native silver was primary and that downward enrichment operated on only a minor scale, if at all.<sup>6</sup> Their belief is based mainly upon the presence of "blind" (not outcropping) veins rich in native silver, the extension of ores carrying native silver in places to depths of 1,600 feet below the surface, and the presence of rich silver ores in veins that lie beneath the Nipissing diabase sill and so should have been protected by it from downward enrichment. On the whole, the field evidence at Cobalt, which is obviously entitled to first consideration in any attempt to determine the origin of the ores, appears to offer insuperable obstacles to the hypothesis of downward enrichment.

The Monte Cristo ores that form the subject of this report show conclusively that native silver may occur as a primary associate of nickel and cobalt arsenides and therefore support the view that the silver at Cobalt is primary. The mineral relations observed in the Monte Cristo ores made it desirable to review the Survey's small collection of typical ores from Cobalt in order to determine whether any evidences of a primary origin of the silver had been overlooked in previous studies.<sup>7</sup>

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<sup>5</sup> Palmer, Chase, and Bastin, E. S., *Metallic minerals as precipitants of silver and gold*: Econ. Geology, vol. 8, pp. 140-155, 1913.

<sup>6</sup> Miller, W. G., *The cobalt-nickel arsenides and silver deposits of Temiskaming*: Ontario Bur. Mines Rept., vol. 19, pt. 2, 1913. Whitehead, W. L., *The veins of Cobalt, Ontario*: Econ. Geology, vol. 15, pp. 103-135, 1920.

<sup>7</sup> Bastin, E. S., *Significant mineralogical relations in silver ores of Cobalt, Ontario*: Econ. Geology, vol. 12, pp. 219-236, 1917.

The results of this review confirm in most particulars the relations previously reported, which may be summarized as follows:

1. Native silver in the Cobalt ores studied is nowhere of the same age as nickel and cobalt arsenides and antimonides. It has replaced niccolite, breithauptite, smaltite, and locally ferruginous calcite. A study of many specimens from all parts of the district might of

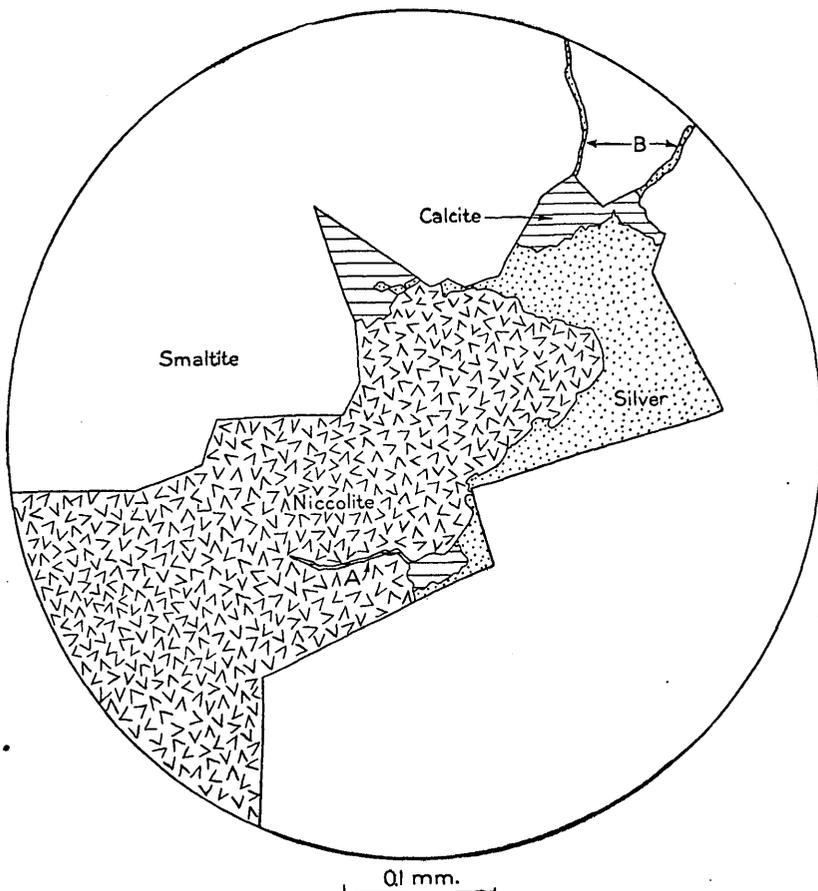


FIGURE 43.—Part of a "nest" of niccolite within smaltite, Kerr Lake mine, Cobalt, Ontario. At vulnerable angles the niccolite has been replaced by native silver and calcite. A is a veinlet of calcite traversing niccolite, and at B are veinlets of silver traversing smaltite. Depth 250 feet. Camera lucida drawing from polished specimen.

course reveal other relations. Evidence of replacement is found in such relations as are shown in figures 43, 44, and 45. All transitions are observable from cores of niccolite alone (or of breithauptite, or both) within smaltite to others in which corners and edges evidently once niccolite are now silver (see fig. 43), to others that are mainly silver inclosing large semirounded niccolite remnants (see fig. 44), and finally to cores that consist wholly of silver except

for very minute and well-rounded niccolite remnants (see fig. 45). These relations are in marked contrast to those at the Monte Cristo mine, where native silver nowhere replaces other minerals, and therefore demand special explanation.

2. The replacements at Cobalt apparently involved chemical interchange between the nickel and cobalt sulphides and arsenides and the

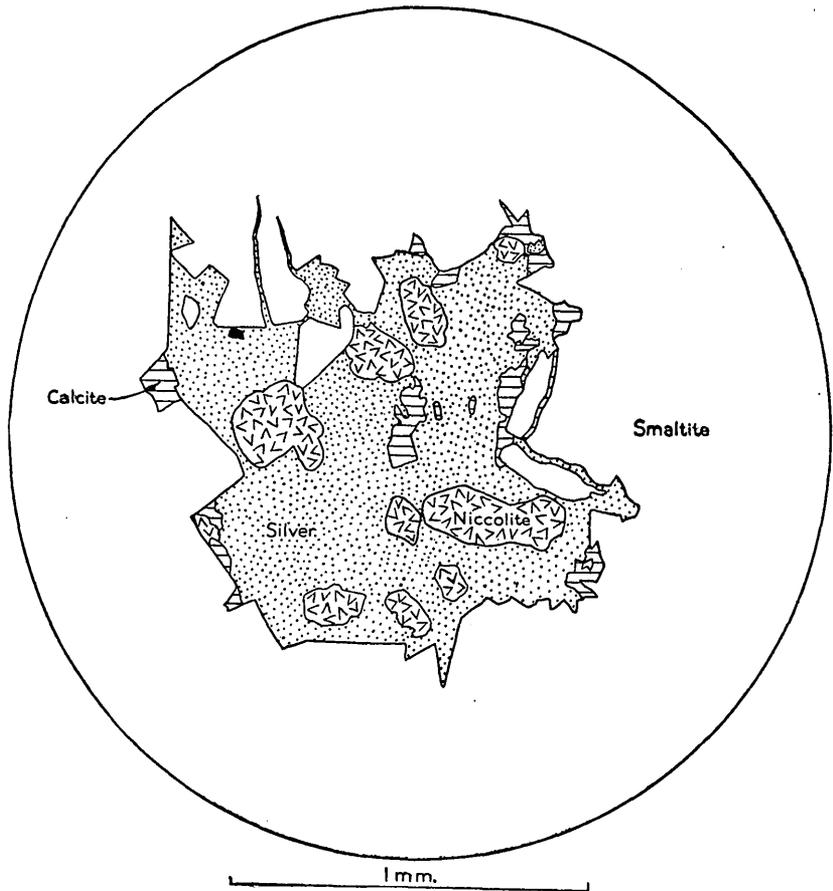


FIGURE 44.—“Nest” of niccolite and silver within smaltite, Kerr Lake mine, Cobalt, Ontario. The niccolite has been partly replaced by silver and a little calcite, leaving several semirounded unreplaced remnants. Camera lucida drawing from polished specimen.

solutions concerned in the replacement and therefore differ from such well-known phenomena as the replacement of calcite by pyrite or of silicified wood by chalcocite. This inference is drawn from the fact that simple arsenides and antimonides of nickel and cobalt have been replaced by silver, whereas sulpharsenides and sulphantimonides have not. In the laboratory the same arsenides and antimonides are rapidly attacked by silver sulphate solution, with the precipitation of

metallic silver, whereas the sulpharsenides and sulphantimonides are not attacked. Furthermore, the replacement of the nickel and cobalt arsenides and antimonides by silver has been selective or preferential. Cores of niccolite are commonly in large part replaced by silver before the replacement of the surrounding smaltite begins. In the laboratory niccolite is attacked much more rapidly by silver sulphate solution than smaltite.

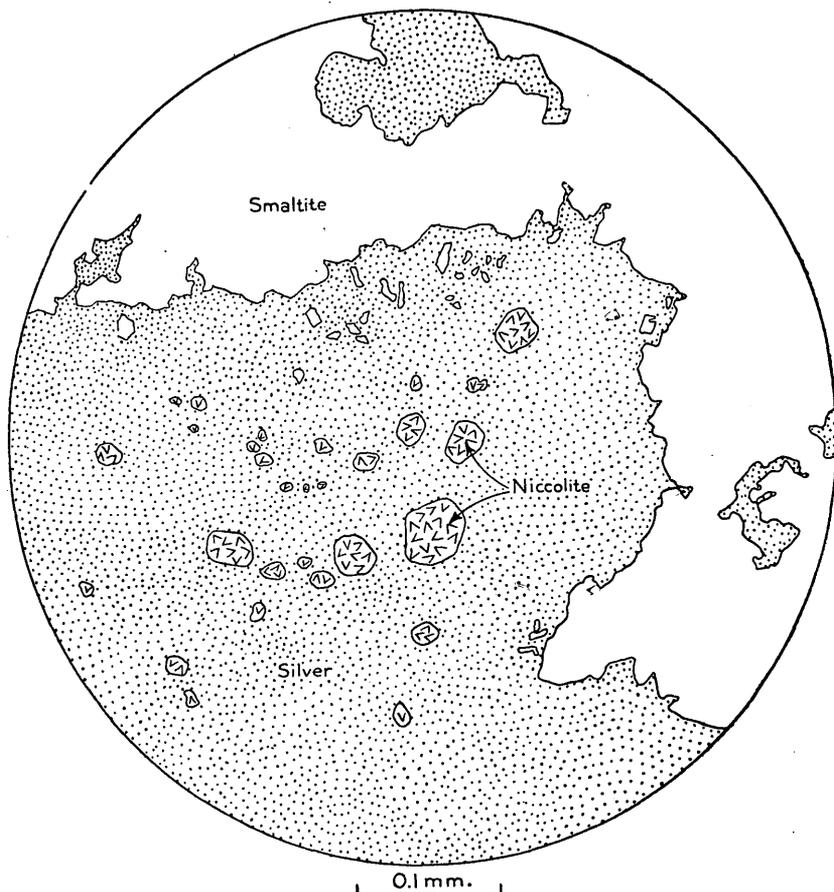


FIGURE 45.—View on larger scale of a part of a “nest” of silver in smaltite similar to that shown in figure 44, except that replacement of niccolite has proceeded farther, leaving only minute rounded niccolite remnants; replacement of smaltite has also begun. From Kerr Lake mine, Cobalt, Ontario. Depth 250 feet. Camera lucida drawing from polished specimen.

#### NATURE OF SILVER-DEPOSITING SOLUTIONS AT COBALT, ONTARIO.

On the basis of the facts just outlined the writer in his earlier paper<sup>8</sup> concluded that much if not all of the native silver at Cobalt had probably been deposited from sulphate solutions through reac-

<sup>8</sup> Op. cit., p. 236.

tions analogous to those which took place in the laboratory. Certain features of the ores, however, have always been somewhat inharmonious with this view. First among these inharmonious features is the abundance of carbonates in the ores. Palmer has shown that the precipitation of silver by nickel and cobalt arsenides and antimonides may proceed under neutral conditions, but metallic sulphides and free sulphuric acid are products of the reactions. If such reactions have brought about the abundant deposition of native silver at Cobalt it would be logical to expect a considerable destruction of carbonate gangue minerals. Some ferruginous calcite has been replaced by silver in these ores, but there is also evidence, cited below, that calcite and silver have jointly replaced niccolite—that is, that they have been deposited simultaneously from the same solution. In the second place the field studies have failed to disclose any sulphates in the ores.<sup>9</sup> If silver was present in the mineralizing solutions in balance with the sulphate radicle we might reasonably expect to find some gypsum, anhydrite, barite, or other sulphate as a gangue mineral. With these facts in mind the writer at the conclusion of his earlier paper on the Cobalt ores stated that “The study of reactions that would take place if the same suite of primary minerals [the nickel and cobalt arsenides and antimonides] were brought in contact with silver-bearing solutions having properties analogous to those of hypogene ore-bearing solutions offers an attractive field for geochemical research.”

The reexamination of the Cobalt collections brings out one fact whose significance was previously overlooked. Some calcite appears to have been deposited contemporaneously with native silver in replacement of niccolite and subordinately of smaltite. In figure 46 is shown, for example, niccolite traversed by veinlets that are part calcite and part silver. Figure 43 shows what appears to be the contemporaneous replacement of niccolite by calcite and silver at vulnerable corners and angles of a niccolite “nest” inclosed by smaltite. The alternative explanation that the silver has replaced both calcite and niccolite is rendered improbable by the fact, apparent under high power, that the calcite-silver contacts are numerous straight crystal faces and have not the irregularities characteristic of replacement. In the specimen shown in figure 44 calcite and silver are also intergrown, apparently contemporaneously, with crystal faces between them.

Miller<sup>10</sup> illustrates branching crystals of silver in calcite. This relation suggests that the two minerals were deposited contempo-

<sup>9</sup> Barite has not been found in the veins of cobalt proper, although it occurs with silver-cobalt ores in one or two veins near Elk Lake, in the Porcupine district, Ontario (Miller, *op. cit.*, p. 9, footnote).

<sup>10</sup> *Op. cit.*, fig. 9, p. 14.

raniously, for silver that has replaced ferruginous calcite in these ores is characteristically devoid of crystal outlines.

All these relations suggest that in the mineralizing solutions at Cobalt the silver was carried in balance with the carbonate or more probably the bicarbonate radicle, and not in balance with the sulphate

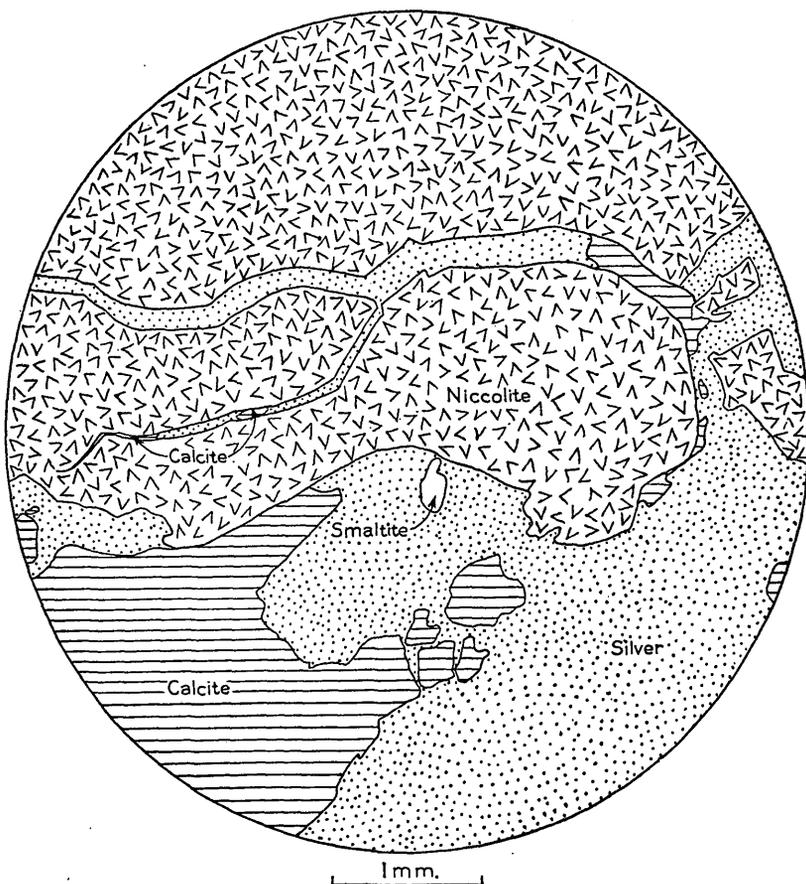


FIGURE 46.—Veinlets of calcite and native silver traversing niccolite, Kerr Lake mine, Cobalt, Ontario. An example of calcite apparently contemporaneous with silver, and both later than niccolite. Camera lucida drawing from polished specimen.

radicle, and the writer therefore proceeded to test this possibility chemically.

Freshly precipitated silver carbonate<sup>11</sup> in a beaker of distilled water was redissolved as bicarbonate by stirring the precipitate and at the same time passing purified carbon dioxide gas through the

<sup>11</sup> Silver carbonate was precipitated from silver sulphate solution by potassium carbonate in excess. The precipitate was washed repeatedly with distilled water until the wash water failed to give any precipitate of barium sulphate with barium nitrate. The washing was continued somewhat longer, to make sure of complete elimination of the sulphate radicle.

water. After filtering, the clear solution of silver bicarbonate, which was neutral toward litmus paper and free from the sulphate radicle, was used in the following experiments.

1. Experiment with niccolite fragments: Fragments of niccolite in an evaporating dish were covered with the clear solution of silver bicarbonate and set aside in the dark for one hour. At the end of that time branching fan-shaped masses of lustrous metallic silver mixed with a dark-gray substance of unknown composition had grown out from the niccolite. Some of these "fans" of skeleton crystals of silver were a quarter of an inch long. Nickel had at the same time gone into solution, as shown by the crimson solution and precipitate obtained when dimethylglyoxime was added to the filtrate. A yellow precipitate of silver carbonate also formed, which redissolved when carbon dioxide was passed into the solution. The solution at the end of the reaction was neutral toward litmus paper.

2. Experiment with powdered niccolite: Reactions like that reported above proceed much more rapidly if the mineral used is pulverized, for a much larger surface is thereby exposed to the attack of the solution. About a gram of powdered niccolite was shaken in a test tube with about 10 cubic centimeters of silver bicarbonate solution. Before the reaction the solution gave a pronounced precipitate of silver chloride when treated with hydrochloric acid. After the mixture had been shaken a few times and filtered the clear filtrate gave no precipitate of silver chloride when treated with hydrochloric acid, showing that silver bicarbonate had been completely removed from solution. With dimethylglyoxime the filtrate gave a marked crimson color and precipitate, showing that nickel had gone into solution.

3. Experiments with powdered breithauptite and maucherite: The procedure just described was repeated with the substitution of breithauptite ( $\text{NiSb}$ ) and of maucherite ( $\text{Ni}_4\text{As}_3$ ) for niccolite ( $\text{NiAs}$ ) and similar results were obtained. In both experiments silver was rapidly and completely removed from solution and nickel was taken into solution. The solutions at the end of the reactions were neutral toward litmus paper. Breithauptite and maucherite are both present in the ores of the Cobalt district and have locally been replaced by native silver. The complete removal of silver from the solutions in experiments 2 and 3 shows that the results obtained were not due to unrecognized traces of silver sulphate remaining as impurities in the solution but involved reaction with silver bicarbonate.

4. Experiment with fragments of smaltite: The experiment described in paragraph 1 was repeated with the substitution of smaltite ( $\text{CoAs}_2$ ) for niccolite ( $\text{NiAs}$ ). At the end of 20 minutes the specimen was examined, and lustrous silver was found to have formed in abundance on the smaltite. The solution was neutral toward litmus paper. After filtering the clear solution was evaporated to dryness.

The residue imparted the characteristic cobalt-blue color to a borax bead, showing that cobalt had gone into solution concomitant with the deposition of silver.

These experiments, though purely qualitative, are perfectly definite and show conclusively that when cobalt and nickel arsenides and antimonides are in contact with a solution of silver bicarbonate a series of reactions ensues which results in the precipitation of metallic silver. These reactions are analogous to the reactions worked out quantitatively for the action of the same minerals on silver sulphate, but they do not develop acidity in the solutions. It is hoped that through cooperative study the reactions with silver bicarbonate may soon be worked out quantitatively and all the products definitely determined.

These experiments develop, therefore, a rational chemical explanation of the selective replacement of nickel and cobalt arsenides and antimonides by native silver in the ores of Cobalt, Ontario, based upon the transportation of the silver in solution as the bicarbonate rather than the sulphate. This explanation appears to be in harmony with the observed abundance of carbonates in the ores and the absence of sulphate and conforms also to the microscopic evidences that in places silver and calcite have simultaneously replaced niccolite and similar minerals. It is likewise harmonious with the field evidence, which points strongly to a primary (hypogene) origin for the rich silver ores.

#### SUMMARY AND CONCLUSIONS.

1. The ores of the Monte Cristo mine, near Wickenburg, Ariz., occur as replacement veins in rocks of probable pre-Cambrian age. There is no direct evidence of the age of the mineralization. If, as seems likely, these veins were formed contemporaneously with most other ore deposits of this region, their age is probably late Tertiary.

2. The minerals listed below were noted in the Monte Cristo ores; the commoner ones are shown in italics.

Primary (hypogene): *Chalcopyrite*, *pyrite*, *arsenopyrite*, sphalerite, galena, *tennantite*, enargite, specular hematite, *quartz*, *barite*, magnetite, *niccolite*, *chloanthite*, gersdorffite, *native silver*, proustite, pearceite, argentite, *calcite*, and *siderite*.

Secondary (supergene): Argentite (?), erythrite (cobalt bloom), annabergite (nickel bloom), and limonite.

3. Although several ore types are recognizable there is no clear evidence of more than one general period of primary mineralization.

4. The microscopic relations in the Monte Cristo ores show clearly that the silver-bearing minerals—native silver, proustite, and pearceite—are primary (hypogene), having crystallized contemporaneously with several of the commoner and unquestionably primary ore minerals. These three silver minerals never replace other minerals in these ores.

5. In some of the Monte Cristo ores argentite has replaced native silver. This argentite is clearly contemporaneous with calcite and is believed to be late primary (hypogene) rather than secondary (supergene).

6. Downward enrichment in silver is negligible unless some argentite is to be interpreted as secondary (supergene). Downward enrichment in copper is limited to the formation of peacock tarnishes on chalcopyrite.

7. Waters dripping through the vein are neutral.

8. Oxidation has been slight.

9. The undoubted primary association of native silver with nickel arsenides in the Monte Cristo mine lends credence to the view that the native silver associated with cobalt and nickel arsenides and antimonides at Cobalt, Ontario, and elsewhere may also be mainly primary.

10. The native silver at Cobalt differs from that at the Monte Cristo mine in that it is not contemporaneously intergrown with the cobalt and nickel arsenides and antimonides but has replaced them. For this reason it has been thought by some to be a product of downward enrichment through the agency of solutions carrying silver in balance with the sulphate radicle. The field relations at Cobalt indicate, however, that the rich silver ores are primary and offer apparently insuperable obstacles to the hypothesis of downward enrichment.

11. The abundance of carbonates and the absence of sulphates in the Cobalt ores suggest that in the mineralizing solutions silver was carried in balance with the bicarbonate rather than the sulphate radicle.

12. A restudy of typical Cobalt ores showing that silver and calcite have simultaneously replaced niccolite also suggests that silver deposition was accomplished by carbonate rather than sulphate solutions.

13. Qualitative experiments prove conclusively that cobalt and nickel arsenides and antimonides are effective precipitants of metallic silver from silver bicarbonate solutions, nickel and cobalt being simultaneously taken into solution. The reactions are analogous to those previously worked out quantitatively for silver sulphate solutions, except that the solutions remain neutral after the reactions.

14. The field relations of the Cobalt deposits, the microscopic relations of the silver to the other ore minerals, experimental work with silver bicarbonate solutions, and partial analogy with the Monte Cristo ores all appear to favor the hypothesis that the rich native silver ores of the Cobalt district are late primary (hypogene) deposits from bicarbonate solutions.

