THE HALOGEN SALTS OF SILVER AND ASSOCIATED MINERALS AT TONOPAH, NEVADA.

J. A. BURGESS.

OCCURRENCE AND GENESIS OF THE SILVER HALOIDS.

The halogen salts of silver have been found in considerable abundance in the Tonopah ores, and the manner of their occurrence in this place is such as to throw some light on the way in which they were formed. It is characteristic in silver mines located in desert regions, to find metallic chlorides, and to a less extent bromides and iodides, in the oxidized parts of the veins, since the downward percolating waters effecting the alteration of the sulphides are charged with alkaline haloids. Penrose¹ has discussed the formation of haloids in arid regions and cites localities where they have been abundantly formed by the action of surface waters.

Character of the Veins.—The ore at Tonopah occurs almost entirely in quartz veins in the "earlier andesite,"² a rock which was so named by Spurr in his professional paper on this region, but which has been more recently determined by him to be trachyte. Much of this rock is covered with a capping of "later andesite" and where so covered the ore consists mostly of primary sulphides, but where the "earlier andesite" outcrops the ore is much oxidized and it is in this oxidized material that the silver haloids are found. The primary ore consists of gold, argentite and the sulphosalt of silver, polybasite, in a gangue of quartz and adularia feldspar. In subsidiary amounts pyrite, chalcopyrite, rhodonite and various carbonates are also present.

¹R. A. F. Penrose, Jr., "The Formation of Haloid Compounds in Ore Deposits in Arid Regions," *Journ. Geol.*, 1894, Vol. 2, p. 314.

²J. E. Spurr, "Geology of the Tonopah Mining District, Nevada," U. S. Geol. Surv. Professional Paper No. 42, 1905. J. A. Burgess, "Geology of the Producing Part of the Tonopah Mining District, 1909," *ECONOMIC GEOLOGY*, Vol. IV., pp. 681-712.

The appearance of the characteristic unoxidized ore is that of white quartz blotched and banded with black sulphides of silver, and frequently containing much pink rhodonite. The base metal sulphides are inconspicuous. The oxidized ore is stained brown and black with the oxidized forms of iron and manganese, and contains both the silver haloids and the remnants of unaltered sulphides. It also contains various other decomposition products.

The "earlier andesite" and the veins are broken by many faults and by a multitude of small fissures and seams, and where the vein is not protected by capping these have served as channels for the percolation of the waters that have brought about the alteration of the primary ore.

Occurrence of the Silver Haloids.—The three secondary silver salts formed in the oxidized ore are the chloride, cerargyrite; the chlorobromide, embolite; and the iodide, iodyrite. They are found as deep as the oxidized ore extends, that is to the 700-foot level. Cerargyrite occurs in far greater abundance than embolite or iodyrite. As regards the distribution of the silver in its different forms, it is probable that in a few places the larger part of it is in the form of cerargyrite, but in general the unaltered sulphides hold most of the silver of the deposit. The commonly associated minerals in the oxidized zone are quartz, sericite, kaolin, talc, gypsum, hematite, limonite, and the manganese oxides. The most thoroughly oxidized veins are usually so crushed and porous as to afford an easy path for percolating waters, and open fissures sometimes occur.

The distribution of the haloids with respect to depth has a significant bearing on their origin. In general it may be said that cerargyrite occupies the upper zone, embolite the middle zone and iodyrite the lower zone of the oxidized veins; or more specifically, where the three minerals are found in a given part of the vein, cerargyrite is the highest and grades downward into embolite, while the iodyrite zone is the lowest and is often rather sharply separated from the embolite zone. These zones are not usually distinct and sometimes two of the minerals are found together; instances occur however which justify their separation

into zones. As an example, iodyrite was found in considerable abundance in the Mizpah vein at the 400-foot and 500-foot levels, between the Mizpah fault and the Desert Queen fault. These faults isolated a rich strip of vein about 50 feet in horizontal extent and left it in a crushed condition favorable to the passage of water. On following this ore upward the iodyrite disappeared and thirty feet above the 400-foot level no iodyrite was found, while greenish embolite was present in some abundance. The character of the transition upward from the embolite was not observed in this place on account of the loss of the upper part of the vein by faulting just below the 300-foot level. The embolite zone is never a well-defined one; while in general occupying an intermediate position between the cerargyrite and the iodyrite, it is usually accompanied by cerargyrite and sometimes by iodyrite.

Genesis of the Silver Haloids.—The alteration of the primary minerals was due to the action of descending oxidizing surface water, which contained in solution salts of chlorine, and a lesser quantity of bromine and iodine salts; and it was from the silver sulphate solutions formed by this water that the haloid silver salts were deposited.

The order of crystallization was chloride, bromo-chloride, iodide; which is contrary to what would be expected from their respective solubilities, since iodide is the least soluble and would be expected to precipitate first. The reason for this reversal may be involved in the complicated set of conditions under which the reactions occurred, and the numerous other minerals present. The most obvious explanation seems to be that the chloride was precipitated first because of the great excess of alkaline chlorides in the solution, and that as the chlorine became reduced in quantity it was partly replaced by bromine, and that the iodide was formed only after the concentration of the other halogens was considerably reduced. The presence of manganese dioxide and sulphuric acid with the liberation of free chlorine, may also have influenced the order of reaction; or the fact that the minerals were deposited in the crystalline form and not as amorphous precipitates, may have modified the results.

The explanation will arise that the order of precipitation may not have been reversed but that the haloid-bearing solutions were ascending instead of descending waters. The objection to this is that this form of alteration occurred only in the veins that outcrop at the surface, and to the greatest extent where the downward passage of water is facilitated by the presence of faults or crushed zones. It did not occur where the veins were covered by capping. The chloride is found in greatest quantity in rich ore close to the surface. The fact that this form of alteration has taken place only in the oxidized and outcropping veins, and to the greatest extent at the places where they were most exposed to the action of surface water, seems to be sufficient evidence of the agency of the surface water in its production.

The condition necessary for the formation of the three haloids in the order in which they are found at Tonopah was the percolation of small quantities of solutions through ore in the process of oxidation; the water travelling at a rate sufficiently slow to permit the diminution by precipitation first of the chlorine and next of the bromine, so that finally the iodine could act as a precipitant. It seems that the conditions best adapted to achieve this result would be a seepage rather than a flow of water. The silver was in no case carried far from the original sulphide ore, and the haloid salts were deposited almost immediately after the oxidation of the sulphide. The water during these reactions is best regarded as a solution of the alkaline haloids, to which a small amount of silver sulphate was being continuously added, permitting the selective precipitation of the silver haloids.

The alteration of iodyrite to cerargyrite or embolite would seem to be an improbable one, since it is a change from a more soluble to a less soluble form, but it seems to have occurred in one locality. In a part of the vein heavily charged with manganese dioxide, corroded crystals of iodyrite were found adhering to psilomelane and closely surrounded with embolite or cerargyrite, the secondary minerals not having been precisely determined. Some of the iodyrite remnants are almost entirely encased in the secondary material in such a way as to leave no doubt of

their relative age and origin. It is probable that the presence of chlorine set free by sulphuric acid and manganese dioxide is accountable for this result.

DESCRIPTION OF THE SILVER HALOGENS.

Cerargyrite.—The silver chloride is most abundant in partly decomposed sulphide ore, or in close proximity to it. It occurs as scales, coatings and fissure fillings, and frequently as minute cubic crystals. In the Mizpah vein, fifty feet below the surface, cerargyrite was found in platy masses one-sixteenth to one-eighth of an inch thick, filling fissures in quartz and adhering tightly to both sides of the fissure, but it is more frequent as coatings on one side of a fissure only. Coatings like this have been found almost completely covering surfaces of four or five square inches. Crystals are found most abundantly in finely crushed ore, and where there is a considerable admixture of altered porphyritic rock. Very perfect crystals are scattered through the soft kaolinized rock. They are translucent with a brilliant adamantine to greasy lustre, usually grayish white in color, but frequently with a faint green or olive tinge. Qualitative analyses seldom fail to show traces of bromine and probably there is a gradation to the chlorobromide.

The crystals are invariably a combination of the cube and octahedron, the cube usually predominating. Many of them are characteristically elongated into tetragonal and orthorhombic shapes. The deposition of the mineral from a solution is well shown in some of the cavities where the crystals have long slender twisted and curved shapes.

Embolite.—The chlorobromide is much less abundant than the simple chloride and was formed under conditions similar to the cerargyrite. It occurs as olive-green coatings and groupings of deformed crystals. Small groups of imperfect cubes are found implanted on massive psilomelane or other gangue material, and some of the best of these crystals show a combination of the cube, octohedron and narrow faces of the rhombic dodecahedron. Specimens are occasionally found with groups of these crystals in

parallel orientation so that bright light reflections are obtained from all at the same angle.

Iodyrite.—The iodide is found commonly as brilliant sulphur-yellow crystals lying loose in fissures in the vein. The largest crystals were accompanied by much flaky brown jarosite which formed a soft, loose matrix that did not interfere with the crystal growth. Other good crystals occurred in a soft, kaolinized substance, but the most perfect ones were found attached to quartz in open fissures. Gypsum is a common associate. One of the largest pockets of iodyrite was found in an open fissure, containing much fine-grained nodular manganese dioxide as loose fragments, in the Valley View vein just above the 500-foot level. These crystals occurred loose and were of a deeper yellow color than usual, and with a somewhat different habit from most of those found. The best specimen found was taken from the Mizpah Vein at a depth of 500 feet and consisted of a lump of small adhering crystals. It weighed six ounces and contained no impurities. The iodyrite also occurs as drusy crystalline crusts and as a powder. No analysis has been made of these crusts, so it is not certain that they are identical in composition with the more perfectly formed crystals.

Iodyrite is interesting as being one of the few representatives of the hemimorphic class of hexagonal crystals. The characteristic habit is a unit hexagonal prism terminated on one end by narrow faces of a steep pyramid ($20\bar{2}1$) and broad base, while the lower end tapers almost or quite to a point by successive alternations of narrow faces of the same steep pyramid and unit prism. This habit is often modified by the relative sizes of the faces, so that short prismatic, long prismatic, tabular to base or prism, and other subordinate types can be differentiated. The crystals are frequently twinned, with $(30\bar{3}4)$ as twinning plane. Measurements have been made of many of the crystals but the oscillations in the growth of the pyramid and prism have produced horizontal furrows and striations and a step-like structure on most of the crystals for their whole length making good readings impossible. Kraus and Cook have recently described

them, giving several drawings to illustrate types and citing several new forms for the crystals.¹

The crystals are sectile and often slightly bent or curved even to a distortion of the angles so that readings on one side of a crystal may vary from one to two or more degrees from the corresponding readings on the opposite side. The forms on the crystals which appear to be unquestionable are (0001), (10 $\bar{1}$ 1), (20 $\bar{2}$ 1), (30 $\bar{3}$ 1), (40 $\bar{4}$ 1), (10 $\bar{1}$ 0), (20 $\bar{2}$ 1) and (000 $\bar{1}$).

DESCRIPTION OF THE ASSOCIATED MINERALS.

Mineral Associations.—The ore deposited at Tonopah is of especial mineralogical interest because of the great variety of associated minerals found with the veins and in the oxidized zone. The successive crystallization of the secondary minerals is well shown in many of the specimens collected, and the majority of the minerals are well crystallized and admit of good measurements with the goniometer. Some of the more prominent and unusual species accompanying the deposit will be briefly described in this paper. The prominent secondary silver minerals in addition to the haloids are argentite, polybasite and pyrrargyrite, all of which occur as direct alteration products of the primary sulphides. The oxides of manganese and iron are very abundant and some of the best occurrences of crystals are in immediate association with these oxides. Sulphates, carbonates, tungstates, molybdates and phosphates are all represented by species in good crystal aggregates.

Jarosite.—One of the prominent minerals associated with the iodyrite is the hydrous basic sulphate of iron, jarosite. One of its occurrences is in the form of minute dark brown scales, resembling mica scales. This is found loose in broken quartz sometimes with yellow iodyrite. Under the microscope these plates are seen to be brown and golden yellow basal plates of rhombohedrons. The mineral also is found as fine drusy crystallizations lining cavities and seams in ferruginous rock. A later

¹ E. H. Kraus and C. W. Cook, "Iodyrite from Tonopah, Nevada," *Amer. Journ. Science*, 1909, Vol. 27, p. 210.

generation of larger crystals with brilliant vitreous luster occurs implanted on the druses and on thin coatings of wad or manganese dioxide. These larger crystals are a combination of the base and unit rhombohedron in approximately equal development, resembling cubes with tetrahedrons. No analysis has been made to determine whether the crystals are true jarosite or natrojarosite.

Hübnerite and Scheelite.—The two tungstates occur associated with the veins but not in large amounts. Hübnerite is found in the cavities of cellular quartz as platy masses showing a good zone of prismatic faces, vertically striated. Some of the thin crystals have a number of pyramidal terminations, but most of the thin plates have broken ends. Light brown scheelite in small masses occurs in the quartz associated with the hübnerite.

Wulfenite.—The molybdate of lead occurs sparingly in some of the porous quartz masses, associated with iodyrite and gypsum of a later generation. Some of the best and most transparent crystals of the silver iodide have been deposited on the thin plates of the wulfenite. The characteristic yellow and orange-red colors of wulfenite are lacking, the plates being practically colorless or with a slight tinge of yellow. The crystals are very thin basal plates with the diametral pyramids on the edges. Barite is in the gangue which carries the wulfenite.

Phosphates.—In some portions of the deposit the porous quartz masses have all their cavities and seams lined with snow-white crystals of apatite. The crystals are very small and of approximately the same size. They consist of short prisms and bases in about equal development, with occasional line faces of the unit pyramid. Bronze-yellow isolated crystals of iodyrite occur implanted on the apatite. The apatite has been covered in places by a flow of pure colorless colloidal silica, forming botryoidal surfaces of glassy hyalite, which is spotted here and there with included yellow iodyrite. Turquoise, the hydrous phosphate of alumina colored with copper, occurs in the form of concretions; and wavellite, another form of the phosphate of alumina is found as little white spherules. These phosphates are all of later age than the body of the ore.

Cinnabar.—This mineral is of a very rare occurrence and is found only in the West End mine, where fissures in the vein are coated successively with botryoidal pyrite or marcasite, and afterwards with botryoidal cinnabar. The cinnabar is of comparatively recent deposition, probably as the result of solfataric action.

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