# CHARACTERISTICS OF THE SILVER-ANTIMONY MINERALS

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## Abstract

The silver-antimony minerals in the Cobalt-Gowganda ores are silver, allargentum and dyscrasite. Three varieties of silver are present, and are classified as silver$_1$, silver$_2$ and normal native silver on the basis of their compositions and modes of occurrence. Silver$_1$ is the main type, and it generally contains some antimony and mercury in solid solution. Silver$_2$ contains large amounts of antimony and some mercury, and is interpreted as being an exsolution from allargentum. Normal native silver is a late variety that is present as veinlets, disseminated grains and wire silver, and it does not contain appreciable amounts of antimony or mercury in solid solution.

Allargentum ($Ag_{0.86}Sb_{0.14}$) is present as discrete grains in silver$_1$, as lamellae in silver$_2$, and as veinlets in calcite. Its compositional range is Ag 84.0–85.6 weight %, Sb 14.4–15.9 weight %, and Hg 0.0–0.9 weight %. Dyscrasite is rare in the Cobalt-Gowganda ores, and was found only as intergrowths with allargentum. Its composition in one sample is equivalent to $Ag_{4.55}Sb_{0.99}Hg_{0.01}$.

## Introduction

The main silver-bearing minerals in the Cobalt-Gowganda ores are antimony- and mercury-bearing silver, allargentum, and dyscrasite, and they all have the appearance of native silver in hand specimens. The characteristics and modes of occurrence of these minerals are described in this paper. These characteristics were determined by ore microscopy, *x*-ray diffraction studies, electron microprobe analyses and by comparison to synthetic antimony silver, synthetic allargentum and synthetic dyscrasite according to the methods described by Petruk *et al.* (1970).

## Minerals

The silver-antimony minerals in the Cobalt-Gowganda ores are silver, allargentum and dyscrasite. Their compositions in 33 samples are plotted as points on a ternary diagram (Fig. 123). Boundaries between the various minerals have been tentatively drawn on the ternary diagram to show the approximate extent of the stability fields of these minerals as deduced from compositional data. Actual stability fields are not known because the phase relations of the Ag-Sb-Hg systems have not yet been determined.

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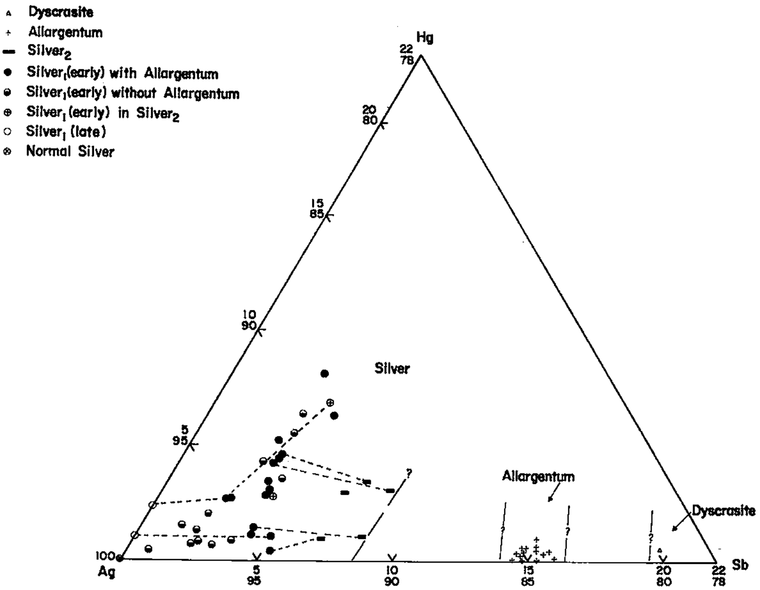


FIG. 123. Ternary diagram of the silver-rich corner of the Ag-Sb-Hg system showing the compositions (in weight percentages) of the silver-antimony minerals in the Cobalt-Gowganda ores. The dashed lines between points connect compositions of silver$_1$ and silver$_2$ found in the same sample.

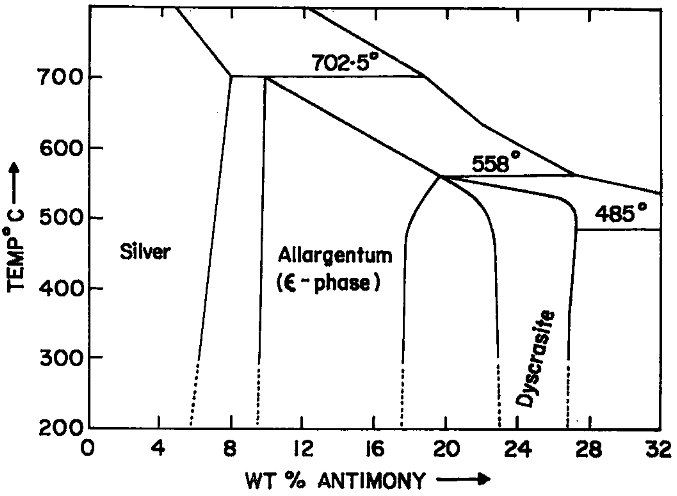


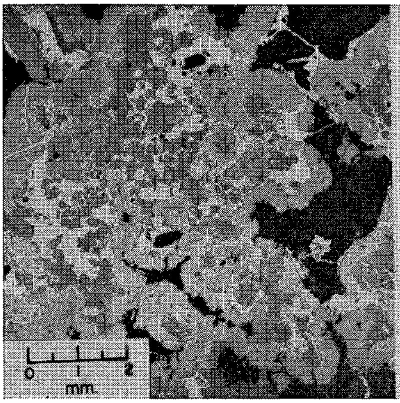
FIG. 124. Phase equilibrium diagram of the silver-rich end of the Ag-Sb system (From Somanchi 1966 and slightly modified by the authors).

The Ag-Sb binary system above 300°C (Somanchi 1966) is shown in Figure 124 to provide some idea of the stability fields in the synthetic system. Keighin (1966) found that at 200°C the stability fields of synthetic ε-phase (allargentum) and dyscrasite are narrower than at 400°C.

*Silver*

Three varieties of silver can be recognized in the Cobalt-Gowganda ores and these have been classified as silver$_1$, silver$_2$ and normal native silver on the basis of their compositions and modes of occurrence. Silver$_1$ is the main variety in these ores. It contains variable amounts of both antimony and mercury, and is optically isotropic. Two ages of it are present : the early variety occurs in the ore veins as cores of rosettes (Fig. 125), and as veinlets and disseminated grains in arsenides and carbonates (Fig. 126) ; the late variety occurs as sub-veinlets and irregular grains in the early one.

Silver$_2$ is present only as a constituent of complex silver$_2$-allargentum intergrowths enclosed in silver$_1$ in those parts of the veins that contain the Ni-Co-As assemblage (Petruk 1970). It contains lamellae of allargentum and silver$_1$, and is bordered by a rim of allargentum (Fig. 127). The allargentum lamellae are at 90° and 45° to each other, and those of silver$_1$ at 75° to one direction of the allargentum lamellae. Silver$_2$ contains somewhat more antimony than does silver$_1$, and is weakly anisotropic between crossed nicols, which agrees with the observation that synthetic



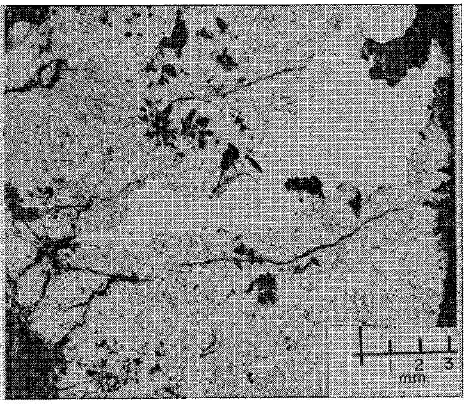


FIG. 125. (Left) Photomicrograph of a polished section showing silver$_1$ (white) at the cores of rosettes, and around the rosettes. The dark grey area is nickeline, the light grey is safflorite, and the black is dolomite.

FIG. 126. Photomicrograph of a polished section showing veinlets of silver$_1$ (white) in arsenides (grey). The black area is dolomite.

antimonial silver is also anisotropic (Keighin 1966). Peacock (1940) suggested that the anisotropy may be due to deformation of the cubic silver lattice by partial replacement of silver atoms by antimony. Silver$_2$ was recognized as a distinct variety of silver by the early workers (Walker 1921, and Peacock 1940), but it was subsequently interpreted as a hexagonal on the basis of its anisotropy and the direction of enclosed lamellae. Thus it was assumed to be the natural occurrence of the ε-phase of the Ag-Sb system and named allargentum (Ramdohr 1960). Its *x*-ray diffraction pattern, however, shows that it is a variety of silver with a larger cubic unit cell than normal silver (Tables 37 and 38).

Normal native silver accounts for only a small proportion of the silver in the ore, and is interpreted as the latest ore mineral to have been deposited. It occurs as wire silver and as disseminated grains in geodes, as coatings on joints and fracture surfaces in the wall rock, and as veinlets in late quartz veins. Late native silver is also present as veinlets cutting sulphides, as borders around sulphides, and as exsolutions of nearly submicroscopic rounded grains in acanthite. The late native silver associated with the sulphides was not analysed because the grains are too small, but it is assumed to have the composition of normal native silver (Table 39).

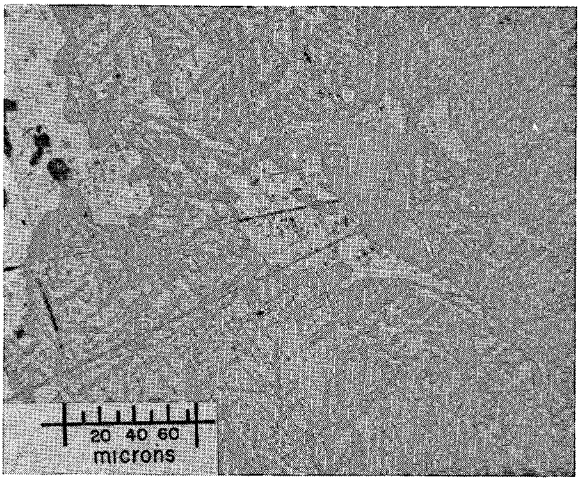


FIG. 127. Photomicrograph of a polished section of a complex grain composed of silver$_1$, silver$_2$ and allargentum. The silver$_1$ is white and is present as irregular grains and as lamellae in the complex grain. The silver$_2$ is light grey and forms the main part of the complex grain, and the allargentum is dark grey and is present as lamellae in silver$_2$ and as borders on the complex grain.

The cell parameters and compositions of silver$_1$, silver$_2$ and normal native silver in typical samples are given in Table 38. It is noted that the unit cell increases from normal silver, through silver$_1$, to silver$_2$ with increasing antimony and mercury content.

TABLE 37. X-RAY DIFFRACTION PATTERNS OF DIFFERENT TYPES OF SILVER

| Silver (99.99% purity) (Swanson & Tatge 1953) | | Normal silver no. 128 | | Silver$_1$ no. 4 | | Silver$_2$* no. 125 | |
|---|---|---|---|---|---|---|---|
| I(est) | d(meas)Å | *I*(est) | *d*(meas)Å | *I*(est) | *d*(meas)Å | *I*(est) | *d*(meas)Å |
| 100 | 2.359 | 10 | 2.35 | 10 | 2.38 | 10 | 2.38 |
| 38 | 2.044 | 6 | 2.04 | 4 | 2.06 | 4 | 2.08 |
| 25 | 1.445 | 5 | 1.442 | 5 | 1.454 | 5 | 1.454 |
| 26 | 1.231 | 7 | 1.230 | 5 | 1.240 | 5 | 1.242 |
| 13 | 1.1796 | 4 | 1.179 | 3 | 1.187 | 3 | 1.192 |
| 4 | 1.0215 | 3 | 1.021 | 2 | 1.021 | 1 | 1.025 |
| 15 | 0.9375 | 6 | 0.9374 | 6 | 0.943 | 6 | 0.9449 |
| 10 | 0.9137 | 4 | 0.9134 | | | 6 | 0.9226 |

* This sample also contained allargentum, but the allargentum lines were omitted from the pattern.

TABLE 38. CELL PARAMETERS AND COMPOSITIONS OF DIFFERENT TYPES OF SILVER

| Type of silver | Sample | Composition in weight per cent Ag | Sb | Hg | Cell parameter * in angstroms |
|---|---|---|---|---|---|
| Normal native silver | 128 | 100.0 | — | — | 4.08 |
| Silver$_1$ | 4 | 92.3 | 3.5 | 4.2 | 4.11 |
| Silver$_2$ | 125 | 90.6 | 8.4 | 1.0 | 4.12 |

* Estimated error = 0.1%

TABLE 39. COMPOSITIONAL RANGES OF DIFFERENT VARIETIES OF SILVER

| Variety of silver | No. of samples analysed | Compositional range in weight per cent | | |
|---|---|---|---|---|
| | | Ag | Sb | Hg |
| Normal silver | 3 | 100.0 | not detected | not detected |
| Silver$_1$ (late) | 3 | 97.3–99.3 | not detected | 0.7–2.7 |
| Silver$_1$ (early) | 29 | 88.5–98.8 | 0.8–5.3 | 0.4–8.1 |
| Silver$_2$ | 5 | 88.6–92.2 | 6.9–8.4 | 0.9–3.3 |

The compositions of $silver_1$, $silver_2$ and normal native silver in individual samples are plotted as points on a ternary Ag-Sb-Hg diagram (Fig. 123), and the compositional ranges of the different varieties of silver are given in Table 39. The results show that $silver_1$ contains variable amounts of antimony and mercury, that $silver_2$ contains large amounts of antimony and some mercury, and that normal native silver is silver with no significant impurities. It was also observed that the silver from the Gowganda area has a lower maximum value of antimony and mercury (2.5 weight % Sb, and 2.5 weight % Hg), than the silver from the Cobalt area. The significance of this is not apparent.

The reflectivity spectra of the various types of silver, allargentum and dyscrasite are given in Fig. 128. The spectra are essentially parallel within the errors of measurements, and it is evident that the reflectivity is quite sensitive to composition. The inset in Figure 128 shows that there is an approximately linear relationship between reflectivity and the combined content of antimony and mercury. Incidentally, the reflectivities of the early and late stages of silver are so similar that the two types can be distin-

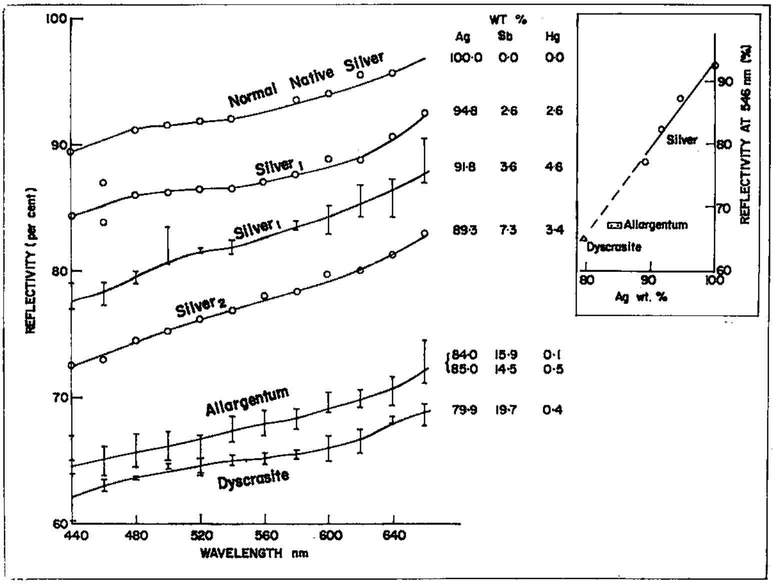


FIG. 128. Reflectivity spectra of silver, allargentum and dyscrasite from Cobalt. The inset in the upper right hand corner shows the relationship between these minerals at 546 nm and weight per cent silver contained in them. The circles show values obtained from one set of readings, and the vertical lines show the range of values obtained from more than one set of readings.

guished only where they are intergrown. The microhardness values and the reflectivity percentages at the four standard wavelengths are shown in Table 40.

### *Allargentum* ($Ag_{1-x}Sb_x$)

The allargentum in the Cobalt ores was referred to as dyscrasite by the early workers (Ellsworth 1916, Walker 1921, and Peacock 1940) and this led to some confusion in the nomenclature and in understanding the relations of the silver-antimony minerals in these ores. A hint of its true identity was provided by Halls *et al.* (1967) who determined its approximate composition, and by Somanchi & Clark (1966) who found a mineral in the Cobalt ores that corresponds to the synthetic ε-phase of the Ag-Sb system. Petruk *et al.* (1970) redefined allargentum, and showed that most of the material previously referred to as dyscrasite in the Cobalt ores is in fact, allargentum. Its compositional range, as determined by analysing 15 samples, is Ag 84.0-85.6 weight %, Sb 14.4-15.9 weight %, and Hg 0.0-0.9 weight %. Its mean composition is equivalent to $Ag_{0.86}Sb_{0.14}$.

The allargentum occurs in silver$_1$ in the parts of the veins that contain the Ni-Co-As assemblage (page 112), and in calcite veins beyond the zone of arsenide mineralization. That in silver$_1$ is present as separate irregular grains, and as a constituent of the complex silver$_2$-allargentum intergrowths shown in Fig. 127. The allargentum in calcite veins occurs as veinlets in pockets of very high-grade silver ore beyond the zone of arsenide mineral-

TABLE 40. MICROHARDNESS AND REFLECTIVITY VALUES

| Mineral | Microhardness VHN in kg/mm² 25 g load | Reflectivity % | | | |
|---|---|---|---|---|---|
| | | 470 | 546 | 589 | 650 |
| Normal silver<br>Ag = 100% | 44.5–74.7<br>61.1(av) | 90.7 | 92.2 | 93.5 | 96.2 |
| Silver$_1$ (sample 16)<br>Ag = 94.8, Sb = 2.6, Hg = 2.6 | — | 85.6 | 86.7 | 87.8 | 91.2 |
| Silver$_1$ (sample 9501)<br>Ag = 91.8, Sb = 3.6, Hg = 4.6 | 79.5–99.7<br>90.7(av) | 78.2–80.0<br>78.9(av) | 81.5–82.6<br>82.1(av) | 83.2–84.5<br>83.9(av) | 85.6–89.2<br>87.0(av) |
| Silver$_2$ (sample 9501)<br>Ag = 89.3, Sb = 7.3, Hg = 3.4 | — | 73.8 | 77.2 | 78.7 | 82.0 |
| Allargentum (sample 9501)<br>Ag = 85.0, Sb = 14.5, Hg = 0.5 | 172–203<br>189 (av) | 64.2–66.8<br>65.4(av) | 66.6–68.6<br>67.5(av) | 68.0–69.7<br>68.7(av) | 70.2–73.0<br>71.3(av) |
| Dyscrasite (sample 1035) | — | 62.7–64.3<br>63.4(av) | 64.5–65.5<br>65.0(av) | 65.0–66.4<br>65.7(av) | 67.5–69.3<br>68.3(av) |

ization, and was observed only in the Deer Horn mine, where it is intergrown with dyscrasite.

The allargentum has a hexagonal close-packed structure. The powder pattern of allargentum, whose composition is Ag 84.3 weight %, Sb 15.3 weight %, and Hg 0.3 weight %, gives a hexagonal unit cell with $a$ = 2.952 Å and $c$ = 4.773 Å. Its calculated specific gravity is 10.12. The reflectivities and microhardness of allargentum are included in Table 40, and its reflectivity spectrum is included in Fig. 128.

### *Dyscrasite*

Dyscrasite was found only in one sample from a pocket of high-grade silver ore in the Deer Horn mine. It is intergrown with allargentum in an allargentum-dyscrasite veinlet in calcite. Its composition is equivalent to $Ag_{4.55}Sb_{0.99}Hg_{0.01}$, and its cell parameters, based on an orthorhombic indexing are $a$ = 2.987, $b$ = 5.178 and c = 4.794 Å. The reflectivities, microhardness and reflectivity spectrum of the dyscrasite are included in Table 40 and Figure 128 respectively.

## DISCUSSION

The silver-antimony minerals in this ore display a number of unusual properties, some of which cannot be explained by our present knowledge on the Ag-Sb-Hg system. These properties are :

(1) The $silver_2$ contains up to 8.4 wt % antimony which exceeds the maximum limits of antimony solubility in silver in the binary Ag-Sb system (Fig. 124). This suggests that the presence of mercury increases the solubility limit of antimony in silver.

(2) The $silver_2$ occurs only in the complex intergrowths with allargentum. It is interpreted that this mineral represents exsolutions from an original allargentum that contained more silver than the present allargentum. Somanchi & Clark (1966) found that a complex intergrowth of $silver_2$ and allargentum, such as the one shown in Fig. 127, forms a homogeneous phase by annealing. They, therefore, suggested that the $silver_2$-allargentum intergrowths were formed by deposition of a homogeneous solid solution which subsequently exsolved into antimonial silver ($silver_2$) and allargentum on cooling.

(3) The $silver_2$-allargentum intergrowth contains lamellae of $silver_1$ which presumably exsolved from the intergrowth and represents a second stage exsolution (Fig. 127). It is not clear why two varieties of silver

would exsolve at two different times from an original silver-rich allargentum.

(4) The silver$_2$ and the early and late varieties of silver$_1$ in the same sample all contain similar amounts of mercury. The significance of this is not apparent.

(5) The allargentum has a very narrow compositional range which suggests that it was formed under conditions where allargentum has a narrow stability field. The Ag-Sb equilibrium diagram, however, shows that allargentum has a wide solid solution field at high temperatures. It is, therefore, suggested that allargentum may have a narrow solid solution field at low temperatures, and that, in the Cobalt-Gowganda ores, this field was reached during cooling. This has also been tentatively suggested by Keighin (1966).

(6) Only a small amount of dyscrasite is present in the ore, and this particular occurrence does not appear to have been previously recognized. The composition of this dyscrasite falls beyond the limits of the stability field indicated on the phase equilibrium diagram. However it contains trace amounts of mercury, and it is possible that the mercury may have caused its stability field to be extended.