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## DYSCRASITE AND THE SILVER-ANTIMONY CONSTITUTION DIAGRAM

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### INTRODUCTION

In connection with an investigation of certain silver ores it was found that etching tests on a lump of supposed native silver from Cobalt, Ontario, gave an excellent etch pattern which did not correspond to results of etching tests on native silver from other localities. The pattern may be obtained by treating with either  $\text{HNO}_3$ ,  $\text{CuCl}_2$ ,  $\text{KCN}$ , or  $\text{KMnO}_4$ . Concentrated  $\text{HCl}$  will develop the pattern if left on for several minutes. The general nature of the intergrowths is similar to that identified by Van der Veen<sup>1</sup> as dyscrasite and native silver. The intergrowth is explained by him as due to a segregation from a solid solution. Inasmuch as the system silver-antimony has been investigated it seemed desirable to make some comparisons of data on natural dyscrasites with data developed by studies of the silver-antimony constitution diagram.

### THE SILVER-ANTIMONY CONSTITUTION DIAGRAM

The silver-antimony constitution diagram has been investigated in detail by Petrenko<sup>2</sup> and by Liebisch<sup>2</sup>, although several workers had previously worked on parts of the diagram. Guertler<sup>3</sup> gives a summary of the work on the system and a graph showing the probable diagram. According to the diagram (see Fig. 1) neither silver nor antimony form as a pure solid from a melt containing both metals. Silver will contain antimony in solid solution up to about 10 per cent by weight. Antimony will hold about 5 per cent of silver in solution at temperatures below 485°C. When

<sup>1</sup> Van der Veen, R. W., *Mineralography and Ore Deposition*, The Hague, 1925, figure 111.

<sup>2</sup> Petrenko, G. J., *Zeit. anorg. chem.*, Vol. 50, p. 133, 1906. Liebisch, T., *Monatsber.*, Berliner A. K., p. 365, 1910.

<sup>3</sup> Guertler, W., *Metallographie*, Berlin, Vol. 1, 1912, p. 769.

the composition of a mixture of the two metals lies between 25 and 35 per cent antimony with 75 to 67 per cent silver, an intermetallic compound  $\text{Ag}_3\text{Sb}$  exists for low temperatures. This intermetallic compound has the composition of the natural mineral dyscrasite. As has been noted by Rastall<sup>4</sup>, dyscrasite may form at  $560^\circ$  by a reaction between the solid solution of antimony

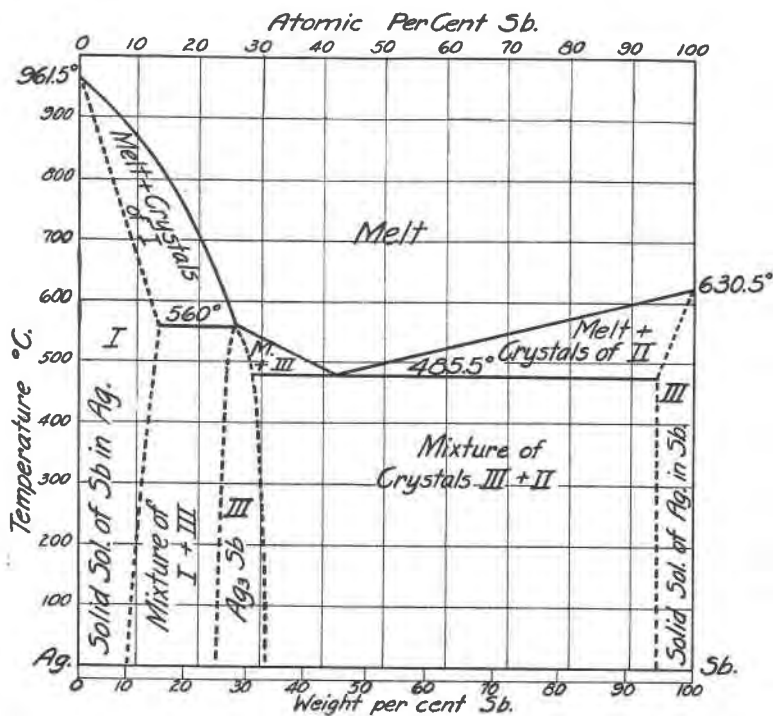


FIG. 1. Silver-Antimony Constitution Diagram. From Guertler, *Metallographie*, Vol. 1, page 769.

in silver and the fused liquid. If the system contains less than 25 per cent and more than 10 per cent antimony, dyscrasite will be formed accompanied by the solid solution  $\text{Ag}+\text{Sb}$ . The dyscrasite forms at  $560^\circ\text{C}$ . whereas the silver solid solution forms between  $560^\circ$  and  $961^\circ\text{C}$ . If the weight per cent of antimony is greater than 33, dyscrasite will be accompanied by the solid solution

<sup>4</sup> Rastall, R. H., *Geology of the Metalliferous Deposits*, Cambridge, 1925, p. 225.

Sb+Ag. In this case the temperature of formation of dyscrasite is 485.5°C., the eutectic temperature. The eutectic composition is about 45.5 per cent by weight of antimony and 54.5 per cent by weight of silver, or 41.5 atomic per cent antimony and 58.5 atomic per cent silver.

So far as the writer is aware the known minerals are limited to the silver side of the diagram, that is, mainly from the intermetallic compound  $\text{Ag}_3\text{Sb}$  to pure silver.

#### APPLICATION OF DATA TO VEINS

In attempting to apply the data available in the constitution diagram shown in Figure 1, the point that at once presents itself is that the Cobalt deposits could scarcely have been deposited as a melt. There is, of course, no necessity for distinguishing between a melt and a solution and it may be accepted that the Cobalt veins were deposited by solutions. If the solutions were of such a nature that the silver and antimony in ratio of 89 to 11 would crystallize out at, for example, 300°C. then a solid solution would probably form. At least we have no very good reason to suppose that it would not. As this solid solution cooled it would become saturated with  $\text{Ag}_3\text{Sb}$  which would precipitate out. Of this we may be certain if the diagram given by Guertler is correct. It may be argued that the presence of water which probably is the main constituent of the depositing solution introduces a new phase and, therefore, the binary constitution diagram does not hold good. This is doubtless true as long as the antimony and silver are in water solution, but on precipitation the water phase is excluded and the antimony-silver equilibrium holds. If the two elements were deposited as separate phases at elevated temperatures they would soon form a solid solution if that were the stable phase at the temperature existing. This point is one of the utmost importance in considering ore minerals which are believed to be precipitated from fairly complex solutions. It enables us to utilize part of the work which has been so laboriously done by the physical chemists and metallographers. The limitations of the possibilities must, however, be clearly recognized.

#### SILVER-DYSCRASITE INTERGROWTH FROM COBALT, ONTARIO

Dyscrasite has long been known as a constituent of the ores in the Cobalt district. That it occurred as an intergrowth with silver

was noted by Ellsworth<sup>5</sup>. Analyses showed too small amounts of antimony to form theoretical dyscrasite and a microphotograph shows skeleton crystals of dyscrasite in native silver.

The significance of the occurrence of varying amounts of antimony in the silver from this region was recognized by Walker<sup>6</sup> who gives several analyses. Walker states, "From information available it seems probable that the material commonly called dyscrasite is made up of a eutectic intergrowth of silver and an antimonide of silver, probably  $\text{Ag}_3\text{Sb}$ , which should contain 27.1 per cent of antimony."

The specimen labelled "native silver" from which the intergrowths here described were obtained was an irregularly rounded mass about four centimeters in diameter. It contained some intergrown calcite, but otherwise seemed fairly pure. It was sawed in two, polished, and smaller pieces sawed off later for analysis and experimental purposes. Previous to etching the polished surface shows a brilliant mirror surface when freshly polished, but faint outlines of the intergrowth may be seen at places. All parts polished thus far show the intergrowths on etching. It was difficult to identify the constituents of the intergrowth found in the specimen described. Following the determinative tables of either Murdoch or Davy and Farnum it would seem that the blades were native silver and the groundmass dyscrasite. From the illustrations by Ellsworth, Walker, and Van der Veen<sup>7</sup> it is obvious that they have identified the blades as dyscrasite and the groundmass as silver. This would accord with results predicted from the constitution diagram. The groundmass is probably a solid-solution of antimony in silver, as noted above.

Microchemical tests on polished surfaces gave the following results:

	DYSCRASITE BLADES	SILVER GROUNDMASS
$\text{HNO}_3$ (1-1)	Iridescent-brownish	Darkens
$\text{HCl}$ (1-1)	Negative	Negative
$\text{HCl}$ (con.)	Negative	Tarnishes brown very slowly
$\text{KCN}$ (20%)	Negative	Tarnishes brown slowly
$\text{FeCl}_3$ (20%)	Iridescent	Iridescent
$\text{KOH}$ (sat.)	Negative	Negative
$\text{HgCl}_2$ (sat.)	Tarnished yellow-brown	Brown to iridescent

<sup>5</sup> Ellsworth, H. V., *Report Ont. Bureau of Mines*, Vol. 25, pt. 1, p. 203, 1916.

<sup>6</sup> Walker, T. L., Dyscrasite from Cobalt, Ontario. *Univ. of Toronto Studies, Contr. to Canadian Mineralogy*, No. 12, pp 20-22, 1921.

<sup>7</sup> *Op. cit.*

Figures 2, 3, and 4 show characteristic intergrowths. The intergrowths are not unlike others which have been attributed to segregation from a solid solution<sup>8</sup>. This suggested the possibility

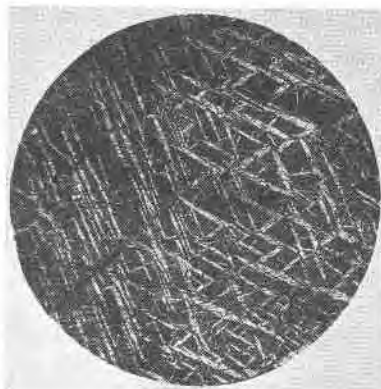


FIG. 2. Photomicrograph showing native silver, or solid solution Ag + Sb (dark), containing blades and lattice of dyscrasite (light). Etched. Cobalt, Ontario. Mag. X. 18.

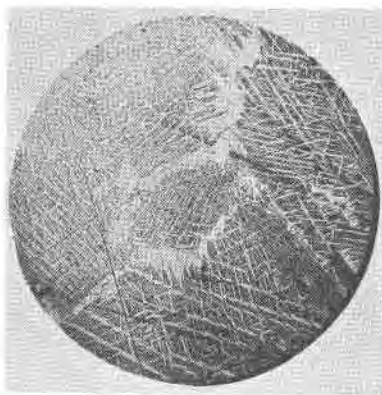


FIG. 3. Field of same surface as Fig. 2, more highly magnified. Mag. X55.

of correlating the intergrowths with the constitution diagram. A partial analysis of a typical piece of the specimen cut off with a diamond saw gave the following results. The writer is indebted

<sup>8</sup> Schneiderhöhn, H., *Untersuchung von Erzen*, Berlin, 1922, Van der Veen, F. W., *op. cit.* Schwartz, G. M., Intergrowths of Chalcopyrite and Cubanite, *Economic Geology*, Vol. 22, pp. 44-61, 1927.

to the University of Minnesota Mines Experiment Station for the analysis.

Silver.....	81.67 per cent
Antimony.....	10.32 per cent
Arsenic.....	0.44 per cent

The impurity is mainly calcite. If the silver and antimony are recalculated to 100 per cent the results are: silver, 88.78 per cent antimony 11.22 per cent. It is probable that arsenic atoms would substitute for antimony in which event the percentages would be: silver, 88.25 per cent, and antimony plus arsenic, 11.75 per cent.

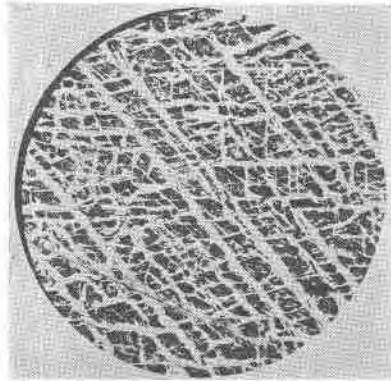


Fig. 4. Intergrowth of slightly different type than that shown in Figs. 2 and 3. Dyscrasite (light) as a more continuous network. Etched and repolished. Cobalt, Ontario. Mag. X 55.

Referring now to Fig. 1, it may be observed that in the case of a melt of either of the above compositions a solid solution of silver and antimony would form when the melt completely solidifies at 560°C., but as cooling progressed the solid solution would break down due, it is apparent, to saturation of the solid solution with  $\text{Ag}_3\text{Sb}$ , which would precipitate out. For eleven per cent antimony the temperature of the break-down would be about 250°C. It should be noted that the boundaries of the various components are dotted, indicating that they are not accurately determined, but represent the probable diagram. It might be logically inferred that the Cobalt native silver-dyscrasite was deposited at a temperature of 250°C., or higher. The fact that the line separating the two states of equilibrium makes the exact temperature of the breakdown rather uncertain.

## EXPERIMENTAL DATA

If the specimen described above represents a mixture of  $\text{Ag}_3\text{Sb}$  and the solid solution ( $\text{Ag} + \text{Sb}$ ) which has formed by the breaking down of a solid solution during cooling, it should form a solid solution on heating. A small piece was sawed off, polished, and etched to observe the intergrowth. This was sealed in a pyrex tube and heated at  $500^\circ \text{C}$ . for three hours and then quenched. Microscopic examination and etching tests fail to give any evidence of the original intergrowth. The specimen appeared perfectly homogeneous and had the appearance of native silver in most respects.

The specimen was reheated and slowly cooled at varying rates, but thus far the two phases have not been reprecipitated in a recognizable form. Possibly extremely slow cooling is necessary or possibly some antimony was volatilized at the higher temperatures. A slight deposit was noted on the tube used for the first test, but this did not appear in later experiments. A small reduction in the antimony present would be sufficient to prevent saturation with  $\text{Ag}_3\text{Sb}$ .

## COMPOSITION OF DYSCRASITE

Dyscrasite has been described as of an extremely variable composition, ranging from  $\text{Ag}_2\text{Sb}$  to  $\text{Ag}_{18}\text{Sb}$ . Dana<sup>9</sup> summarizes the data on composition showing a wide variation. Two of the analyses quoted in the sixth edition agree with  $\text{Ag}_3\text{Sb}$ . A greater number of analyses are given in the 5th edition.

In a more recent paper Smith<sup>10</sup> describes the occurrence of large masses of dyscrasite at the Consols Mine, Broken Hill. He gives the most common types as  $\text{Ag}_3\text{Sb}$  and  $\text{Ag}_6\text{Sb}$ , followed by  $\text{Ag}_4\text{Sb}$ ,  $\text{Ag}_5\text{Sb}$ ,  $\text{Ag}_9\text{Sb}$ ,  $\text{Ag}_{12}\text{Sb}$ , and  $\text{Ag}_{18}\text{Sb}$ .

Doelter<sup>11</sup> gives a more extended summary of the composition and quotes many analyses and concludes that  $\text{Ag}_3\text{Sb}$  is the most common and that dyscrasite is often a solid solution of silver in  $\text{Ag}_3\text{Sb}$ . The constitution diagram shown by Guertler indicates, however, that the so-called dyscrasite is a physical mixture of true dyscrasite,  $\text{Ag}_3\text{Sb}$ , and the solid solution ( $\text{Ag} + \text{Sb}$ ).

<sup>9</sup> Dana, *System of Mineralogy*, 1911, 6th Ed., p. 43; also 5th. Ed., p. 35.

<sup>10</sup> Smith, George, On the Occurrence of Dyscrasite in Australia. *Am. J. Sc.*, Vol. 49, pp. 278-280, 1920.

<sup>11</sup> Doelter, C., *Handbuch der Mineralchemie*, Band IV, 234-238, 1926.

The Cobalt specimen described above appears homogeneous at first sight even on the polished surface, unless it is etched. The analysis would indicate a formula of  $\text{Ag}_9\text{Sb}$ , but etching and microscopic examination show that it is in reality composed of two phases. One of these corresponds to native silver, the other to dyscrasite.

From a consideration of the constitution diagram of silver and antimony it seems quite probable that the variable composition reported for dyscrasite is due to an intergrowth of the intermetallic compound  $\text{Ag}_3\text{Sb}$  with the silver-antimony solid solution, or antimony-silver solid solution in the case of  $\text{Ag}_2\text{Sb}$ . The formula for pure dyscrasite existing as a single homogeneous phase is evidently  $\text{Ag}_3\text{Sb}$ .

#### SIGNIFICANCE OF DYSCRASITE

Dyscrasite has been described as both a hypogene and as a supergene mineral. At Cobalt, for example, perhaps all would agree that it is primary. Whitehead<sup>12</sup> describes its occurrences at Chañarcillo, Chile, where it is supergene. It is probably significant that no intergrowths were described by Whitehead. If they are formed as suggested above they would not occur in ores deposited by cold waters. Further data are necessary to be certain, but it appears probable that supergene dyscrasite would not show crystallographic intergrowths of the type described above. If intergrowths are found they would seem to indicate deposition at temperatures ranging up to  $560^\circ\text{C}$ . and a breaking down on cooling. The presence of intergrowths would be a criterion indicating hypogene deposits. Their absence would have no necessary significance, but would indicate supergene origin as one of the possibilities.

#### CONCLUSIONS

1. It is concluded that the formula of dyscrasite is  $\text{Ag}_3\text{Sb}$ , which is also known as an intermetallic compound in the system Ag-Sb. Dyscrasite with this formula should be homogeneous.

2. Compositions other than  $\text{Ag}_3\text{Sb}$  are due to: (a) the solid solution of antimony in silver (0-10% Sb), (b) a mixture of  $\text{Ag}_3\text{Sb}$  and the solid solution (alloy) of antimony in silver (10-26% Sb), (c) a mixture of  $\text{Ag}_3\text{Sb}$  and the solid solution of silver in antimony (33-95% Sb).

<sup>12</sup> Whitehead, W. L., *The Veins of Chañarcillo, Chile, Ec. Geol.*, Vol. 14, pp. 1-45, 1919.



3. A solid solution of 0.5% of silver in antimony has been produced artificially, but is not known as a mineral.

4. Mixtures of  $\text{Ag}_3\text{Sb}$  and the solid solution  $\text{Ag} + \text{Sb}$  occur as crystallographic intergrowths, as illustrated by the photomicrographs.

5. An intergrowth such as is shown to exist in the ores from Cobalt, Ontario, may originate by (a) the crystallization of the solid solution ( $\text{Ag} + \text{Sb}$ ) above  $560^\circ\text{C}$ ., and the crystallization of  $\text{Ag}_3\text{Sb}$  at  $560^\circ\text{C}$ .; (b) the formation of the solid solution ( $\text{Ag} + \text{Sb}$ ) in the narrow range of 10 to 15% Sb and its breakdown into ( $\text{Ag} + \text{Sb}$ ) and  $\text{Ag}_3\text{Sb}$  on cooling.

6. The wide range in analyses of so-called dyscrasite is inferred to be due to mixtures of the type described, which may be recognized only by etching the polished surfaces and examination under the microscope.