ALLARGENTUM, REDEFINED

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ABSTRACT

It is proposed that the name allargentum be retained for the ε-phase of the Ag–Sb system. This had been proposed by Ramdohr (1949, 1950, 1960), but due to lack of compositional knowledge and *x*-ray diffraction data of the type material, the name was applied to a variety of silver rather than to the natural occurrence of the ε-phase (allargentum) which is also present in the ores from Cobalt, Ontario. This led to confusing interpretations of Ag–Sb assemblages containing allargentum. A recent detailed study of samples from the Cobalt area has permitted a re-appraisal of these assemblages. Allargentum is now redefined as the natural occurring equivalent of the ε-phase of the Ag–Sb system usually, but not necessarily, containing some mercury. It has a hexagonal close-packed structure with a = 2.95 Å and c = 4.77 Å, Z = 2, calculated s.g. = 10.12, and unit cell formulae $Ag_{0.86}Sb_{0.14}$. It is weakly anisotropic under crossed nicols, its reflectivity is less than that of silver, and its microhardness is 189 kg/mm^2.

INTRODUCTION

Ramdohr (1949, 1950, 1960) described a complex assemblage from the ores of the Cobalt area, Ontario, as consisting of native silver, dyscrasite and a new mineral that he called allargentum. He described this new mineral as anisotropic and containing a hexagonal network of lamellae which he interpreted as dyscrasite and late silver. On this evidence, *i.e.*, the anisotropism, the hexagonal network, and the presence of native silver, together with what was assumed to be dyscrasite, he suggested that allargentum was the ε-phase of the Ag–Sb system, which is hexagonal and lies between silver and dyscrasite in composition. No *x*-ray or compositional evidence was given, but the captions under his photomicrographs (Figs. 330 and 331 on pp. 385 and 386 of Ramdohr 1960), clearly show that he called the white mineral silver, the light grey one allargentum, and the dark grey one dyscrasite. This led subsequent workers to use the optical properties in this type of intergrowth as the identifying criteria (*e.g.*, Markham & Lawrence 1962, Petruk 1966). Later work, using the electron probe microanalyser, however, indicated that what was called dyscrasite, using Ramdohr's optical criteria, had, in fact, too little antimony to be dyscrasite, and the apparent allargentum did not have enough antimony to be the ε-phase of the Ag–Sb system (Halls *et al.*, 1967). The simultaneous occurrence of the three minerals described by Ramdohr—silver, allargentum (ε-phase) and dyscrasite—is also not consistent with equilibrium conditions as inferred from the Ag–Sb binary system.

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It thus became apparent that the description of allargentum by optical properties, angles of lamellae, mineral assemblage and analogy to the ϵ-phase of the Ag–Sb system was not sufficient to unequivocally define allargentum. That the ϵ-phase of the Ag–Sb system does occur at Cobalt had been shown by the *x*-ray work of Somanchi & Clark (1966).

The purpose of this paper is to quantitatively redefine allargentum as the ϵ-phase of the Ag–Sb system and to prove that Ramdohr's optical description was erroneously applied to a mercury-bearing antimonial silver and that the "dyscrasite" of his description is, in fact, the natural equivalent of the ϵ-phase of the Ag–Sb system.

METHOD OF INVESTIGATION

The silver-antimony minerals in the Cobalt-Gowganda ores were found in about 700 samples of the ores and studied by means of ore microscopy, *x*-ray diffraction studies, electron probe microanalyses, and by comparison with synthetic antimonial silver, synthetic ϵ-phase and synthetic dyscrasite. The *x*-ray data and unit cell dimensions were obtained by the film method using 114.6 mm diameter Debye-Scherrer powder cameras, and Fe-filtered Co radiation. Film-shrinkage corrections were applied and the intensities were estimated visually. Single crystal work was done on the synthetic ϵ-phase.

The compositions of the minerals were determined by using a Materials Analysis Company (MAC) model 400 electron probe microanalyser. Synthetic dyscrasite, ϵ-phase, and antimony- and mercury-bearing silver were used as standards.

The synthetic Ag–Sb and Ag–Sb–Hg standards were prepared from high purity elements by difference weighing in silica glass. After evacuation and sealing, they were subjected to different heat treatments. The silver charges were heated for half an hour at 640°, for 17 hours at 800° and subsequently were annealed for 67 days at 500° ± 3° in a horizontal tube furnace. After quenching rapidly in an ice-water bath, the sample tubes were opened and some powder was obtained from each sample by using a small hand drill. This powder was annealed for 12–24 hours in an evacuated tube at 500° and then poured into glass capillaries for *x*-ray diffraction. The *x*-ray powder patterns so produced were sharp, and usually contained more reflections than the natural unannealed Ag–Sb minerals. The ϵ-phase runs were heated for 15 hours at 745° and annealed at 500° for 72 days. The rest of the treatment was the same as for the silvers. Small pieces of these synthetic standards were cut off with pliers and mounted in a cold-setting plastic for polished section preparation. They were checked for homogeneity with the electron probe.

The specific gravity was determined on a synthetic sample weighing

98 mg by a hydrostatic method using hexachloro-1,3 butadiene (Cabri 1969).

The ore microscopy, including reflectivity measurements and microhardness determinations, was performed on samples mounted in cold-setting Araldite resin and polished on lead laps with graded diamond abrasives down to 0–2 μ. Final buffing was done for 1½ minutes on a cloth lap with Linde B 0.05 μ metallographic polishing compound.

Reflectivity measurements were made on a Leitz Ortholux-Pol microscope equipped for reflectivity measurements by a Leitz MPE microscope photometer, containing a Dumont 6467 photomultiplier tube, two six-volt storage batteries connected in parallel and maintained under constant charge during operation by a battery charger, and a Veril B 200 continuous band interference filter. A 45:1 objective with a numerical aperture of 0.85 was used.

The microhardness of the minerals was measured on a Leitz Durimet microhardness tester equipped with polarizing filters and rotating stage. The values were determined from 10 readings taken with a 25 gm load. They are given in terms of Vickers hardness number (VHN).

General Description of the Mineral Assemblage

The textures of the silver-antimony minerals from Cobalt were first described by Ramdohr (1950), and these textures are displayed in most samples of high grade silver ore from there. The main texture is a complex intergrowth of three phases, which will be referred to here as phases 1, 2 and 3. (Fig. 1). Phase 1 is present as lamellae in the complex intergrowths. Phase 2 forms the main part of the intergrowths, and phase 3 is present as borders around phase 2 and as lamellae in phase 2. The phase 3 lamellae are at 90° and 45° to each other, and one set is at 75° to the phase 1 lamellae.

Detailed Mineralogy

Phase 1 (silver)

Phase 1 is an antimony- and mercury-bearing silver that contains up to 5% Sb and 8% Hg, and has a cubic unit cell with a cell edge of approximately 4.113 Å. Since the identity of this phase is not at issue, no further details are given here; but it will be described more fully in another paper in preparation.

Phase 2 (silver)

Phase 2 had been previously interpreted by Ramdohr (1960) as a natural occurrence of the ε-phase of the Ag–Sb system (Fig. 2), and he

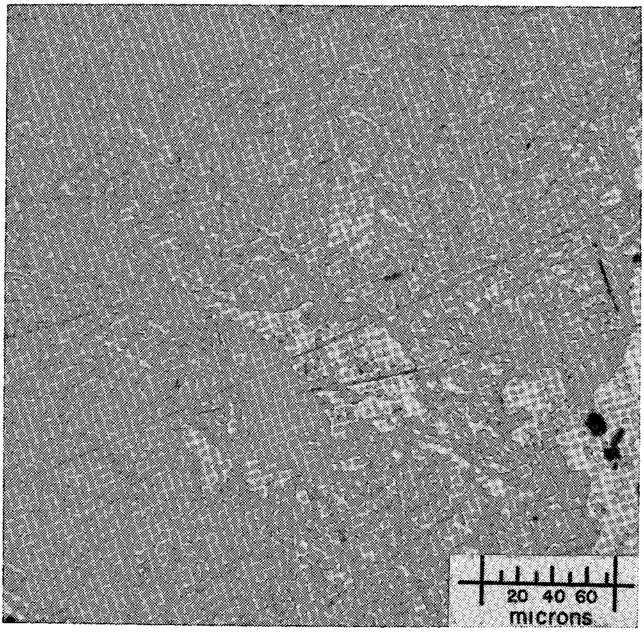

FIG. 1. Photomicrograph of a polished section showing the texture of silver-antimony minerals in the Cobalt ores. The white irregular areas and white lamellae represent phase 1. The light grey area forming the main part of the photograph represents phase 2, and the dark grey areas around phase 2 as well as the lamellae in phase 2 represent phase 3 (allargentum). (This photograph was taken in oil immersion to enhance contrast.)

named it allargentum. Its *x*-ray diffraction pattern, however, corresponds to that of silver (Table 1), and its crystallographic unit cell, 4.120–4.122 Å, is larger than any cell previously reported for silver. The cell parameters of a sample of analysed phase 2, and of the synthetic silvers that were used in this study (Table 2) show that the unit cell increases with increasing antimony and mercury contents. The compositional range of phase 2, in weight percent, determined by microprobe analyses on 5 samples, is Ag 88.6–92.2, Sb 6.9–8.4, and Hg 0.9–3.3. Its reflectivity is lower than that of the phase 1 silver (Fig. 3), which contains less antimony in solid solution. Phase 2 is weakly anisotropic under crossed nicols, which agrees with the observation that synthetic antimonial silver is anisotropic (Keighin 1966). Peacock (1940) suggested that the anisotropy of antimonial silver may be due to deformation of the cubic silver lattice by partial replacement of silver atoms by antimony. These data show that phase 2 is an essentially cubic antimony- and mercury-bearing silver and the name allargentum cannot be applied to it. It is suggested, rather, that phase 2 is a variety of silver that contains maximum or nearly

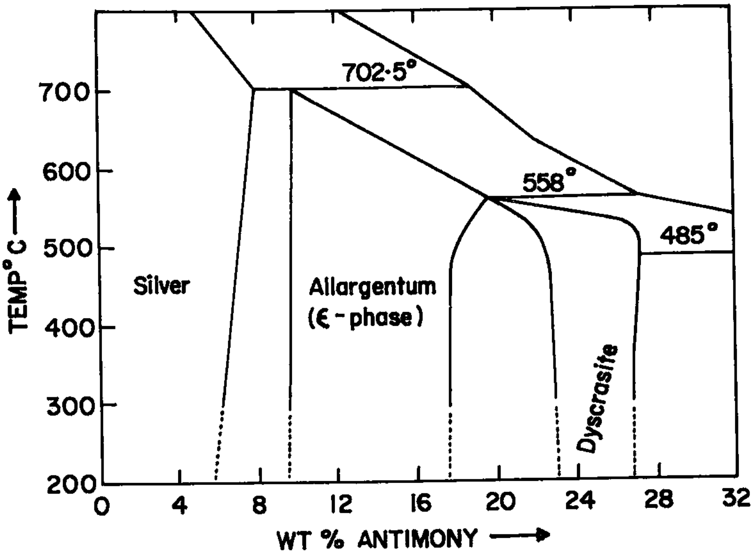

FIG. 2. Phase equilibrium diagram of the silver-rich end of the Ag–Sb system (from Somanchi 1966, slightly modified by the authors).

TABLE 1. X-RAY DIFFRACTION PATTERNS OF SILVER AND PHASE 2 (SILVER)

	Silver (99.999% purity) Swanson & Tatge, 1953		Phase 2 (silver) (Sample No. 125)		Synthetic Cabri 25	
I	*d*(meas)Å	*hkl*	*I*(est)	*d*(meas)Å*	*I*(est)	*d*(meas)Å†
100	2.359	111	10	2.38	10	2.37
38	2.044	002	4	2.08	5	2.05
25	1.445	022	5	1.454	5	1.456
26	1.231	113	5	1.242	7	1.240
13	1.1796	222	3	1.192	4	1.186
4	1.0215	004	1	1.025	3	1.030
15	0.9375	133	6	0.9449	6	0.9458
10	0.9137	024	6	0.9226	6	0.9218

*The pattern also contains the strong lines of ε-phase but they have been deleted here. Estimated accuracy of measured *d* values according to guide lines given by Azaroff & Buerger (1958, p. 218) is ±1%.

†Estimated accuracy ±0.005%.

TABLE 2. CELL PARAMETERS OF PHASE 2 (SILVER) AND SYNTHETIC SILVER USED IN THIS STUDY

		Composition (in weight %)			
Type of Silver	Sample No.	Ag	Sb	Hg	Unit Cell Å
Phase 2	125	90.6	8.4	1.0	4.120 ± 0.01
Synthetic	Cabri 25	91.50	6.03	2.47	4.117 ± 0.004
Synthetic	Cabri 26	92.99	6.05	0.96	4.113 ± 0.004
Synthetic	Cabri 23	93.00	5.00	2.00	4.113 ± 0.003
Synthetic	Cabri 28	93.00	4.02	2.98	4.109 ± 0.003
Synthetic	Cabri 21	94.07	5.93	0.00	4.109 ± 0.002

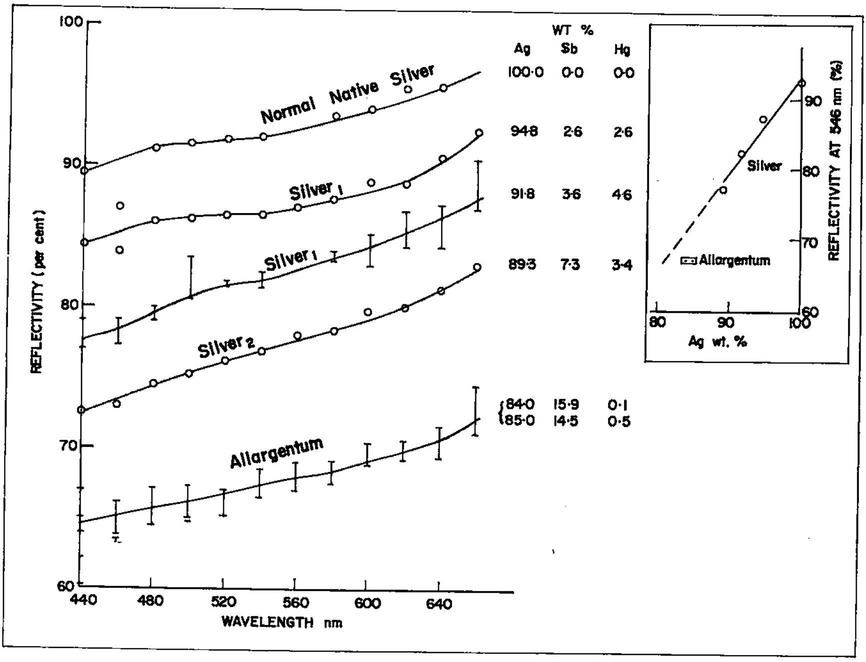

FIG. 3. Reflectivity spectra of silver and allargentum from Cobalt. The graph in the upper right-hand corner shows the relationship between reflectivity of these minerals at 546 nm and the weight per cent silver.

maximum amounts of antimony and mercury in solid solution. These amounts (up to 8.4 wt.% Sb and 3.3 wt.% Hg) are higher than the reported maximum limits of antimony in silver at 700° for the Ag–Sb system (Fig. 2). This suggests that mercury increases the solubility of antimony in silver, and that the phase diagram of the binary system does not strictly apply to the Cobalt assemblage. Hence, an investigation of the silver-rich corner of the Ag–Sb–Hg ternary system has been undertaken to clarify this relationship.

Phase 3 (allargentum)

The mineral referred to as phase 3 in this paper was previously described as dyscrasite from Cobalt (Walker 1921; Peacock 1940; Ramdohr, 1950 and 1960). Its x-ray diffraction pattern corresponds to that of the synthetic ϵ-phase (Table 3), which was indexed on a hexagonal unit cell with $a = 2.96$ and $c = 4.78$ Å by Westgren *et al.* (1929) and Weibke & Efinger (1940). A comparison of unit cell parameters calculated from the powder patterns of the naturally occurring mineral and of several synthetic compositions is given in Table 4.

TABLE 3. X-RAY DIFFRACTION PATTERNS OF ALLARGENTUM

	Cobalt, area, Sample No. 4		Synthetic (Cabri 19)		Calculated for $a = 2.945$* and $c = 4.780$
hkl	*I*(est)	*d*Å†	*I*(est)	*d*Å‡	*d*Å
001					4.780
100	4	2.548	7	2.545	2.551
002	10	2.370	7	2.396	2.390
101	6	2.252	10	2.245	2.250
102	3	1.756	4	1.744	1.744
003					1.593
110	2	1.473	4	1.469	1.473
111					1.407
103	4	1.353	6	1.352	1.351
200			1	1.273	1.275
112	2	1.253	5	1.252	1.254
201	2	1.236	4	1.228	1.232
004	1	1.193	3	1.195	1.195
202			2	1.122	1.125
104 113	1	1.081	4	1.082	1.082
203	1	0.997	4	0.995	0.996
210			2	0.962	0.964
005					0.956
211	3	0.943	5	0.943	0.945
114			6	0.928	0.928

*This pattern gives all the calculated *hkl*'s for a hexagonal pattern.
†Estimated accuracy of measured *d* (Azaroff & Buerger 1958) ±0.02%.
‡Estimated accuracy ±0.005%.

TABLE 4. CELL PARAMETERS OF ALLARGENTUM

	Composition of allargentum in weight per cent			Cell parameters in Å	
Sample No.	Ag	Sb	Hg	*a*	*b*
Cobalt ore (No. 4)	84.3	15.3	0.3	2.952	4.773 ± 0.003
Synthetic (Cabri 18)	84.05	15.95	0.0	2.951	4.794 ± 0.001
Synthetic (Cabri 19)	87.03	12.97	0.00	2.945	4.780 ± 0.002
Synthetic (Cabri 20)	89.99	10.01	0.00	2.935	4.783 ± 0.003

The specific gravity of one sample of synthetic ϵ-phase (Cabri 18) was measured as 10.0, which, together with the unit-cell parameters and composition reported in Table 4, gives a Z value of 2. On the basis of two atoms per unit cell, the unit cell parameters may be explained by assuming a close-packed hexagonal structure. Single crystal x-ray photographs have confirmed the basic hexagonal cell unit, but on the basis of hexagonal close packing a space group cannot be readily assigned. The complete elucidation of the structure is in progress.

The unit cell content suggests that the formula should be expressed as $Ag_{1-x}Sb_x$, where $x = 0.09$ to 0.16. This is in contrast to Ag_6Sb as proposed by Somanchi & Clark (1966). The compositional range and the atomic proportions of the natural mineral, based on analyses of 15 samples, are:

	Compositional Range	Atomic Proportions
Ag	84.0–85.6 wt. %	0.860–0.870
Sb	14.4–15.9 wt. %	0.130–0.138
Hg	0.0– 0.9 wt. %	0.000–0.005

The mean composition of the natural material is equivalent to

$$Ag_{0.865}Sb_{0.134}Hg_{0.001}, \quad \text{or} \quad (Ag, Hg)_{6.46}Sb$$

on the basis of one Sb atom.

These data show that phase 3 is a natural occurrence of the ϵ-phase of the Ag–Sb system, and that it may contain small amounts of mercury in solid solution. It is proposed that the name allargentum be applied to this phase, thereby retaining that part of Ramdohr's (1960) suggestion that allargentum represents the ϵ-phase.[1]

Some of the properties of allargentum are as follows: Vickers microhardness varies between 172 and 203, with an average value of 189; reflectivity values at the four standard wavelengths are 65.4% at 470 nm, 67.5% at 546 nm, 68.7% at 589 nm and 71.3% at 650 nm; and reactions to various chemical reagents are given by Somanchi & Clark (1966).

A type sample containing allargentum, from the Hi–Ho Mine, Cobalt, is deposited with the National Mineral Collection in Ottawa.

Other occurrences of allargentum

Allargentum, in addition to its occurrence in complex intergrowths described here, also occurs in the Cobalt ores as separate grains. A second Canadian occurrence, mercury-free, was reported very recently by Cabri & Harris (1969) in ore from the Red Lake area of Ontario. Allargentum has also been reported in ore from the Consols Mine, Broken Hill, Australia (Markham & Lawrence 1962), and the accompanying photomicrographs are somewhat similar to Fig. 1 of this report. This suggests that the phase referred to as allargentum in the Consols Mine may be a variety of silver, while that referred to as dyscrasite may be allargentum.

CONCLUSIONS

We propose that allargentum be defined as a natural occurrence of the ϵ-phase of the Ag–Sb system, and that it can contain some mercury in

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[1] This proposal was approved by the I.M.A. Commission on New Minerals and Mineral Names in September, 1969.

solid solution. The type material is abundant in high-grade silver ores from many mines in Cobalt, Ontario, and its properties are as follows:

1. Approximate composition in units of wt.% is Ag = 85.0, Sb = 14.6, and Hg = 0.4. Deviations from this composition can be expected in other ores because of the wide solid-solution field of the ϵ-phase in the Ag–Sb system.
2. Unit cell formula is $Ag_{1-x}Sb_x$ where x varies from 0.09 to 0.16, and the mean composition of the natural material is $Ag_{0.86}Sb_{0.14}$ with trace amounts of mercury.
3. It is hexagonal with unit cell parameters of $a = 2.95$ Å, $c = 4.77$ Å, and the unit cell contains two atoms probably in a close-packed arrangement.
4. Measured specific gravity of a synthetic equivalent is 10.0, and the calculated specific gravity of the natural material is 10.12.
5. Vickers microhardness is about 189.
6. Reflectivity values at the standard wavelengths are 65.4% at 470 nm, 67.5% at 546 nm, 68.7% at 589 nm and 71.3% at 650 nm.

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