

## THE SILVER – MERCURY – ANTIMONY MINERALS OF SALA, SWEDEN

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### ABSTRACT

Minerals in the ternary system Ag–Hg–Sb are important carriers of Ag in the Proterozoic Pb–Zn ores of Sala, central Sweden. The ores with pyrrhotite, sphalerite, galena and magnetite as main constituents are hosted by a skarn-bearing dolomite. Sphalerite may contain up to 1 wt. % Hg. The Ag–Hg–Sb minerals plot in five compositional fields: a) native silver and antimonial silver, forming a continuous series with  $\alpha$ -Ag–Hg–amalgam with up to 51–52 wt. % Hg; b) schachnerite with approximately 60 wt. % Hg and probable paraschachnerite; c) allargentum with up to 5 wt. % Hg; d) Hg-bearing dyscrasite forming a continuous solid-solution series along the join  $\text{Ag}_3\text{Sb} - \text{Ag}_3\text{Hg}$ , with up to 23 wt. % Hg; in the samples richest in Hg the structural position of Sb is occupied mainly by Hg; e) native Sb, only present in very minor amounts. Important miscibility gaps exist in this system. The coexistence of two phases is widespread, and the coexistence of three phases occurs only occasionally. Lamellar intergrowths between allargentum and antimonial silver or  $\alpha$ -amalgam indicate unmixing due to low-temperature re-equilibration; their presence suggests that the stability fields, especially those of allargentum and Sb-bearing  $\alpha$ -amalgam, were larger at the original temperature of crystallization, which did not exceed 280°C, the upper stability limit of gudmundite, a trace constituent of most samples.

**Keywords:** ternary system Ag–Hg–Sb, native Ag,  $\alpha$ -amalgam, schachnerite, allargentum, Hg-bearing dyscrasite, miscibility gap, Sala, Sweden.

### SOMMAIRE

Les minéraux du système ternaire Ag–Hg–Sb sont des hôtes importants de l'argent dans le minerai de Pb–Zn d'âge protérozoïque de Sala, en Suède centrale. Le minerai de pyrrhotine, sphalérite, galène et magnétite se trouve dans une dolomie skarnifiée. La sphalérite peut contenir jusqu'à 1 % de mercure (en poids). Les minéraux du système Ag–Hg–Sb définissent cinq champs de composition: a) argent natif et argent antimoniaux, qui forment une solution solide avec un amalgame  $\alpha$  de Ag et Hg qui contient jusqu'à 51 ou 52 % de Hg, b) schachnerite contenant environ 60 % de Hg, et paraschachnerite probable, c) allargentum contenant

jusqu'à 5 % de Hg, d) dyscrasite porteuse de mercure, qui forme une solution solide continue  $\text{Ag}_3\text{Sb} - \text{Ag}_3\text{Hg}$ , contenant jusqu'à 23 % de Hg (dans les échantillons les plus riches en Hg, le Hg occupe la position structurale du Sb), et e) antimoine natif, que l'on trouve en quantités infimes. Des lacunes de miscibilité importantes existent dans ce système. La coexistence de deux phases est répandue, et la coexistence de trois phases est assez rare. La présence d'intercroissances lamellaires d'allargentum et d'argent antimonial ou d'amalgame  $\alpha$  indique qu'il y a eu démixion due à une ré-équilibration à basse température. Ce phénomène laisse supposer que les champs de stabilité, surtout ceux de l'allargentum et de l'amalgame  $\alpha$  antimonial, étaient plus étendus à la température originelle de la cristallisation; celle-ci n'a pas dépassé 280°C, limite supérieure de la gudmundite, présente à l'état de traces dans la plupart des échantillons.

(Traduit par la Rédaction)

**Mots-clés:** système ternaire Ag–Hg–Sb, argent natif, amalgame  $\alpha$ , schachnerite, allargentum, dyscrasite mercurifère, lacune de miscibilité, Sala, Suède.

### INTRODUCTION

The famous Sala Pb–Zn–Ag mines, near the town of Sala in the Proterozoic Bergslagen ore province, south-central Sweden, were in production from the 16th century until 1962. Exceptionally high Ag-contents of up to 7,000 g/tonne were reported to occur in some parts of the old mines (Sjögren 1910). In 1982 the Boliden Mineral Company started a drilling program to investigate a recently discovered lateral extension of the known mineralization.

Ore samples from both the old mines and the newly discovered mineralization carry abundant mineral phases belonging to the system Ag–Hg–Sb. The known natural phases in the system Ag–Hg–Sb belong essentially to two binary systems. Native Ag (cubic, may contain several wt. % Hg and Sb in varying proportions), allargentum (hexagonal, approximately  $\text{Ag}_6\text{Sb}$ ), dyscrasite (orthorhombic, approximately  $\text{Ag}_3\text{Sb}$ ) and native Sb (hexagonal) belong to the system Ag–Sb. Dyscrasite and allargentum may

contain small amounts of Hg. In the binary system Ag–Hg, the phases are commonly described as Ag–Hg amalgams. The mineral phases in this system are:  $\alpha$ -phase (cubic, Ag-rich amalgam, up to 50 wt.% Hg), schachnerite (hexagonal, approximately  $\text{Ag}_{1.1}\text{Hg}_{0.9}$ , 60 wt.% Hg), paraschachnerite (orthorhombic, approximately  $\text{Ag}_{1.2}\text{Hg}_{0.8}$ , 55 wt.% Hg) and moschellandsbergite (cubic, approximately  $\text{Ag}_4\text{Hg}_5$ , 70 wt.% Hg). Ternary phases in the system Ag–Hg–Sb have not been reported, to our knowledge..

An Ag–Hg amalgam has long been known to occur in the upper levels of the mine. Zakrzewski & Burke (1987) have noted the presence of schachnerite and paraschachnerite in old museum samples.

In the present study the results of microprobe analyses of Ag–Sb–Hg minerals in about a hundred drill-cores samples of Sala ore are given. These findings shed light on the phase relations in the ternary system.

#### DESCRIPTION OF THE ORES

The ores at Sala are located in a dolomitic limestone, which is intruded and underlain by granitic rocks. The mineralization is accompanied by the formation of abundant skarn minerals: diopside, tremolite, minor garnet and (clino)humite, and other minerals such as chlorite, phlogopite and talc. Locally, diopside and tremolite are completely al-

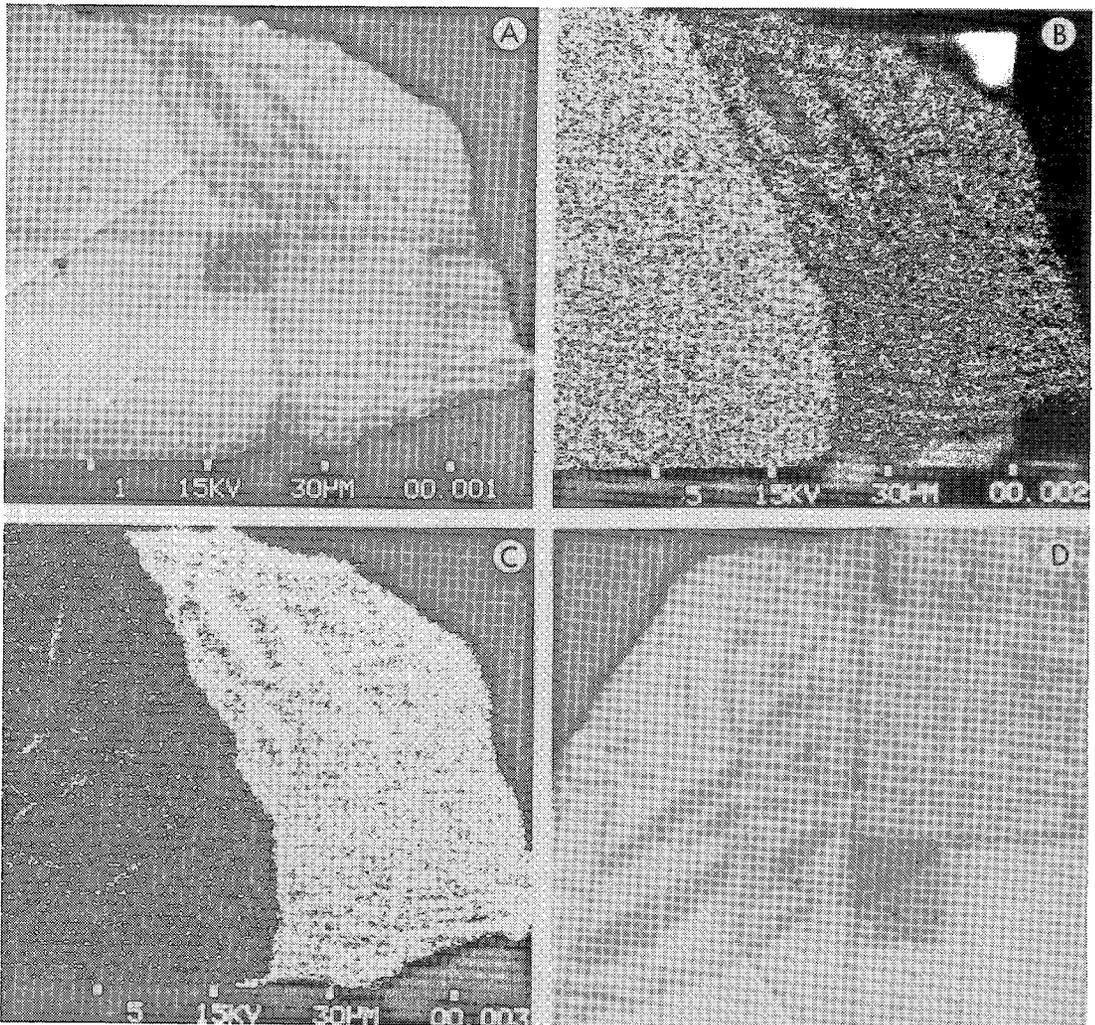


FIG. 1. Complex intergrowth of amalgam-allargentum. Left: Sb-poor amalgam with occasional lamellae of allargentum. Right: lamellar intergrowth of amalgam and allargentum. A. Backscattered electron image. B.  $\text{HgM}\alpha$  X-ray emission image. C.  $\text{SbL}\alpha$  X-ray emission image. D. Higher magnification of part of photo A (scale in  $\mu\text{m}$  indicated on photographs A, B and C). Note: dark grey square in the centre is due to contamination.

tered to carbonates, chlorite, and talc. Late formation of fine serpentine needles is very common, especially along shear zones.

The ore minerals are mostly present as disseminations and in stringers or small veinlets, and only locally as nearly massive galena- and sphalerite-ores. The ore and gangue minerals commonly show a more-or-less granoblastic texture.

#### *Ore-mineral parageneses and textural relations*

The main primary ore minerals are Fe-rich sphalerite ( $(\text{Zn},\text{Fe})\text{S}$ ), pyrrhotite (with compositions between  $\text{Fe}_{0.87}\text{S}_1$  and  $\text{Fe}_{0.9}\text{S}_1$ , and minor FeS) and galena  $\text{PbS}$ ; magnetite  $\text{Fe}_3\text{O}_4$  and pyrite  $\text{FeS}_2$  are locally present in varying amounts. The most important accessory and trace minerals are: chalcopyrite  $\text{CuFeS}_2$ , cubanite  $\text{CuFe}_2\text{S}_3$ , gudmundite  $\text{FeSbS}$ , cobaltite  $\text{CoAsS}$ , arsenopyrite  $\text{FeAsS}$ , (para)costibite  $\text{CoSbS}$ , breithauptite  $\text{NiSb}$ , ullmannite  $\text{NiSbS}$ , molybdenite  $\text{MoS}_2$ , boulangerite  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ , diaphorite  $\text{Pb}_2\text{Ag}_3\text{Sb}_3\text{S}_8$ , pyrargyrite  $\text{Ag}_6\text{Sb}_2\text{S}_6$ , freibergite  $(\text{Ag},\text{Cu},\text{Fe},\text{Zn})_{12}\text{Sb}_4\text{S}_{13}$ , hessite  $\text{Ag}_2\text{Te}$ , miargyrite  $\text{AgSbS}_2$ , acanthite  $\text{Ag}_2\text{S}$ , and the minerals in the Ag-Hg-Sb system, described in this paper.

In certain parts of the old mines, where Sb minerals are more abundant, the most common carriers of Ag are pyrargyrite, Ag-Pb-Sb-sulfosalts and freibergite. In the newly discovered extension of the mine, however, Ag-Hg-Sb minerals are by far the most important minerals of Ag.

The Ag-Hg-Sb minerals occur in submillimetre-size anhedral grains; only very occasionally schacherite shows a hexagonal outline. Some grains are located between the gangue minerals, but mostly the Ag-Hg-Sb minerals occur intergrown with the main ore-minerals sphalerite, pyrrhotite, galena, magnetite, pyrite and chalcopyrite. Intergrowths with other Sb- and Ag-bearing minerals such as gudmundite, breithauptite, (para)costibite, pyrargyrite and native Sb are rather common. The Ag-Hg-Sb minerals are locally also present in veinlets, together with other ore minerals, and as small-scale fracture fillings in the host rock. The occasional presence of a thin rim of acanthite or native Sb around the Ag-Hg-Sb minerals indicates incipient alteration of these minerals.

In several samples two or three different types of Ag-Hg-Sb minerals are present; intergrowth relations between them are rather common. Four types of textures of coexisting phases are found: 1) lamellar intergrowths of two phases: they are limited to the Ag-rich corner of the Ag-Hg-Sb field (between allargentum and native silver or  $\alpha$ -phase amalgam). These intergrowths generally consist of a network of cross-cutting lamellae in several directions (Fig. 1). In some intergrowths, the two phases are present

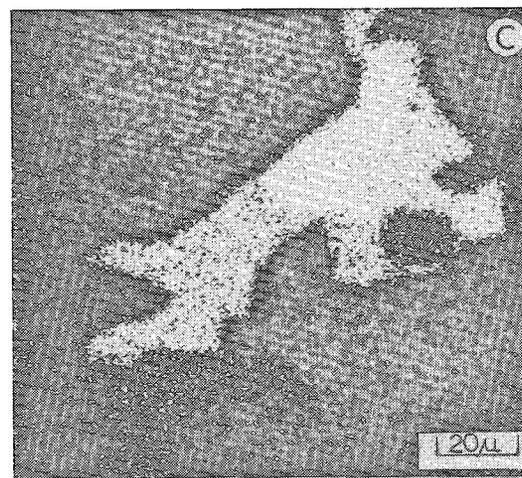
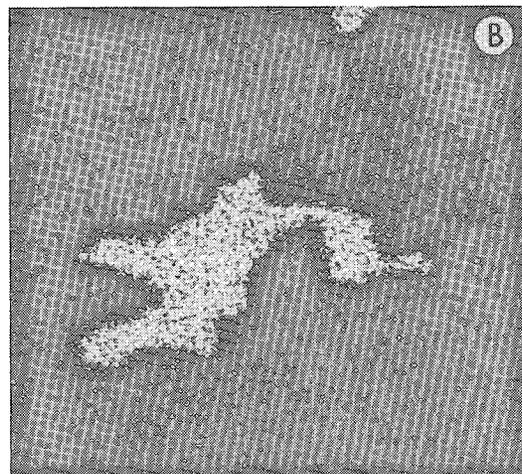
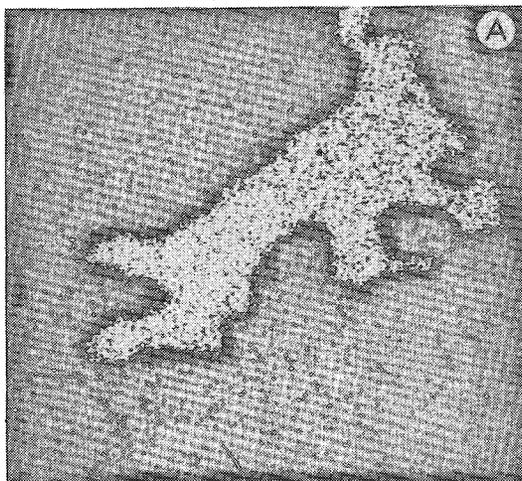


FIG. 2. X-ray emission images of an intergrowth of Hg-Ag  $\alpha$ -amalgam and Hg-bearing dyscrasite. A.  $\text{AgL}\alpha$ , B.  $\text{SbL}\alpha$ , and C.  $\text{HgM}\alpha$ . (Scale bar 20  $\mu$ m).

in approximately equal proportions; in others, only a few lamellae of allargentum are present in a matrix of  $\alpha$ -amalgam. 2) Rim of one phase bordering the second phase: rim of native silver on Hg-free allargentum, rim of allargentum on Hg-poor dyscrasite. 3) Aggregates of two intimately associated Ag-Hg-Sb minerals showing frequent mutual contact: these textures are described below as "side-by-side" intergrowths. Side-by-side intergrowths between  $\alpha$ -amalgam and allargentum, between allargentum and dyscrasite, between Hg-bearing dyscrasite and native Sb, between dyscrasite and Hg-rich  $\alpha$ -amalgam (Figs. 2, 3), and between Hg-rich  $\alpha$ -amalgam and paraschacherite have been observed. 4) Discrete grains of two phases not in mutual contact.

The textures described under 3) and 4) are of common occurrence and locally found in the same sample, but generally not in samples with lamellar intergrowths. Small inclusions of amalgam and dyscrasite (only a few micrometres across) are locally present in galena and sphalerite and are interpreted as exsolution bodies. Galena contains Ag and Sb in amounts up to 0.15 wt.%, and inclusions of dyscrasite, which are exceptionally Hg-free; sphalerite shows contents of Hg up to 1.0 wt.%, and inclusions of Hg-rich dyscrasite and amalgam. The inclusions in galena may show a prismatic or polygonal outline and, occasionally, a regular arrangement. In a few samples, galena contains both exsolved dyscrasite and freibergite. The exsolution blebs in sphalerite are very commonly intergrown with pyrrhotite of the same or somewhat larger size and occasionally with very small grains

of breithauptite. The intergrowths with pyrrhotite may be located along sphalerite grain-boundaries and twin planes, even preferentially at the intersections of two different sets of twin planes. In both galena and sphalerite, the occurrence of larger grains of Ag-Hg-Sb minerals suggests segregation of the fine-grained exsolution bodies.

The primary ore-mineral paragenesis locally shows extensive alteration. Pyrrhotite is transformed into pyrite and marcasite, or into a symplectitic intergrowth of pyrite and magnetite; this is associated with late formation of pyrite, magnetite, and even some hematite. Usually sphalerite is not affected, but in an ultimate stage of alteration, Fe-rich sphalerite (commonly 7-9 wt.% Fe) is transformed into nearly Fe-free sphalerite (< 0.5 wt.% Fe).

The altered ores are characterized by late-crystallized nearly Sb-free Ag-Hg amalgam, occurring in grains that locally show a very irregular outline, as very small inclusions in late pyrite, in small veinlets, and as a rim on other ore minerals. In partly altered ores, indications of two generations of amalgam are locally present.

Although the effects of supergene alteration cannot be precluded, we believe that the late alteration is generally related to low-temperature equilibration during cooling of the primary assemblage. In fact, the assemblage of Ag-Hg-Sb minerals described in this paper also shows the effects of low-temperature equilibration during cooling. The late alteration may show a relationship to the formation of numerous shear-zones.

#### MINERAL CHEMISTRY: ANALYTICAL PROCEDURE

Parts of the analyses were made at the Free University at Amsterdam with a Cambridge Instruments Microscan 9 electron microprobe, at 15 or 20 kV, with on-line ZAF matrix correction. At 15 kV, the HgM $\alpha$  line was used, and at 20 kV, the HgL $\alpha$  line. The minerals are rather unstable under the electron beam; for that reason, short counting-times of 5 or 10 seconds were used, with a probe current of 40 nA at 15 kV and 25 nA at 20 kV. The following standards were used: pure Ag, synthetic HgTe and natural Sb<sub>2</sub>S<sub>3</sub>. The determinations of Hg in sphalerite were made at 15 kV (M line) and 30 kV (L and M lines); the detection limit is approximately 0.02-0.03 wt.%. Another series of analyses was carried out at the University of Uppsala, with a Cambridge Instruments Geoscan electron microprobe run at 15 or 20 kV, with an external correction programme called SGU mk 13.

Freshly polished samples of Ag-Hg-Sb minerals tarnish very rapidly, sometimes within one day; immediate carbon-coating after repolishing, and analysis in the following days, is a prerequisite for reliable data. Several months after the polishing a

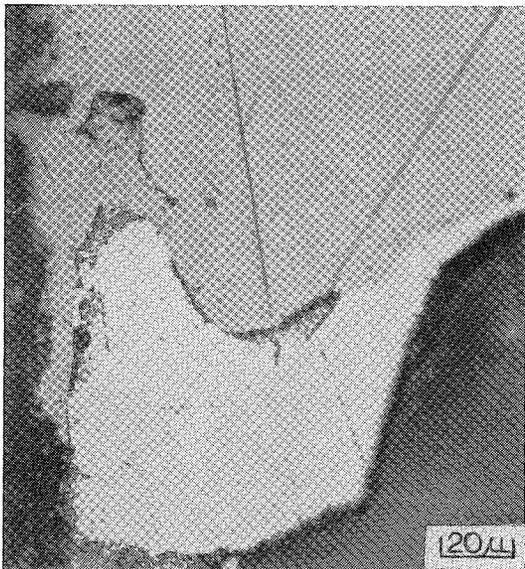


FIG. 3. Hg-bearing dyscrasite (light grey) and Hg-Ag-amalgam (white), intergrown with galena (grey); plane light, air. (Scale bar 20  $\mu$ m).



Figure 5, the coexisting phases are shown. Five groups of compositions, corresponding to mineral phases in the system Ag-Hg-Sb, can be distinguished.

*$\alpha$ -phase native silver and Ag-Hg-amalgam*

The compositions in this wide field of continuous solid-solution between pure silver and approximately  $\text{Ag}_{0.48}\text{Hg}_{0.52}$  belong to several sets of samples, each characterized by specific properties, such as mineral paragenesis, a limited range in Ag/Hg ratio and Sb content of the amalgam. (1) *Sb-bearing, Ag-rich Ag-Hg amalgam* (up to 20 wt. % Hg and up to 5 wt. % Sb). This subgroup consists of: a) nearly pure

native silver, Hg-free antimonial silver and Hg-bearing antimonial silver. In sample 95, lamellar intergrowths with allargentum are present. b) *Sb-bearing Ag-rich amalgam* (samples 64, 79 and 80). The grains are all very small and show a highly variable composition; some are nearly Sb-free ( $\leq 1$  wt. %). The Sb content decreases with increasing Hg content. (2)  *$\alpha$ -phase amalgam with 15-25 wt. % Hg and  $\leq 1$  wt. % Sb*. These overlap partly with the Sb-poor ( $\leq 1$  wt. %), Hg-richest members of subgroup 1. Part of the samples contains amalgam formed in the alteration stage. The amalgam in the unaltered primary ores shows lamellar intergrowths with allargentum. (3)  *$\alpha$ -phase amalgam with 26-33 wt. % Hg*. The Sb contents are very low ( $< 0.5$  wt. %). Most

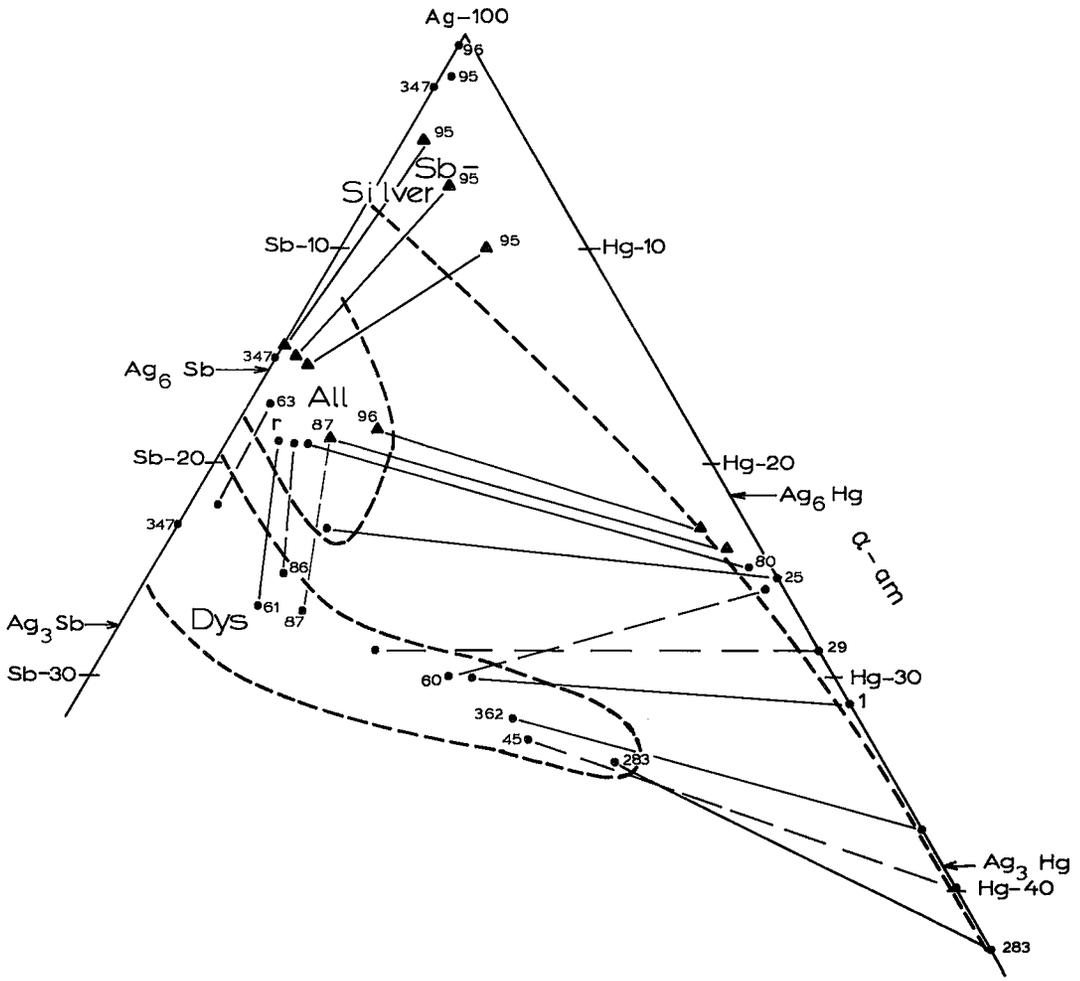


FIG. 5. The Ag-rich corner of the ternary system Ag-Sb-Hg, showing compositions (in wt. %) of coexisting phases and tie-lines. ▲—▲: lamellar intergrowths; ●—●: side-by-side intergrowths and intergrowths constituted by one phase rimmed by another (r); ● - - - ●: phases not intergrown; — - - : compositional limits of different minerals at low temperature.

samples contain amalgam formed in the alteration stage. Amalgam in the primary ore-mineral paragenesis shows intergrowths with (or is associated with) dyscrasite of intermediate Hg-contents. (4)  $\alpha$ -phase amalgam with 33-52 wt. % Hg. The Hg-rich limit of the  $\alpha$ -phase is somewhat problematic because the identity of some small grains with 51-52 wt. % Hg is not certain. Sb is absent or present only in very minor amounts. With only one exception (sample 9), all examples of amalgam of this important subgroup occur in unaltered ores. Side-by-side intergrowths of amalgam with less than 43 wt. % Hg and Hg-rich dyscrasite are common. Amalgam with more than 43 wt. % Hg is occasionally associated or intergrown with schachnerite and paraschachnerite. Sb-bearing minerals such as gudmundite and minor breithauptite are rather frequently found intergrown with the amalgam of this subgroup.

*Schachnerite and probable paraschachnerite*

Most grains containing between 55 and 61 wt. % Hg have a composition corresponding to the mineral schachnerite (59-61 wt. % Hg). In samples 82 and 88, schachnerite is the only Ag-Hg phase; in samples 81 and 518 schachnerite is present only in minor amount (Fig. 6). Sample 81 shows an especially wide range of compositions; most grains have between 50 and 51 wt. % Hg ( $\alpha$ -amalgam), some grains contain between 51 and 52 wt. % Hg (possibly  $\alpha$ -amalgam also), one grain shows 59.4 wt. % Hg (schachnerite) and two grains show a composition of approximately 55 wt. % Hg. These two grains are intergrown with  $\alpha$ -phase Ag-Hg amalgam. In these intergrowths the

TABLE 1. REPRESENTATIVE COMPOSITIONS OF Ag-Hg-Sb MINERALS

Sample:	80	a	b	c	d	e	f	g
Ag wt. %	86.0	85.6	83.3	82.7	81.5	80.4	81.1	
Hg	12.5	13.6	16.0	17.0	3.0	4.8	5.5	
Sb	2.5	1.6	1.3	0.2	15.8	14.9	14.4	
Total	101.0	100.8	100.6	99.9	100.3	100.1	101.0	

Sample:	94	a	b	c	d	e	f	g
Ag wt. %	48.5	48.9	48.6	49.1	49.4	48.9	49.3	
Hg	51.8	50.5	50.4	50.6	50.7	50.5	50.5	
Sb	-	-	-	-	-	-	-	
Total	100.3	99.4	99.0	99.7	100.1	99.4	99.8	

Sample:	95	a	b	c	d	96	a	b	c
Ag wt. %	92.4	83.6	95.2	85.2	76.4	79.4	81.3		
Hg	3.0	0.3	0.6	-	21.3	6.3	5.7		
Sb	4.2	15.1	4.3	15.5	2.2	14.2	13.2		
Total	99.6	99.1	100.1	100.7	99.9	99.9	100.2		

sample 80: a-d different grains of Sb-bearing  $\alpha$ -amalgam; c-g allargentum in lamellar intergrowth with  $\alpha$ -amalgam; sample 94: different grains of Hg-rich  $\alpha$ -amalgam; sample 95: a-b and c-d antimonial silver and allargentum, in lamellar intergrowth; sample 96: a.  $\alpha$ -amalgam; b-c allargentum in lamellar intergrowth with  $\alpha$ -amalgam.

phases with 55 wt. % Hg can be optically distinguished from  $\alpha$ -phase amalgam by extremely slight differences in polishing hardness and reflectance values and by a slight anisotropy.

The presence of schachnerite (59-61 wt. % Hg) is confirmed by an X-ray powder-diffraction pattern.

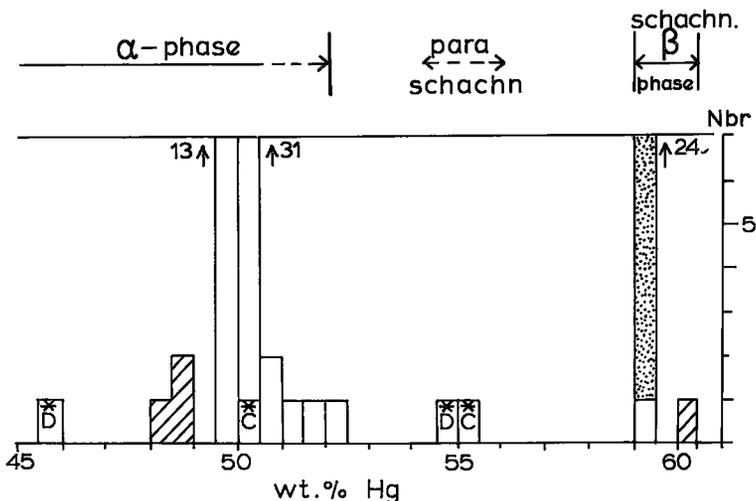


FIG. 6. Frequency of amalgam compositions in individual grains in 4 samples (sample 81: blank, samples 82 and 83 dotted, sample 518: diagonally hatched; C\* and D\*: grains consisting of two phases).

However, the presence of paraschachnerite (about 55 wt. % Hg) is inferred only from the measured composition. The observed slight anisotropy of the grains, which is not in good agreement with the distinct anisotropy of paraschachnerite as described by Seeliger & Mücke (1972), does not constitute a definitive identification.

### Allargentum

In one sample (347), allargentum contains no Hg, whereas in the other samples, Hg contents up to 5 wt. % are present. However, part of the allargentum is intergrown with amalgam, and it is possible that the compositions richest in Hg contain too much Hg, owing to the influence of the Hg-rich phase in the intergrowth. Allargentum is intergrown or associated with  $\alpha$ -phase Ag-Hg-amalgam and dyscrasite.

### Hg-bearing dyscrasite

The abundant dyscrasite occupies a rather narrow compositional field, following approximately the join  $\text{Ag}_3\text{Sb} - \text{Ag}_3\text{Hg}$ . Dyscrasite compositions with high Sb contents show deviations from this join toward a higher content of Ag (approximately  $\text{Ag}_{3.8}\text{Sb}$ ). In dyscrasite with the highest content of Hg (23 wt. %, sample 283), the structural position of Sb is occupied mainly by Hg; the formula is  $\text{Ag}_3(\text{Hg}_{0.56}\text{Sb}_{0.44})_{\Sigma 1.00}$ . Hg-bearing dyscrasite commonly shows large variations in Hg-content within one sample.

### Native Sb

Native Sb is only a very minor constituent; it is intergrown or associated with Hg-bearing dyscrasite.

## COMPOSITION OF Ag-Hg-Sb PHASES IN RELATION TO OTHER ORE MINERALS

The composition of the Ag-Hg-Sb minerals is not exclusively determined by the proportions of Ag, Hg and Sb in the ore, but depends also on the presence

of other components, *e.g.*, Fe, Ni, S. The affinity of Ag is greater for Hg than for Sb. This is shown by the common intergrowth-relations between Ag-Hg amalgam and Sb-bearing minerals such as gudmundite and breithauptite.

The abundance of Hg is indicated by the ratio Hg/Ag in the ore (only known for part of the samples) and the Hg-content of sphalerite, which is approximately proportional to Hg/Ag. The samples plotting in the Ag-rich part of the Ag-Hg-Sb compositional field are characterized by a Hg/Ag value less than 0.5 and Hg-contents in sphalerite lower than 0.05 wt. %. These values are higher in samples containing Hg-rich dyscrasite, and significantly higher in the samples containing amalgam with more than 40 wt. % Hg. The average Hg/Ag value in the ore increases from 1.3 in samples containing amalgam with 40-46 wt. % Hg to 4.1 in samples containing amalgam with 46-51 wt. % Hg; there is a corresponding increase in the average Hg-content in sphalerite from 0.2 to 0.3 wt. %. In the ores containing schachnerite and paraschachnerite, the average Hg content in sphalerite is 0.55 wt. %; the Hg/Ag value in the ore (known only for 2 samples) is 3.9.

The exsolved phases of Ag-Hg-Sb minerals in galena and sphalerite generally have a composition different from that of the larger discrete grains in the same sample. The inclusions in galena are richer in Sb and lower in Hg, and those in sphalerite richer in Hg (Table 2). This is easily explained by the original distribution of Ag, Sb and Hg as trace elements in galena and sphalerite. Galena still contains Ag and Sb in amounts up to 0.15 wt. %, and Hg is still present in many sphalerite grains in amounts up to 1 wt. %.

## DISCUSSION OF THE RESULTS

The results plotted in the triangular diagram Ag-Hg-Sb (Fig. 4) indicate several solid-solution fields in which the compositions are concentrated and other areas in which no compositions have been found. The different fields will be discussed successively.

### Hg-bearing Ag-Sb phases

The phase relations in the binary system Ag-Sb have been determined down to 300°C by Somanchi (1966). He found three phases: antimonial silver, allargentum ( $\epsilon$ -phase) and dyscrasite (Fig. 7).

Somanchi & Clark (1966) compiled the published data on natural phases and found the following compositional ranges for the three phases: antimonial silver 5.9-6.8 wt. % Sb, allargentum 11.2-16.2 wt. % Sb, and dyscrasite 22.0-28.0 wt. % Sb, confirming the experimental results. Petruk *et al.* (1971) described natural Hg-bearing phases from the

TABLE 2. COMPOSITION OF DYSCRASITE AND AMALGAM (WT. %) OF LARGE GRAINS AND EXSOLUTION BLEBS

Sample nr	Large grains	Inclusions in galena	Inclusions in sphalerite
518	44,48,61 % Hg (Am+Sch)		appr. 70% Hg
49	43 % Hg (Am)		> 50% Hg
54	43 % Hg (Am)		> 51 % Hg
35	22 % Sb, 5 % Hg (Dys)		very low Sb
37	19 % Sb, 10 % Hg (Dys)	3 % Hg	min. 1 % Sb
46	14 % Sb, 19% Hg (Dys)	8 % Hg	
89	18 % Sb, 14 % Hg (Dys)	27 % Sb, 6 % Hg	2-4 % Sb, 24-27 % Hg

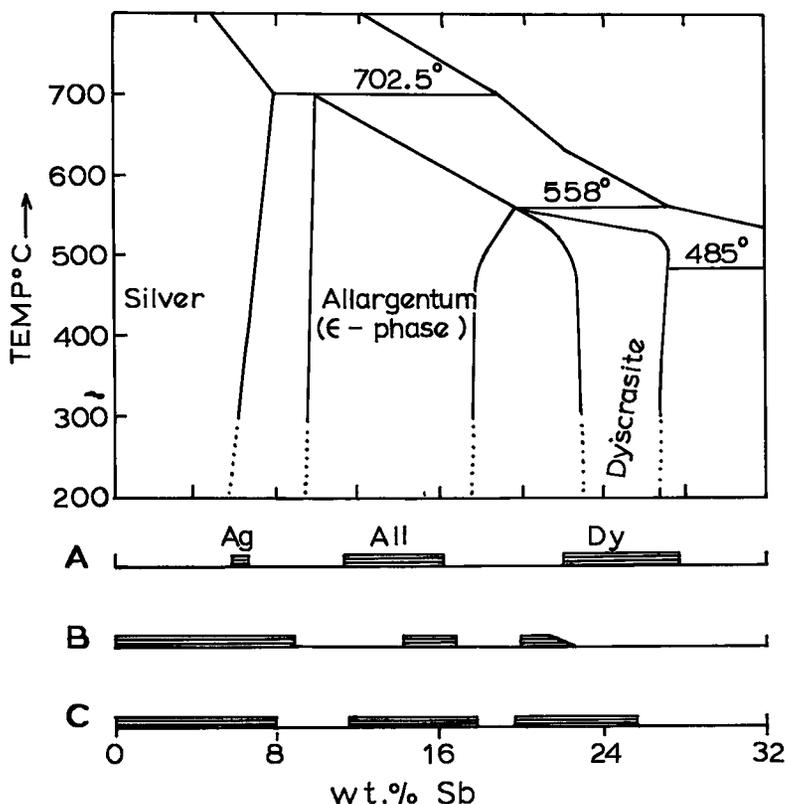


FIG. 7. Phase-equilibrium diagram of the silver-rich end of the system Ag-Sb, from Somanchi (1966) and slightly modified by Petruk *et al.* (1969). A. Literature data compiled by Somanchi & Clark (1966). B. Stability limits of the phases, as tentatively suggested by Petruk *et al.* (1969). C. Compositional limits suggested in this study (Ag: native silver and antimonial silver, All: allargentum, Dy: dyscrasite).

famous Cobalt-Gowganda ores, which show complex intergrowth-textures. They also reported high Hg contents (up to 8 wt.%) in native Ag and lower ones in allargentum and dyscrasite. Compared with the phase diagram of Somanchi (1966), somewhat different compositional limits were suggested for the three phases.

The results of the present study of mineral phases along the Ag-Sb join of the Ag-Sb-Hg system are in fair agreement with those of Petruk *et al.* (1971), although the Hg contents in the Sala ores are higher. Some characteristic features are: a) antimonial silver forms a continuous solid-solution series with Ag-Hg amalgam, b) allargentum contains up to 5-6 wt.% Hg, c) dyscrasite forms a continuous series with Hg-rich dyscrasite containing up to 23 wt.% Hg; the solid-solution field occupies a narrow band extending more than half-way along the  $\text{Ag}_3\text{Sb} - \text{Ag}_3\text{Hg}$  join.

When we compare our inferred solid-solution

limits for the phases along the Ag-Sb join with those determined experimentally by Somanchi (1966), some differences can be noted (Fig. 7). In particular, the Sb-poor limit of dyscrasite is located at a lower Sb content: approximately 20 wt.% instead of 22-23 wt.%. The differences with the solid-solution limits suggested by Petruk *et al.* (1971) are minor; the Sala results suggest an upper limit of the allargentum field at about 18 wt.% Sb, whereas Petruk *et al.* (1971) tentatively proposed 16.5 wt.% Sb.

These results indicate minor discrepancies with the phase boundaries proposed by Somanchi (1966). We suggest that Somanchi's diagram shows some inaccuracies; in particular, the boundaries of the T-X stability fields may show a significant slope rather than being vertical. In fact, Somanchi & Clark (1966) annealed an intergrowth between antimonial silver and allargentum. They obtained a homogeneous solid-solution with 13.9 wt.% Sb, which contradicts the phase diagram of Somanchi (1966).

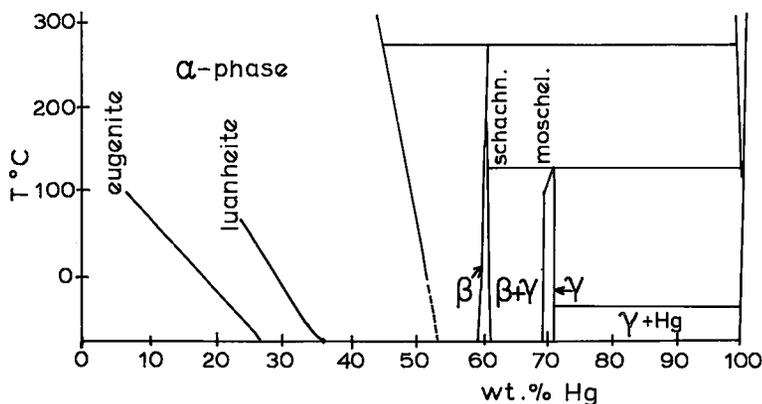


FIG. 8. Phase diagram of the low-temperature part of the system Ag-Hg according to Murphy & Preston (1931), with modifications suggested by Seeliger & Mücke (1972) and indicated by the results of the present study.

### Ag-Hg amalgam phases

The binary system Ag-Hg has been examined by Murphy & Preston (1931); they distinguished three phases (Fig. 8): a)  $\alpha$ -phase: 0–50 wt.% Hg, b)  $\beta$ -phase: approximately 60 wt.% Hg, c)  $\gamma$ -phase: approximately 70 wt.% Hg, corresponding to the natural phase moschellandsbergite. Our results indicate a continuous solid-solution series of  $\alpha$ -Ag-Hg amalgam phases containing between 0 and 51–52 wt.% Hg, broadening at the low Hg side and connected with antimonial silver with up to 5 wt.% Sb.

In the region between 51 and 60 wt.% Hg along the Ag-Hg binary join, Seeliger & Mücke (1972) described two phases: the natural  $\beta$ -phase schachnerite (hexagonal), with 58 wt.% Hg, and the orthorhombic phase paraschachnerite, with approximately 54 wt.% Hg. The stability limits of the latter compound are not known; Seeliger & Mücke (1972) suggested that it is an intermediate phase between the  $\alpha$ - and  $\beta$ -phases.

In the upper levels of the old Sala mines, amalgam was found as lumps and crystals in druses or cavities, quite commonly accompanied by native mercury (Sjögren 1900). Zakrzewski & Burke (1987) have described Ag-Hg amalgams in an old sample of Sala, preserved at the Swedish Natural History Museum in Stockholm. They have also found schachnerite (59–61 wt.% Hg), paraschachnerite with a variable composition between 50 and 57 wt.% Hg, and Hg-rich  $\alpha$ -amalgam.

Our results (Fig. 6) also indicate the presence of schachnerite (59–61 wt.% Hg), which is also confirmed by an X-ray powder-diffraction pattern, and of a phase containing 54–56 wt.% Hg (probably paraschachnerite).

The analytical results of paraschachnerite and  $\alpha$ -

amalgam described above seem to indicate that a miscibility gap exists between 51–52 wt.% Hg (the boundary of  $\alpha$ -phase amalgam) and approximately 55 wt.% Hg (the composition of paraschachnerite). Paraschachnerite is intergrown with  $\alpha$ -amalgam. The rarity of paraschachnerite compared with the much higher frequency of  $\alpha$ -amalgam and schachnerite is difficult to explain; paraschachnerite possibly was formed by incipient alteration of schachnerite or by transformation of schachnerite into a low-temperature polymorph richer in Ag.

Seeliger & Mücke (1972) described schachnerite and paraschachnerite from the oxidation zones of sulfide ores. They explained the formation of these phases by the demercuration of moschellandsbergite under oxidizing, low-temperature conditions; the final stage of alteration is an  $\alpha$ -amalgam. Zakrzewski & Burke (1987) explained the origin of these minerals in the Sala ores in a similar way. Experiments by von Barga (1979) showed the development of a 50- $\mu$ m rim of schachnerite on mercurial silver in the presence of mercury at room temperature.

In the Sala samples examined in this study, there are no indications that alteration of  $\alpha$ -amalgam or demercuration of Hg-rich phases is responsible for the formation of schachnerite and paraschachnerite; the latter minerals are present in the unaltered ores.

### Miscibility gaps, coexisting phases

The ternary system Ag-Hg-Sb shows a large miscibility-gap between Hg-bearing dyscrasite, allargentum and Ag-Hg amalgam; the limits of mineral solid-solutions are tentatively indicated in the diagram (Figs. 4, 5).

The occurrence of two- and three-phase assemblages of Ag-Hg-Sb minerals at Sala is consistent with these miscibility gaps. Apart from very uncom-

mon alteration (a very thin rim of possibly secondary native Sb or acanthite), there are no reasons to suspect disequilibrium relations in these mineral assemblages.

The following two-phase assemblages are present: a) Sb-rich, Hg-bearing  $\alpha$ -native Ag + allargentum (lamellar intergrowth); b)  $\alpha$ -Ag-Hg amalgam (1-2 wt. % Sb) + allargentum (lamellar intergrowths); c) Hg-poor dyscrasite + allargentum; d) Hg-rich dyscrasite + Hg-rich  $\alpha$ -Ag-Hg amalgam; e) schachnerite + Hg-rich  $\alpha$ -amalgam; f) paraschachnerite (?) + Hg-rich  $\alpha$ -amalgam; g) Hg-bearing dyscrasite + native Sb.

The three-phase assemblages are of very minor importance: a)  $\alpha$ -amalgam + allargentum + rare dyscrasite; b) Hg-free dyscrasite + allargentum + native Ag (native Ag is present as a thin rim on allargentum and probably formed by exsolution from an original Ag-richer allargentum).

The tie-lines between  $\alpha$ -amalgam and dyscrasite and  $\alpha$ -amalgam and allargentum are generally more or less parallel to the  $Ag_xSb - Ag_xHg$  joins, indicating Sb-for-Hg substitution. There are some deviations from this general trend, but only in samples in which one of the phases is present in minor amounts and as very small grains, conditions that do not guarantee reliable analytical results. The tie-lines between allargentum on the one hand and Hg-poor dyscrasite and Sb-rich, Hg-bearing native Ag on the other, are approximately parallel to the Ag-Sb join, but they point from both sides to lower Hg contents in allargentum (Fig. 5).

Lamellar intergrowths are interpreted as due to unmixing resulting from lower-temperature re-equilibration and decomposition of higher-temperature solid solutions. A rim of one phase on another phase and, possibly in some cases, side-by-side intergrowths, may also be formed by unmixing. Indeed in two samples both lamellar and side-by-side intergrowths of the same minerals occur.

### Conditions of formation

The Ag-Hg-Sb minerals occur in stable association with the main sulfides pyrrhotite, pyrite, Fe-rich sphalerite, galena and chalcopyrite, and with magnetite. In altered ores where the pyrrhotite is transformed into pyrite and late magnetite, only the nearly Sb-free  $\alpha$ -amalgam is stable.

The rather widespread occurrence of small quantities of gudmundite, locally intergrown with Ag-Hg-amalgam, indicates that the temperature of crystallization did not exceed 280°C, which is the upper limit of stability of gudmundite (Clark 1966). The local presence of schachnerite, according to von Bargen (1979) stable below 276°C, is in agreement with this estimate of temperature.

The Ag-Hg-Sb mineral parageneses found are

indicative of re-equilibration at lower-temperature conditions, presumably well below 280°C. Slow cooling rates and the reactive character of the Hg-bearing phases have probably contributed to large-scale re-equilibration. The low-temperature re-equilibrated assemblage of minerals provides indications concerning higher-temperature phase relations in the ternary system Ag-Sb-Hg. Experiments in this system indicate that reaction rates at 300°C are extremely slow (von Bargen 1979) and that the results of the low-temperature experiments are not decisive.

The lamellar exsolution-related intergrowths of allargentum and  $\alpha$ -phase amalgam indicate that at the temperature of original crystallization, presumably somewhat below 280°C, an extensive solid-solution in the Ag-rich corner of the system Ag-Hg-Sb enables the precipitation of Sb-rich solid solutions of the Ag-Hg-Sb amalgam. Thus at temperatures around 280°C, the miscibility gap between antimonial silver and allargentum is rather limited along the Ag-Sb join. However, below 280°C this miscibility gap expands rapidly into the ternary field and, on cooling, the higher-temperature Sb-rich Ag-Hg-Sb amalgam decomposes into lamellar intergrowths of Hg-bearing allargentum and Sb-bearing  $\alpha$ -phase amalgam.

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