

National University, had identified armenite by whole-rock X-ray powder diffractometry in Ba-rich calc-silicate rocks at Purnamoota, an abandoned mining area 30 km north of Broken Hill. A specimen of this rock (33304, Geology Dept., ANU), consists almost entirely of armenite, with a little celsian and accessory minerals. This raises the question as to why the bytownite and celsian in the Piggery rocks have not reacted more completely to armenite; the controlling factor is presumably the H<sub>2</sub>O activity, probably quite low during the metamorphism of the Broken Hill gneisses (amphibolite to granulite facies).

During this research accessory minerals in the Ba-rich gneisses were analysed for barium, in order to see how this element was distributed. The only minerals with considerable amounts were biotite (BaO variable, up to 13%) and muscovite (BaO 5–7%). BaO contents of other minerals were as follows: bytownite, 0.15%; titanite, 0.2%; apatite, trace (< 0.05%); hornblende, 0.16%; zoisite, 0.13%. Clearly under the conditions of crystallization of these gneisses barium formed celsian and armenite and concentrated in potassium minerals, and was essentially rejected by calcium minerals, as would be expected on crystallochemical grounds.

KEYWORDS: armenite, celsian, anorthite, barium, Broken Hill, Australia.

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## Schachnerite, paraschachnerite and silver amalgam from the Sala mine, Sweden

SCHACHNERITE ( $\beta$ -Ag<sub>1.1</sub>Hg<sub>0.9</sub>) and paraschachnerite (Ag<sub>1.2</sub>Hg<sub>0.8</sub>) were discovered in ores from Landsberg (Germany) by Seeliger and Mücke (1972), who suggested that these minerals should also be found in other localities where silver amalgam phases occur. Until recently, however, only one other occurrence of paraschachnerite was noted (in Kremikovci, Bulgaria, by Atanasov, 1979). The Sala material thus represents the third occurrence of paraschachnerite and the second one of schachnerite.

The Sala Pb–Ag–Zn deposit is the oldest known occurrence of natural silver amalgam. In the period between 1506 and 1962 this mine produced about 515 metric tons of silver and 37 000 metric tons of lead; at one time also about 0.6 metric ton

The IMA Commission on New Minerals and Mineral Names has approved the proposal to discredit calciocelsian.

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of mercury was gained (Tegengren, 1924). Macroscopic quantities of amalgam, native mercury and cinnabar were only noted in the higher parts of the mine, especially from the Juthyll shaft. According to Sjögren (1900) 'amalgam' occurred in two different forms: A. as silvery white cubic crystals in small druses filled sometimes with native mercury; B. as yellowish irregular masses in cavities. Chemical analyses of the cubic crystals yielded the composition of moschellandsbergite ( $\gamma$ -phase Ag<sub>4</sub>Hg<sub>5</sub>) with a small excess of mercury; the irregular masses, after subtraction of mechanical impurities, have exactly the composition of the  $\gamma$ -phase. Macroscopically identical irregular material, analysed by Nordström (1881), had a significantly lower Hg content, corresponding well with results of the present

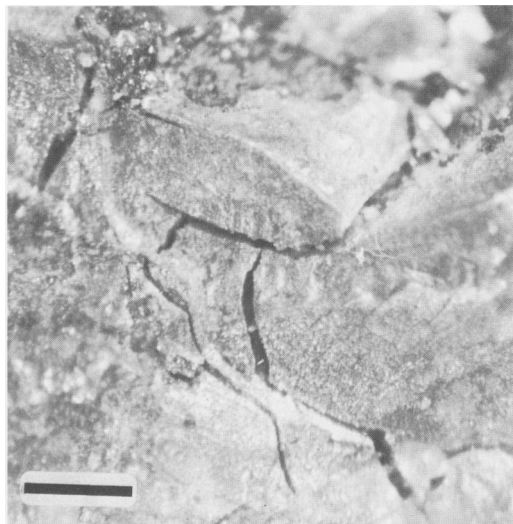


FIG. 1. Irregular masses of Ag-Hg minerals with desiccation fissures (bar is 0.5 mm).

investigation, and indicating a composition intermediate between those of paraschachnerite and  $\alpha$ -amalgam.

*Description of sample.* Schachnerite and paraschachnerite occur in specimen RM 334832 of the Swedish Natural History Museum in Stockholm. Macroscopically it shows a striking similarity with the B-type material of Sjögren (1900, 1910), and with material examined by Nordström (1881). The

sample consists of greenish marble with disseminated calcisilicates. Along cleavage planes, the green silicates are present in greater quantities and are accompanied by sphalerite, chalcopyrite and the yellowish irregular masses of 'amalgam'. These 'amalgam' masses occur in the form of nestlets and platelets up to 6 mm in diameter and up to 1 mm thick. The aggregates show desiccation fissures (Fig. 1), suggesting a secondary origin by demercuration.

*Chemical investigation.* Electron microprobe analyses were performed with a Cambridge Instruments Mark 9 instrument, using as standards metallic Ag and synthetic HgTe. Results were corrected with an on-line ZAF program. No elements other than Ag and Hg were detected. Due to the porous nature of most of the investigated material the totals are in the range of only 97 to 99 wt.%. Several semi-quantitative analyses have even lower totals. The results are plotted in Fig. 2. There are three clusters of results: around  $\text{Ag}_{1.12}\text{Hg}_{0.88}$ , representing schachnerite; a composition  $\text{Ag}_{1.18}\text{Hg}_{0.82}$  which extends the known range of paraschachnerite as indicated by the composition of natural phases from Landsberg and synthetic compounds analysed by Seeliger and Mücke (1972). The third cluster around  $\text{Ag}_{1.3}\text{Hg}_{0.7}$  is close to the estimated bulk composition of the amalgam material in the investigated sample, and also close to the chemical analysis of Nordström (1881). This composition illustrates the transition of paraschachnerite to  $\alpha$ -amalgam. In Fig. 2 are also indicated the results of the chemical analyses of

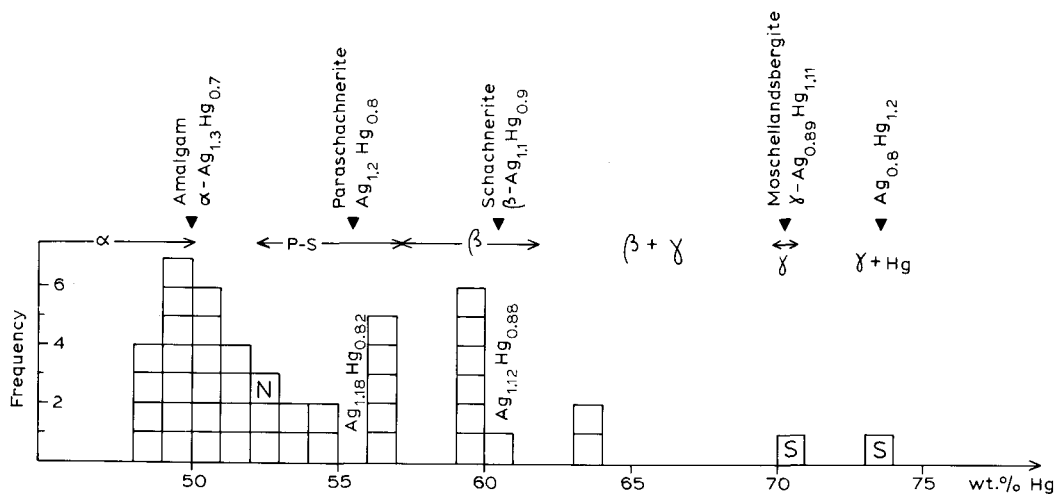


FIG. 2. Chemical composition of Ag-Hg minerals from Sala, representing the Hg-rich portion of the Ag-Hg system. Analytical results are corrected to Ag+Hg = 100 wt.%. The composition and the range of schachnerite and paraschachnerite are after Seeliger and Mücke (1972). Compositions measured by Nordström (N) and Sjögren (S) are also given.

Sjögren (1900): moschellandsbergite ( $\gamma$ -phase) and oversaturated moschellandsbergite ( $\gamma$ -phase + Hg), compositions not found in the present investigation.

*Mineralogical notes.* Microscopic observations in reflected light revealed two types of Ag-Hg minerals: the first type has a smooth polished surface, and the second one has a porous appearance. According to the microprobe results, the smooth type has the composition of schachnerite, whereas the porous type contains two phases: paraschachnerite and  $\alpha$ -amalgam extremely rich in Hg (previously called 'kongsbergite'). These Ag-Hg minerals are accompanied by (in order of decreasing abundance) sphalerite, chalcopyrite, pyrite, pyrrothite, gudmundite, cubanite, ilmenite, galena and possibly pyrargyrite.

*Schachnerite* forms isolated grains up to 150  $\mu\text{m}$  in diameter disseminated in carbonate; it also occurs intergrown with paraschachnerite and other minerals. Schachnerite often replaces cataclastic pyrite. The optical properties of the mineral are similar to those given by Seeliger and Mücke (1972). The distinction from paraschachnerite and amalgam was possible because of the smooth polish of schachnerite and the distinct anisotropy of paraschachnerite.

*Paraschachnerite* occurs intimately intergrown with amalgam and with schachnerite. Optical observations of the mineral are difficult because of the porous nature of the polished surface; its distinct anisotropy, however, is the most striking property. The porous surface is also the reason for the rather low totals of electron-microprobe results, especially when carried out in the raster mode. An X-ray powder diffraction pattern of a mixture containing amalgam, schachnerite and paraschachnerite contained only a few lines of amalgam (see below).

*Amalgam* is the cubic  $\alpha$ -phase with less than 50 wt.% Hg in the Ag-Hg system. The lower limit is not defined; until recently it was thought that amalgam forms a continuous solid solution series with native silver, but the discoveries of eugenite ( $\text{Ag}_{11}\text{Hg}_2$ ) and luanheite ( $\text{Ag}_3\text{Hg}$ ) complicate the Ag-Hg system. Electron microprobe analyses of the Sala material indicate an approximate formula of  $\text{Ag}_{1.3}\text{Hg}_{0.7}$  for the amalgam richest in Hg. This composition and the unit-cell value  $a$  of about 4.19 Å (obtained from Guinier and Gandolfi X-ray patterns of rather poor quality) are compatible with results obtained on Hg-rich amalgam phases ('kongsbergite') from Landsberg by Seeliger and Mücke (1972).

*Discussion.* The results of the present investigation and the data from the Ag-Hg system as presented by Seeliger and Mücke (1972) make

possible a mineralogical interpretation of older works (Nordström, 1881; Sjögren, 1900, 1910) and a reconstruction of the evolution of the Hg-rich phases of the Sala mine. The cubic crystals analysed by Sjögren (1900) were formed in an environment saturated with Hg, and consequently they have the composition of moschellandsbergite with an excess of Hg. Sjögren (1910) noted, moreover, that such crystals were not stable; they could pass into the liquid form by shaking and pressure, or just by moving them from the underground workings to the surface. It is probable that release of excess Hg produced the irregular masses of type B with a moschellandsbergite composition. Although no relics of moschellandsbergite were found in the recently investigated sample, its macroscopic similarity with type B irregular masses suggests that moschellandsbergite must have been the pre-existing phase, which altered first into schachnerite and paraschachnerite, followed by an alteration of these two minerals into Hg-rich amalgam. The same order of events was described from the Landsberg occurrence. Seeliger and Mücke (1972) concluded that schachnerite and paraschachnerite were formed directly from moschellandsbergite by *demercuration*; continuation of this process leads to the formation of amalgam. However, an expected step in this process, the transformation of schachnerite into paraschachnerite, has not been observed, neither in Landsberg, nor in Sala.

For the formation of clearly secondary moschellandsbergite in the Sala mine in an environment of

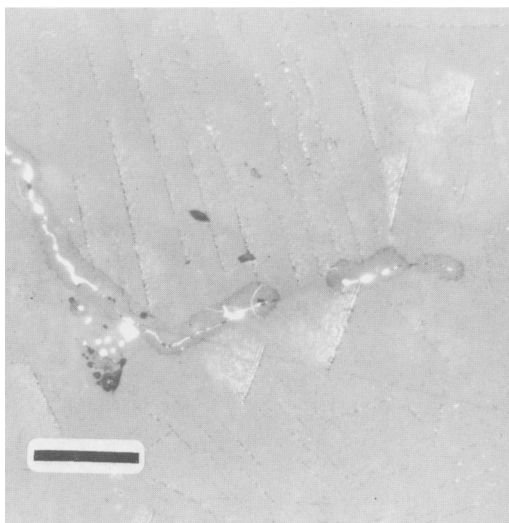


FIG. 3. Oriented exsolution-like inclusions of  $\alpha$ -amalgam in sphalerite (bar is 20  $\mu\text{m}$ ).

native mercury, one has to postulate the release of mercury from some Hg-rich pre-existing phase(s), for example by some thermal effect. It should be stressed here that, although being very spectacular, the occurrence of Ag-Hg minerals in druses and cavities in the upper parts of the mine is only of minor importance for the total balance of mercury involved in the Sala deposit. The majority of Hg is connected with massive Zn-Pb ores; Tegengren (1924) noted in Zn concentrates a minimum of 100 g mercury per ton and 150–200 g silver per ton. These values can be explained by the occurrence of minute exsolution-like inclusions of amalgam in sphalerite (Fig. 3).

The release of Hg from sphalerite and from a pre-existing amalgam phase of unknown composition produced on the one hand Hg-rich phases as native mercury and moschellandsbergite, and on the other hand Ag-rich phases as native silver and mercurian silver. Theoretically this process could have led to the formation of paraschachnerite among the Hg-rich phases. In Sala, however, textural evidence (porous appearance and relics of paraschachnerite inside the aggregates) suggests its origin by demercuration directly from moschellandsbergite, or through schachnerite as an intermediate stage. Further demercuration of paraschachnerite resulted in the formation of Hg-rich amalgam.

KEYWORDS: schachnerite, paraschachnerite, amalgam, system Ag-Hg, Sala, Sweden.

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## Chemical variation in a single crystal of chalcophanite

THE non-stoichiometry of chalcophanite was first recognized by Wadsley (1964), who considered it to be  $Zn_{1+x}Mn_3O_7 \cdot 3H_2O$ ,  $0 < x < 0.25$ . Since then a number of authors (Radtke *et al.*, 1967; Potter and Rossman, 1979; Ostwald, 1985) have shown that the mineral possesses an extremely wide variation in chemical composition associated with a constant X-ray diffraction pattern (JCPDS 15-807). In fact Radtke *et al.* (1967) suggested that the formula of chalcophanite was  $(R) R_3^1O_7 \cdot 3H_2O$ , where  $R$  is commonly Zn but may be  $Mn^{2+}$ , Ag, Ba, Ca, Mg and  $R^1$  is  $Mn^{4+}$ ,  $Fe^{3+}$ . Recently a nickel chalcophanite has been recorded (Elias *et al.*, 1981) thus further expanding this list of elements.

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Although the writer has not been able to examine specimens of all recorded chemical compositions of this mineral, those examined, including high- and low-Zn chalcophanite, nickel chalcophanite, and manganese-enriched chalcophanite (Ostwald, 1985) have remarkably similar determinative properties (optical properties, reflectivity, microhardness, X-ray 'd' spacings, infra-red spectra, etc.) which suggests that these properties are a function of the basic 7 Å layer lattice and are little influenced by the widely variable chemistry.

Chalcophanite was first described by Moore (1875). It is interesting to speculate how recent knowledge of chemical variation in this apparently