MINERALOGIA POLONICA
Vol. 23, No 1 — 1992

Adam PIESTRZYŃSKI[1] *Wojciech TYLKA*[2]

SILVER AMALGAMS FROM THE SIEROSZOWICE COPPER MINE, LUBIN-SIEROSZOWICE DISTRICT, SW POLAND

Abstract. A new occurrence of Ag-Hg native alloys has been found in the Sieroszowice mine, Lubin — Sieroszowice copper district. Silver amalgams ranging in composition from $Ag_{14}Hg_1$ to Ag_6Hg_1, and an eugenite ($Ag_{11}Hg_2$) were found within low grade copper sulphide ore in close proximity to red-stained dolomite beds. The investigated silver amalgams contain detectable Cu, Au and Pd.

INTRODUCTION

The Sieroszowice mine lies within the Lubin — Sieroszowice copper district at the western corner of the economic copper field. The western border of the Sieroszowice mine is in contact with red beds of the rote Fäule facies. Within the Sieroszowice mine field itself, a small area of the red bed facies is present. The red stains are observed in the top part of the Weissliegendes sandstone as well as in the Kupferschiefer and Werra dolomites above (Fig. 1). This area is characterized by completely barren sandstone (Fig. 2), and by low grade copper mineralization in the black shale and carbonate rocks (Fig. 2). The dolomites are characterized by gypsum and anhydrite nests up to 10 cm in size (Phot. 1, 2). They are also interbeded with gypsum-anhydrite veinlets (Phot. 1). Copper minerals occur as big sulphide nests (up to 2 cm), veinlets, and disseminations visible only during microscopic observations. A small concentration of Cu-sulphides has been found on the border between the anhydrite-gypsum nests and carbonate wallrocks.

Rich silver-mercury minerals has been recognized within the sulphide bearing dolomites close to the contact with the red coloured dolomite beds.

The major sulphide minerals are chalcocite, digenite and covellite. According to the earlier work of Kucha 1986, as well as this study, the presence of the following parageneses of the silver-mercury minerals are suggested:

1. Ag-amalgams, connected with the contact of Cu- and Pb-zones running through the Kupferschiefer. In the bottom part of the shale chalcocite and bornite are

1 Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków
2 Sieroszowice mine, 59-320 Polkowice.

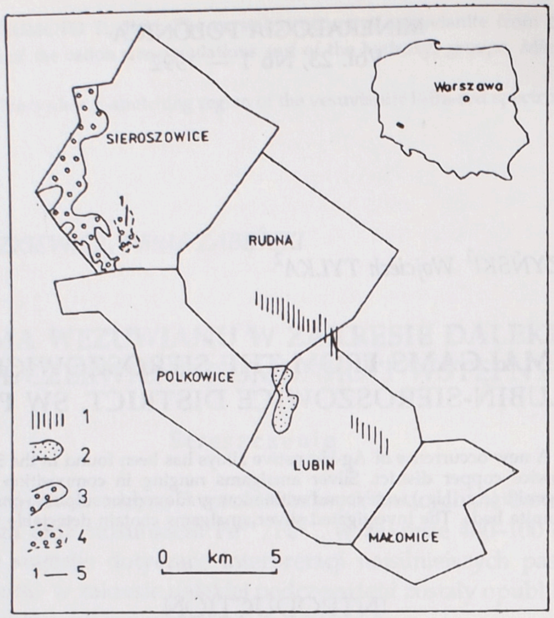

Fig. 1. Distribution of Ag-amalgams and noble metals in the area of the four mines under operation. 1 — Pb-Ag-Hg-Cu, after Kucha (1990); 2 — noble metal, after Kucha (1990); 3 — rote Fäule; 4 — rote Fäule with copper mineralization; 5 — location of the investigated profiles marked on Fig. 2.

Fig. 1. Rozmieszczenie Ag-amalgamatów i metali szlachetnych na eksploatowanych obszarach kopalń miedzi. 1 — Pb-Ag-Hg-Cu wg Kuchy (1990), 2 — metale szlachetne, wg Kuchy (1990), 3 — rote Fäule, 4 — strefa rote Fäule z mineralizacją miedziową, 5 — lokalizacja profili z figury 2.

always present. In the upper part, the shale becomes calcareous and is characterized by galena, sphalerite, pyrite and small amounts of copper and iron-copper sulphides. The transition between the Cu and the Pb-Zn zone is characterized by Ag-Hg alloys and Cu-Ag-Hg-sulphides, and contains up to 3000 ppm Ag (Mayer and Piestrzyński, 1985). Ag-minerals are represented mainly by kongsbergite, native silver, and eugenite (Kucha, 1986). The Hg content in Cu-Ag-sulphides intergrown with Ag-amalgams reaches 11.02 wt % (Mayer and Piestrzyński, 1985). Some mercury is also present in sphalerites (Kucha, 1986).

2. Eugenite + calcite + gypsum + hematite, occurring in the boundary dolomite (lithological unit between the Weissliegendes and the Kupferschiefer, present mostly as a thin, up to 20 cm, layer in the eastern part of the Lubin–Sieroszowice district) (Kucha, 1986).

3. Ag-amalgams + gypsum + hematite, occurring in the uppermost part of the Weissliegendes sandstone characterized by macroscopically visible red-stained gypsum cement with hematite. In this zone chalcocite, covellite and tennantite are major minerals.

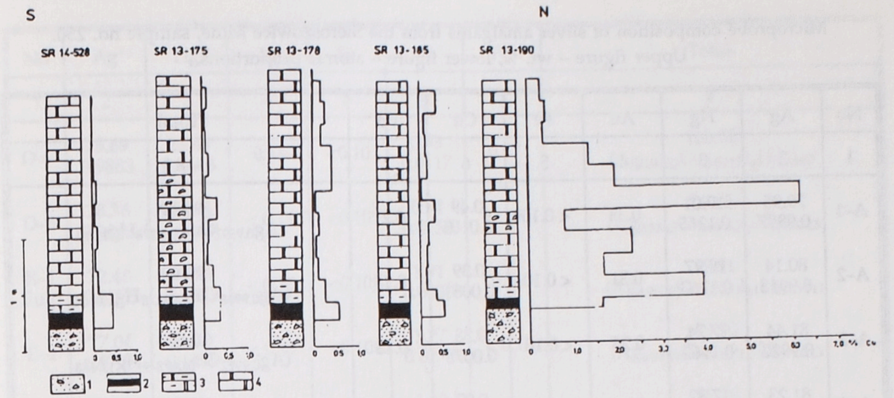

Fig. 2. Distribution of copper in vertical profiles from the red beds zone of the Sieroszowice mine. Location of the profiles is shown on Fig. 1. The distance between profiles is 20 m, 1 — red sandstone, 2 — Kupferschiefer, 3 — clayey dolomite, 4 — dolomite.

Fig. 2. Rozmieszczenie miedzi w profilu pionowym w strefie występowania czerwonych plam w węglanach. Lokalizację profili podano na Fig. 1. Odstępy pomiędzy profilami wynoszą 20 m. 1 — piaskowiec z czerwonymi plamami, 2 — łupek miedzionośny, 3 — dolomit ilasty, 4 — dolomit.

4. Ag-amalgams in dolomite (PZ1) along the transition zone between hematite-bearing and copper sulphide-bearing rocks (this study). This zone is characterized by low copper (about 1%) (Fig. 2) and silver (10–20 ppm) contents. These values are low in comparison to other areas of the Lubin — Sieroszowice copper district (Salamon, 1979). The low silver content in the dolomites is probably related to the thin copper mineralization located mostly in the shale (Fig. 2) as well as with the relatively low amount of Ag in the Kupferschiefer from this area. The elevated silver contents are only present in the Kupferschiefer horizon. No Pb-Zn mineralization is present in this part of the mine. The position of Ag-amalgams is about 1 m above the Weissliegendes sandstone. Ore microscope investigation shows the presence of two different mineral assemblages. The older assemblage is characterized by copper sulphides occurring as nests up to 2 cm in size, and disseminations visible only under the ore microscope. The younger assemblage consists of copper sulphides intergrown with the native alloys. These minerals fill fissures and open spaces between carbonate crystals in secondary veinlets. The veinlets cut copper sulphide nests (Phot. 3, 4). The chalcocite in these nests replaced the carbonate host (Phot. 5) which reveals, under crossed nicols, red internal reflections. In this carbonate, minute hematite needles have been also recognized. Microprobe investigation showed that the carbonate is ankerite. The disseminated copper minerals are characterized by xenomorphic and framboid-like textures of chalcocite (Phot. 6).

Table 1

Microprobe composition of silver amalgams from the Sieroszowice Mine, sample no. 250.
Upper figure – wt. %, lower figure – atomic proportions.

No	Ag	Hg	Au	Fe	Cu	Pd	Total
1	2	3	4	5	6	7	8
A–1	79.95 0.9897	19.01 0.1265	0.33	< 0.10	0.49 0.0103	0.21	99.99 $(Ag_{0.9897}Cu_{0.0103})_8Hg_{1.012}$
A–2	80.14 0.9918	18.97 0.1263	0.31	< 0.10	0.39 0.0081	0.18	99.99 $(Ag_{0.9918}Cu_{0.0081})_8Hg_{1.0104}$
A–3	81.44 0.9922	17.74 0.1162	0.26	< 0.10	0.38 0.0078	0.18	100.00 $(Ag_{0.9922}Cu_{0.0078})_9Hg_{1.0458}$
A–4	81.23 0.9924	17.82 0.1236	0.32	< 0.10	0.37 0.0076	0.24	99.98 $(Ag_{0.9924}Cu_{0.0076})_8Hg_{0.9888}$
A–5	83.16 0.9845	14.68 0.0935	0.23	< 0.10	0.77 0.0155	0.15	98.99 $(Ag_{0.9845}Cu_{0.0155})_{11}Hg_{1.0284}$
A–6	79.60 0.9745	19.54 0.1286	< 0.15	< 0.10	1.23 0.0255	0.13	100.50 $(Ag_{0.9745}Cu_{0.0255})_8Hg_{1.0288}$
A–7	79.24 0.9841	19.78 0.1321	< 0.15	< 0.10	0.76 0.0159	< 0.12	99.78 $(Ag_{0.9841}Cu_{0.0159})_8Hg_{1.0568}$
C–1	79.50 0.9716	18.62 0.1223	0.31	0.11	1.37 0.0283	0.19	99.99 $(Ag_{0.9716}Cu_{0.0283})_8Hg_{0.9784}$
C–2	86.46 0.9681	11.64 0.0701	< 0.15	< 0.10	1.68 0.0318	0.21	99.99 $(Ag_{0.9681}Cu_{0.0318})_{14}Hg_{0.9814}$
C–4 Eug.	73.26 0.9564	24.64 0.1729	< 0.15	< 0.10	1.97 0.0436	< 0.12	99.87 $(Ag_{0.9564}Cu_{0.0436})_{11}Hg_{1.9019}$
C–5	77.03 0.9654	21.18 0.1433	< 0.15	<0.10	1.62 0.0346	< 0.12	99.87 $(Ag_{0.9654}Cu_{0.0346})_7Hg_{1.0031}$
D–1	82.03 0.9766	16,74 0.1054	0.18	<0.10	1.16 0.0234	0.13	99.97 $(Ag_{0.9766}Cu_{0.0234})_{10}Hg_{1.054}$
D–2	82.66 0.9692	15.72 0.0992	< 0.15	<0.10	1.55 0.0308	< 0.12	99.93 $(Ag_{0.9692}Cu_{0.0308})_{10}Hg_{0.992}$
D–3	79.71 0.9807	19.07 0.1262	0.19	<0.10	0.92 0.0176	< 0.12	99.89 $(Ag_{0.9807}Cu_{0.0176})_8Hg_{1.096}$
D–4	80.62 0.9824	18.24 0.1195	0.21	<0.10	0.85 0.0176	< 0.12	99.92 $(Ag_{0.9824}Cu_{0.0176})_8Hg_{0.956}$
D–5	77.70 0.9875	21.37 0,1460	0.25	<0.10	0.58 0.0012	< 0.12	99.90 $(Ag_{0.9875}Cu_{0.0012})_7Hg_{1.022}$
D–6	76.27 0.9832	22.52 0.1561	0.25	<0.10	0.77 0.0168	0.17	99.98 $(Ag_{0.9832}Cu_{0.0168})_6Hg_{0.9366}$

Table 1 cnd

No	Ag	Hg	Au	Fe	Cu	Pd	Total
1	2	3	4	5	6	7	8
D–7	75.69 0.9883	23.43 0.1645	0.18	<0.10	0.53 0.0117	0.17	100.00 $(Ag_{0.9883}Cu_{0.0117})_6Hg_{0.987}$
D–8	78.36 0.9843	20.56 0.1389	< 0.15	<0.10	0.74 0.0157	0.19	99.85 $(Ag_{0.9843}Cu_{0.0157})_7Hg_{0.9723}$
E–1 Eug.	72.48 0.9570	25.36 0.1801	< 0.15	<0.10	1.91 0.0430	0.16	99.91 $(Ag_{0.9570}Cu_{0.0430})_{11}Hg_{1.9811}$
E–2	77.04 0.9729	21.49 0.1459	< 0.15	<0.10	1.27 0.0271	< 0.12	99.80 $(Ag_{0.9729}Cu_{0.0271})_7Hg_{1.0213}$
E–3	79.68 0.9745	18.85 0.1239	< 0.15	<0.10	1.23 0.0255	< 0.12	99.76 $(Ag_{0.9745}Cu_{0.0255})_8Hg_{0.9912}$
E–4	78.38 0.9753	19.94 0.1334	0.30	< 0.10	1.17 0.0247	0.18	99.97 $(Ag_{0.9753}Cu_{0.0247})_8Hg_{1.0672}$
E–5	80.97 0.9760	17.60 0.1142	< 0.15	< 0.10	1.10 0.240	0.19	99.86 $(Ag_{0.9760}Cu_{0.0240})_9Hg_{1.0278}$
E–6	76.96 0.9759	21.80 0.1487	< 0.15	< 0.10	1.12 0.0241	< 0.12	99.88 $(Ag_{0.9759}Cu_{0.0241})_7Hg_{1.0409}$
Sought for but not detected: S, Bi, Pt, As.							

EXPERIMENTAL

The investigations were carried out on samples collected at the Sieroszowice mine. The investigated area is marked on Fig. 1.

The chemical composition of silver amalgams was determined with ARL SEMQ electron-probe under the following conditions: voltage — 20 kV, probe current — 120 μA, sample current 9 nA and counting time 20 s. The following spectral lines and standards were used: SK_α, FeK_α, (FeS_2), AgL_α, (100%), AuL_α, (100%), HgL_α, (HgS), PdL_α (100%). The intensities of characteristic radiation were corrected for absorption (Philibert, 1965) and atomic number difference (Philibert and Tixier, 1968).

RESULTS AND DISCUSSION

Twenty five microprobe analyses of silver amalgams (Tab. 1) show a large variation in chemical composition. The amount of silver is ranging from 72.48 up to 86.46 wt% (Tab. 1). Copper is present only in small quantities (0.38–1.91 wt%) and probably subtitutes for silver. The maximum gold and palladium contents are 0.33 wt% and palladium 0.21 wt% respectively (Tab. 1). Only thirteen Au and fifteen Pd determinations were above detection limits of 0.15 and 0.12 wt% respectively. These results should be confirmed by futher detailed investigations. Previous data published by Kucha (1986) indicate that typical eugenite is without Au and Pd admixtures. The Au and Hg atomic proportions (Tab. 1, lower figure) suggest the presence of eugenite (analyses C-4 and E-1), and a solid solution series ranging from $Ag_{14}Hg_1$ to Ag_6Hg_1 (23 measurements, Tab. 1) with small but significant contents of Cu, Au and Pd. The chemical formula of eugenite from the Sieroszowice mine was determined to be $(Ag_{0.9564}Cu_{0.0436})_{11}Hg_{1.9019}$ and $(Ag_{0.9570}Cu_{0.0430})_{11}Hg_{1.9811}$, which agress well with the formula $Ag_{11}Hg_2$ proposed by Kucha (1986). No differences in microscopic properties of the eugenite and other silver amalgams have been observed. In the reflected light the investigated minerals are white with a light yellow tint. Their reflectance is about 80% as described by Kucha (1986). All investigated minerals are isotropic. The presence of copper in silver amalgams suggests that amalgams originated from a solution containing Ag and Cu. The source of mercury is very controversial, however the small quantities of this metal may have originated from the organic matter and/or from natural gas within the Rotliegendes (Kucha, 1990).

The presence of gold in Ag-amalgams from the Lubin–Sieroszowice copper district is very controversial, because of the high detection limit of Au. However, Healy and Pętruk (1990) have identified an Ag-Au-Hg alloy from the Trout Lake massive sulphide deposit. The composition varies as follows: 17.3 — 76.5% Ag, 1.62 — 79.9% Au and

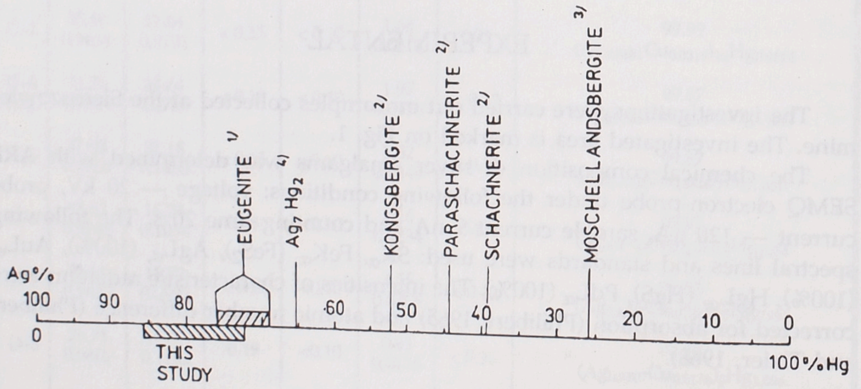

Fig. 3. Position of known Ag-Hg minerals and investigated Ag-alloys in the Ag-Hg binary system (in wt%). 1 — after Kucha (1986), 2 — after Seeligen and Mücke (1972), 3 — after Ramdohr (1975), 4 — after Kucha and Marcinkowski (1976).

Fig. 3. Lokalizacja znanych Ag-minerałów i badanych Ag-stopów rodzimych w binarnym systemie Ag-Hg. 1 — wg Kuchy (1986), 2 — wg Seeliger i Mücke (1972), 3 — wg Ramdohra (1975), 4 — wg Kuchy i Marcinkowskiego (1976).

1.29 — 30.9% Hg. The average composition is 49.2% Ag, 38.7% Au and 11.0% Hg. It is suggested that Au can substitute for Ag in the binary Ag-Hg system forming the ternary system Ag-Au-Hg. In this system it is possible to include the eugenite described by Kucha (1986), Au-Ag amalgams of Nysten (1986), Hg-bearing electrum described by Scott (1977) and Healy and Petruk (1988, 1989), mercurian gold described by Shikazono and Shimizu, (1988) and the Au-bearing Ag-amalgams described in this study. The position of all known mineral phases in the binary Ag-Hg system including Ag_7Hg_2 and $Ag_{10}Hg_2$ (Kucha and Marcinkowski, 1976) are marked on Fig. 3.

CONCLUSIONS

The silver amalgams differ from eugenite and other Ag-Hg alloys in chemical composition, however their microscopic properties are similar. It is suggested that there exists a solid solution series $Ag_{14}Hg_1 - Ag_6Hg_1$. Further work on the Ag-Hg system is needed especially on amalgams containing less than 30 wt% of mercury. In the paragenetic position described above, the amalgams seem to crystallize after main stage of copper sulphide precipitation. Crystallization of amalgams is probably closely connected with weakly reducing environments present after crystallization of the main sulphide stage. It can also be concluded that the silver amalgams form the latest ore parageneses. This work confirms the earlier study presented by Kucha (1986). It is the second report of eugenite in Poland.

Acknowledgments. The authors are indebted to Prof. Wodzicki for the critical reading of the manuscript.

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EXPLANATION OF MICROPHOTOGRAPHS

PLATE III

PHOT. 1. Exposure of red-spotted Lower Zechstein dolomite at the Sieroszowice mine. White — gypsum and anhydrite veinlets and nests. Red spots are arrowed

PHOT. 2. Fragment of a mine working wall with well-visible, large gypsum-anhydrite nests (white) and red spots (arrowed)

PLATE IV

PHOT. 3. Dolo- (do) and calcisparrite (ca) veinlet in chalcocite (cc) nest with silver amalgams (sam). Sieroszowice mine, Zechstein Limestone (PZ1), reflected light.

PHOT. 4. Xenomorphic crystals of silver amalgams (sam) in dolomite-calcite veinlet, Sieroszowice mine, Zechstein Limestone (PZ1), reflected light

PHOT. 5. Replacing structures of massive chalcocite (cc) after ankerite (dark). Sieroszowice mine, Zechstein Limestone (PZ1), reflected light

PHOT. 6. Framboid-like textures of chalcocite (white) in dolomite, Sieroszowice mine, reflected light

Adam PIESTRZYŃSKI, Wojciech TYLKA

AMALGAMATY SREBRA Z KOPALNI SIEROSZOWICE, SW POLSKA

Streszczenie

W kopalni Sieroszowice stwierdzono eugenit i inne amalgamaty srebra. Minerały te występują w strefie czerwonych plam zlokalizowanych zarówno w stropowej części białego spągowca jak również w skałach węglanowych. Skały tej strefy charakteryzują się niskimi zawartościami miedzi oraz widocznymi makroskopowo, licznymi żyłkami gipsowymi i gniazdami gipsowo-anhydrytowymi. Dwa spośród analizowanych amalgamatów srebra posiadają skład chemiczny zbliżony

do opisanego wcześniej przez Kuchę (1986) eugenitu o składzie $Ag_{11}Hg_2$. Skład chemiczny pozostałych amalgamatów jest zmienny w granicach $Ag_{14}Hg_1$–Ag_6Hg_1. Zarówno eugenit jak i pozostałe amalgamaty wykazują stałą domieszkę miedzi w granicach 0,38–1,91 %wag. Zawartość złota oznaczana w niektórych punktach osiąga maksymalną wartość 0,33 % wag. a palladu 0,21 %wag. Ze względu na wysokie granice oznaczalności tych pierwiastków, odpowiednie 0,15 i 0,12 %wag., obecność tych pierwiastków powinna zostać potwierdzona dalszymi badaniami. Skład chemiczny amalgamatów wskazuje na obecność ograniczonego roztworu stałego w binarnym systemie Ag-Hg.

Poza kopalnią Lubin, Sieroszowice są drugim miejscem, w którym stwierdzono nowo opisany minerał o składzie eugenitu.

OBJAŚNIENIA FOTOGRAFII

PLANSZA III

FOT. 1. Ocios wyrobiska górniczego w kopalni Sieroszowice w strefie występowania czerwonych plam w skałach węglanowych. Białe — żyłki i gniazda gipsowo-anhydrytowe. Strzałkami oznaczono miejsca występowania czerwonych plam.

FOT. 2. Fragment ociosu z dobrze widzocznymi gniazdami gipsowo-anhydrytowymi (białe) i czerwonymi plamami wskazanymi przez strzałki.

PLANSZA IV

FOT. 3. Żyłka kalcytowo (ca) — dolomitowa (do) przecinająca gniązdowe skupienie chalkozynu (cc), sam — amalgamaty srebra. Kopalnia Sieroszowice, dolomit, światło odbite.

FOT. 4. Ksenomorficzne kryształy amalgamatów srebra (sam) w żyłce dolomitowe; (do), cc– chalkozyn. Kopalnia Sieroszowice, dolomit, światło odbite.

FOT. 5. Struktury zastępowania ankerytu przez masywny chalkozyn (cc). Kopalnia Sieroszowice, dolomit, światło odbite.

FOT. 6. Frambpido-podobne struktury chalkozynu (biały) w dolomicie. Kopalnia Sieroszowice, światło odbite.

PLATE IV