Textures and geochemistry of silver minerals from Kupferschiefer in the western part of Fore-Sudetic Monocline.

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Abstract. For the last two years the Fore-Sudetic Monocline has been an object of intense investigation by many exploration companies. In the Mozów prospective area, two new boreholes were drilled reaching Kupferschiefer-type deposits. In both of them Cu-Ag mineralisation was observed above the Rote Fäule hematitic footwall alteration. In geological material collected from the copper-bearing series, silver minerals like native silver, silver amalgams, stromeyerite, danielsite and unnamed Ag_9Hg, Ag_7Hg_2 have been recorded as individual grains - microlites, intergrowths - aggregates, and as silver-bearing laminae. The studied textures suggest genetic association of silver minerals with copper mineralisation. The vertical and lateral distribution of silver minerals from the Mozów area and their chemical composition are comparable to the currently mined Cu-Ag ore deposit in the southern part of the Fore-Sudetic Monocline.

silver minerals, silver amalgams, Kupferschiefer, Fore-Sudetic Monocline, Poland

1 Introduction

Silver in the Lower Zechstein copper-bearing series is associated with the occurrence of rich copper concentrations. This element manifests itself as its own minerals, isomorphic additions and organometallic compounds (Salmon 1979; Banaś et al. 1976). Among silver minerals in the Cu-Ag ore deposit in the southern part of the Fore-Sudetic Monocline which undergoes extraction, silver amalgams have been recorded, i.e. eugenite, kongsbergite (Kucha 1986), along with native silver, stromeyerite, acanthite (Harańczyk 1970), jalpaite, argyrodite (Nguyen Van Nhan 1970), mckinstryite (Salamon 1976). Numerous minerals have not yet been named (Kucha and Marcinkowski 1976; Kucha and Głuszek 1983; Mayer and Piestrzyński 1985; Piestrzyński and Tylka 1992). The highest silver contents have been observed in close contact with the oxidised facies and in a belt adjacent to an area of high lead concentrations (Kucha 1990; Kucha and Przybyłowicz 1999). In the present paper, chemical composition of silver minerals has been analysed for the copper-bearing series in new drillholes from the western part of the Fore-Sudetic Monocline. The results of chemical analyses have been presented in element distribution charts as weight percent. Distribution of silver minerals has been assessed against the position of oxidised sediments (Rote Fäule).

2 Geological setting

The material for detailed examinations was collected from cores of two boreholes drilled in 2013. MCC1 and MCC2 boreholes are located in the prognostic “Mozów” Cu-Ag deposit in direct contact with the Zielona Góra oxidised area (Fig. 1). Both the prognostic area and the front of the oxidised facies have been demarcated based on the examinations of historical materials (Speczik and Oszczepalski, 2011). The material for mineralogical examinations has been collected from the profile of Lower Zechstein copper-bearing series comprising the bottom of lower anhydrite, the complete Zechstein limestone with the copper-bearing shale as well as the top part of Rotliegend. In both drillholes the Zechstein limestone is bipartite. The top part of Zechstein limestone is represented by dolomitic-oncolitic limestones, with the bottom part consisting of micritic dolomitic limestones and argillaceous limestones. The copper-bearing shale (Kupferschiefer) in both boreholes takes the form of black clayey-limy shale. The top part of Rotliegend consists of grey and pink quartzy arenites.

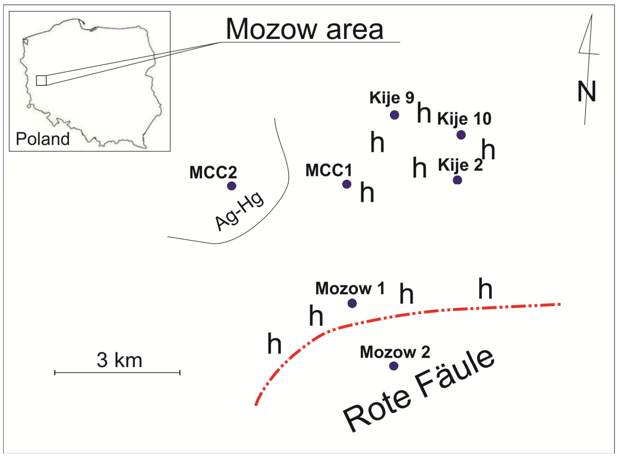

Figure 1. The area of the prognostic Mozów prospect deposit against the distribution of the oxidised zone (Rote Fäule), areas where the oxidised facies penetrates the bottom part of copper-bearing shale (h) and the zone with elevated silver mineral content (Ag-Hg). Boreholes 1 and 2 drilled in 2013; Kije 2, 9, 10, Mozow 1 and 2 historical boreholes drilled in 1980-1990.

2.1 Mineralisation

Silver minerals accompany the main sulphide ore, which in both discussed boreholes occurs in the bottom part of the Zechstein limestone and in the copper-bearing shale. Chalcocite and digenite are the predominant sulphides, and also, in the top part of the metal-bearing profile, bornite, galena and sphalerite have been recorded along with relics of pyrite replaced by copper, lead and zinc sulphides. Sandstone rich in iron oxides and hydroxides (Rote Fäule), in which gold and platinum minerals have been recorded with sparse copper sulphides, underlies the copper-bearing zone (Krzemiński and Speczik 2013). In the MCC1 borehole the most abundant silver minerals are present at the border of oxidised sediments which is in the lower part of the copper-bearing shale, while in the MCC2 borehole numerous silver minerals are present in the whole profile of the metal-bearing series, and the redox interface is located in uppermost of Rotliegend. Native silver has been identified under polarised reflected light along with silver amalgams and stromeyerite. A total of 131 microlites and silver mineral aggregates have been observed, 39 of which are in the profile of the first borehole and 92 are in the profile of the second borehole. In the vertical profile, silver amalgams concentrate mainly in the copper-bearing shale and much less silver amalgams are present in the Zechstein limestone. Native silver has been recorded both in the copper-bearing shale and in the Zechstein limestone. Stromeyerite accompanies the silver amalgams.

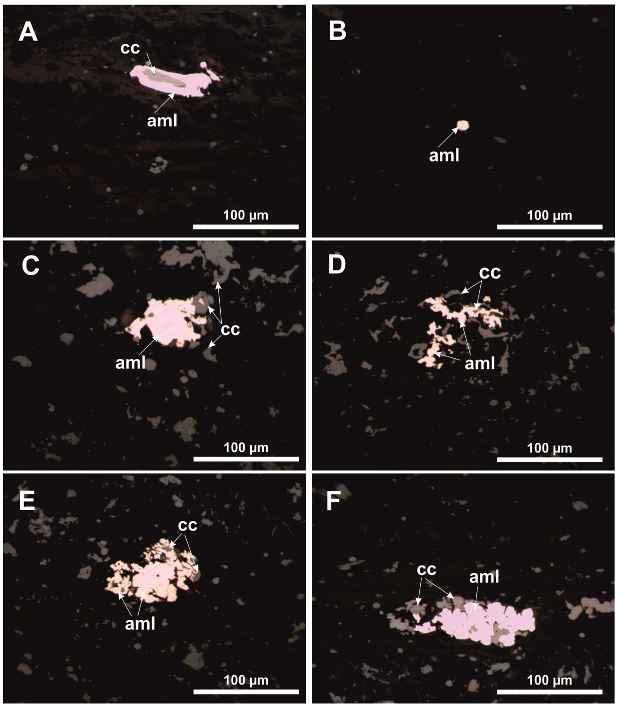

Figure 2. Selected photomicrographs of silver minerals under polarised reflected light. A – intergrowth of ring-forming silver amalgam (aml) with chalcocite (cc), MMC2, copper-bearing shale; B – pyritic framboid completely replaced by silver amalgam shaped as a spherical microlitic form, MCC2, copper-bearing shale; C – aggregate of silver amalgam with chalcocite, MCC2, Zechstein limestone; D – wormlike aggregate of silver amalgam in an intergrowth with chalcocite, MCC2, copper-bearing shale; E – aggregate of silver amalgam with chalcocite, borehole 1, Zechstein limestone; F – aggregate of silver amalgam in an intergrowth with chalcocite, MCC1, copper-bearing shale.

2.2 Textures

Three types of silver mineral textures have been distinguished: microlites, aggregates and silver-bearing laminae. Microlites are individual manifestations of silver minerals with spherical or irregular shape, dispersed among copper sulphides. Silver mineral microlites have been noticed occasionally; these are mainly silver amalgams, rarely native silver, while no individual stromeyerite has been recorded, always coexisting in intergrowths with silver amalgams or native silver. Xenomorphic microlites of silver amalgams and native silver have been noticed in Zechstein limestone; also, individual pyritic framboids completely replaced by silver amalgams have been recorded locally in the copper-bearing shale along with carbonate grains partially replaced by silver minerals. The aggregates are intergrowths of native silver with silver amalgams and stromeyerite along with chalcocite and digenite; they are the most common form of silver ore (Fig. 2). The largest aggregates exhibit zonal structure, with native silver or stromeyerite in the central part and silver amalgams in the outer part (Fig. 3). The shape of them varies; they are massive grains or wormlike and irregular elongated forms. The carbonate laminae replaced by silver minerals and copper and lead sulphides in the copper-bearing shale (Fig. 3). In the case of these forms a pattern is visible in the distribution of individual minerals constituting the laminae: galena is present in the upper part, with silver amalgams and native silver below, followed by stromeyerite and chalcocite.

2.3 Geochemistry

Micro-area analyses have proven high diversity in the chemical composition of silver minerals. The silver amalgams contain between 49.01 and 83.69 wt.% of silver, the additions of copper amount to up to 4.01 wt.%, occasionally present are additions of gold up to 0.71 wt.%. In the amalgams from MCC1 borehole the silver content ranges between 66.91 and 69.89 wt.%. The displayed results of the analyses have indicated the presence of minerals with silver content slightly higher compared to the Ag_7Hg_2 compound and lower compared to eugenite (Fig. 4). The silver content of amalgams ranged between 49.01 and 83.69 wt.% in the second borehole. The results displayed in element distribution charts indicated the presence of eugenite, kongsbergite and minerals intermediate between eugenite and Ag_7Hg_2. The major part of the results fell within the range between 79.69 and 83.69 wt.% of Ag. Furthermore, in the MCC2 borehole it has been noted that the low silver content amalgams are more common in the lower part of Kupfershiefer, while high silver content amalgams are characteristic for the upper part of Kupferschiefer and lower part of the limestone (Fig. 5). No similar pattern has been observed in the first borehole. Analyses of native silver have proven a 98.01 wt.% silver content with a slight addition of mercury up to 1.01 wt.%, copper up to 1.01 wt.% and gold up to 0.49 wt%. The highest additions of mercury have been recorded in the native silver present as intergrowths with silver amalgams. The additions of gold were characteristic for the silver minerals from the bottom part of the profile in both boreholes. Stromeyerite from both boreholes contains 48.70 to 49.89 wt.% of silver, 30.90 to 33.10 wt.% of copper and 13.10 to 16.10 wt.% of sulphur. Locally the stromeyerite contains additions of mercury up to 8.65 wt.%. Moreover, in the case of zonally structured aggregates, danielsite has been indexed, containing 33.30 to 35.20 wt.% of copper, 35.45 to 37.20 wt.% of silver, 9.98 to 12.50 wt.% of mercury and 13.45 to 16.50 wt.% of sulphur.

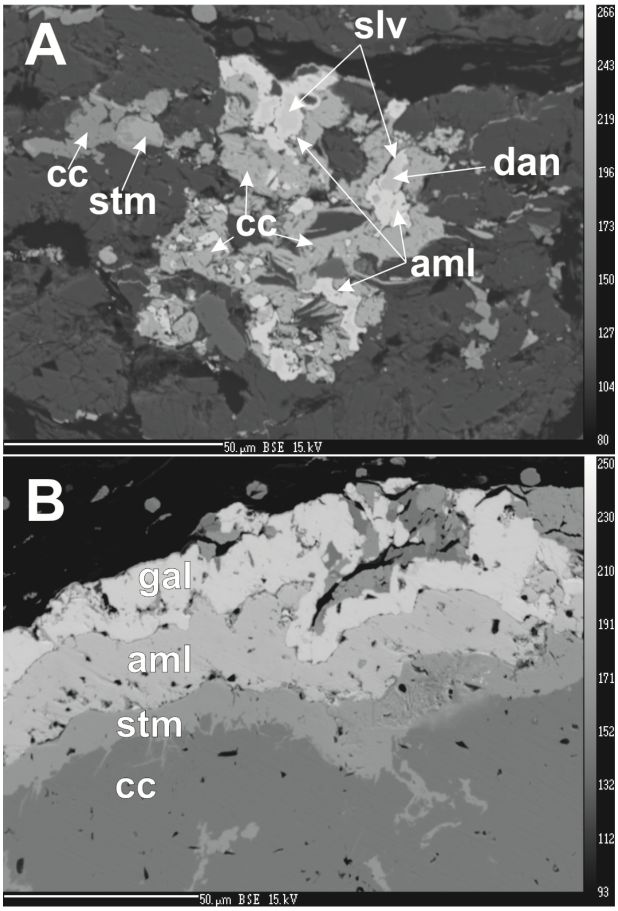

Figure 3. Silver minerals visible under backscattered electrons. A – wormlike aggregate of silver amalgams (aml) with stromeyerite (stm), native silver (slv), danielsite (dan) and chalcocite (cc) in the copper-bearing shale, borehole 2; B – silver-bearing lamina with zonal structure - galena (gal) in the top, with silver amalgam (aml) and stromeyerite (stm) below and chalcocite (cc) in the bottom.

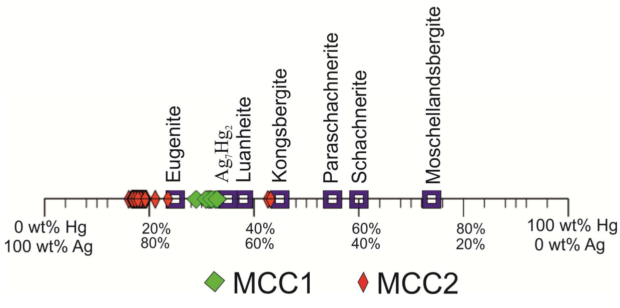

Figure 4. Mercury and silver distribution chart (wt.%) for individual analyses of silver amalgams depending on the borehole.

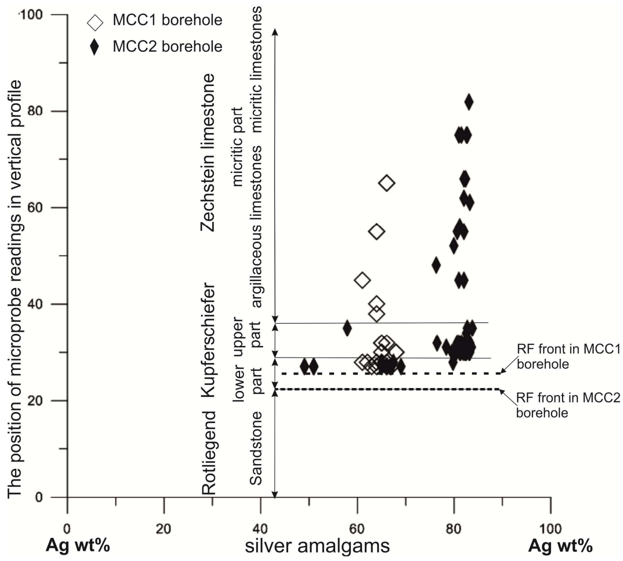

Figure 5. Silver distribution chart (wt.%) for individual analyses of silver amalgams depending on the position in the vertical profile. (RF- Rote Fäule)

3 Discussion and conclusion

The emergence of rich silver mineral concentrations in the copper-bearing shale directly above the oxidised Weissliegend is associated with the impact of metal-rich brines migrating within the sandstone, which upon encountering a hydrodynamic and geochemical barrier of strongly reductive nature reduced the transported metals including silver. The result of this process is the zonal distribution of minerals in horizontal and vertical profiles (Oszczepalski 1989; Pieczonka et al. 2007; Borg et al. 2012). In both boreholes, the vertical zonality in the distribution of copper sulphides has been confirmed (predominance of copper sulphides in the bottom and of lead and zinc sulphides in the upper part), while in the horizontal profile both boreholes belong to the zone of chalcocite predominance which puts them both in close proximity to the oxidised area. The forms of silver minerals, i.e. replacements of carbonate minerals and of framboidal pyrite indicate that the silver ore was created as an effect of diagenetic processes (Jowett 1986; Oszczepalski 1999). The coetaneous origin of native silver and silver amalgams as well as the copper sulphides is confirmed by numerous intergrowths of silver amalgams, native silver with chalcocite, digenite and galena. The textures of stromeyerite and danielsite indicate that those minerals were generated as a result of reaction between silver amalgams and copper sulphides (Ramdohr 1980). The number of recorded instances of silver minerals in the first borehole is three times lower compared to the number of silver minerals in the second borehole. Similar abundant manifestations of silver minerals have been described along the boundaries of areas rich in lead sulphides in relation to copper sulphides in the central part of the extracted Cu-Ag deposit (Kucha 1990; Kucha and Przybyłowicz 1999). Analogically to the abovementioned data, the second borehole may indicate having reached a similar position from the boundary between the areas of copper and lead sulphide predominance (Fig. 6).

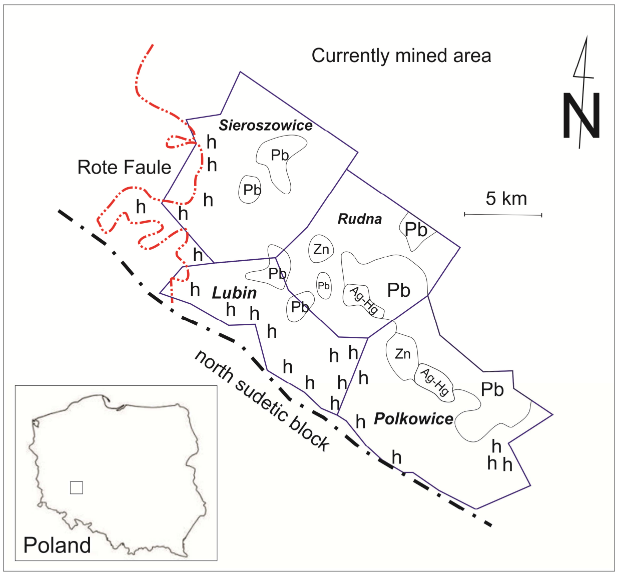

Figure 6. Distribution of zones of elevated galena (Pb), zinc (Zn) and silver amalgam (Ag-Hg) content in relation to the oxidised area (Rote Fäule) and the regions where the oxidised facies penetrates the bottom part of the copper-bearing shale (h). (after Kucha and Przybyłowicz 1999)

The results of determining the chemical composition of silver minerals confirm the presence of: eugenite, kongsbergite, for the first time danielsite, stromeyerite and previously unnamed minerals with similar stoichiometric formulas: Ag_9Hg and Ag_7Hg_2. Silver amalgams with similar chemical composition were recorded during earlier research in the mining area, however their detailed examinations still remain an open issue (Piestrzyński and Tylka 1992). The chemical composition of the silver amalgams is diverse and associated with the zonal distribution of the ore minerals in relation to the oxidised area. The results indicate that closer to the oxidised zone in the horizontal profile the mercury content of silver amalgams increases, while in the vertical profile no pattern in changes in chemical composition has been observed, except for the occasional presence of gold additions along the contact with Rote Fäule.

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