

The first occurrence of cupropearceite in the Kupferschiefer deposit, Lubin mine, SW Poland

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Cupropearceite is a sulphosalt belonging to the pearceite-polybasite group, formed due to Cu-for-Ag substitution. It is a rare mineral of the Earth's crust, described only in four locations so far. This work reports the occurrence of cupropearceite in the upper part of the Weissliegend sandstone from the Cu-Ag deposit in the Fore-Sudetic Monocline. The mineral is associated with stromeyerite, bornite, chalcocite, native silver, silver amalgams and, rarely, pyrite. Formation of cupropearceite is related to fluid activity during low-temperature hydrothermal events responsible for the formation of the Cu-Ag ore mineralization. The identification of cupropearceite is important in terms of constraining minerals bearing associated metals, particularly Ag and As. This work also presents occurrence of this rare mineral in the previously unnoted mineral assemblage mentioned above. The presence of cupropearceite confirms a low-temperature, hydrothermal origin of the Cu-Ag deposit in the Fore-Sudetic Monocline.

Key words: Cu-Ag deposit, cupropearceite, Ag-bearing minerals, pearceite-polybasite group, sulphosalt, Fore-Sudetic Monocline, Lubin mine.

INTRODUCTION

The Cu-Ag deposit of the Fore-Sudetic Monocline comprises over 140 mineral phases documented so far (Piestrzyński, 2007a; Pieczonka, 2011). Ore minerals occurring in the Zechstein sedimentary rocks are mostly copper sulphides: chalcocite, digenite, bornite, chalcopyrite and covellite, with rare pyrite, marcasite, galena, sphalerite, tennantite, tetrahedrite, stromeyerite, native silver and silver amalgams (Nguyen Van Nhan, 1970; Mayer and Piestrzyński, 1985; Piestrzyński and Tylka, 1992; Piestrzyński, 2007a; Pieczonka, 2011). The current study extends the list of minerals in the Cu-Ag deposit from the Fore-Sudetic Monocline to cupropearceite.

Cupropearceite was described as a new mineral by Bindi et al. (2007a). It is a member of the pearceite-polybasite group of minerals (Bindi et al., 2007b). These are Ag-bearing sulphosalts of general formula $[M_6T_2S_7][Ag_9CuS_4]$, where M=Ag, Cu and T = As, Sb (Bindi et al., 2007a, 2013, 2015a). Occasionally, S is replaced by Se and Te (Bindi et al., 2007a, 2015b). Cupropearceite likely forms by the replacement of Ag by Cu

(Bindi et al., 2007a, 2013, 2015a). The pearceite-polybasite group of minerals is relatively common in nature (Harlov and Sack, 1994; Bindi et al., 2007a, b, 2015a), and occurs mostly in epithermal polymetallic deposits (Harlov and Sack, 1994). Despite of that, cupropearceite is a very rare mineral. Until now it was described only in four deposits, i.e. the Sarbay mine, Kostanay Province, North Kazakhstan (Bindi et al., 2007a, 2013; Bindi and Pekov, 2009 *vide* Bindi et al., 2015a), the Tsumeb mine, Namibia (Bindi et al., 2015a), Madersbacher Köpfl, Tyrol, Austria (Kolitsch, 2017), and the Alexandr mine, Vrančice near Příbram, Czech Republic (Sejkora et al., 2010).

Cupropearceite is opaque with a metallic luster and a black streak (Bindi et al., 2007a). The average chemical composition of cupropearceite originally described by Bindi et al. (2007a) is: 60.72 wt.% Ag, 14.03 wt.% Cu, 17.30 wt.% S, 6.31 wt.% As, 1.43 wt.% Sb, 0.03 wt.% Fe. Cu-rich cupropearceite, which has an increased Cu content up to ~25 wt.% and a relatively decreased Ag content >48 wt.%, was documented later in the Tsumeb mine, Namibia (Bindi et al., 2015a), and in the Sarbay mine, Kazakhstan (Bindi and Pekov, 2009 *vide* Bindi et al., 2015a).

GEOLOGICAL SETTING

The Cu-Ag deposit from the Fore-Sudetic Monocline is a world-class deposit of stratabound type (Piestrzyński, 2007b; Pieczonka et al., 2008). The Cu-Ag deposit is located in the SW

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part of the Fore-Sudetic Monocline (Oszczepalski, 1999; Kłapciński and Peryt, 2007; Pieczonka et al., 2008). To the south, the deposit is tectonically bordered by the Fore-Sudetic Block (Fig. 1), whereas the other borders are defined by the last positive drill holes (Pieczonka and Piestrzyński, 2010). The Cu-Ag mineralisation forms an irregular ore body (e.g., quasi-layer, double-layer, vein, nest and impregnating structures) in Permian Rotliegend and Zechstein sedimentary rocks (Kłapciński and Peryt, 2007; Piestrzyński, 2007a; Pieczonka et al., 2008). The economic importance of the ore mineralisation is related to three types of ore: dolomite, black shale and sandstone (Kucha, 1986; Piestrzyński and Salamon, 1986; Oszczepalski, 1999; Piestrzyński, 2007a; Pieczonka et al., 2008; Pieczonka and Piestrzyński, 2010). The deposit is horizontally concordant with the enclosing lowermost Zechstein. Horizontal arrangement of the deposit is disrupted by a disjunctive block tectonic (Piestrzyński and Salamon, 1986; Kłapciński and Peryt, 2007). For detailed description of the geology, ore mineralogy and origin of the Cu-Ag deposit see Mayer and Piestrzyński (1985), Wodzicki and Piestrzyński (1994), Oszczepalski (1999); Kłapciński and Peryt (2007), Piestrzyński (2007a, b), Pieczonka et al. (2008) and Pieczonka (2011).

In the eastern part of the Lubin mine, where cupropearceite was documented, ore mineralisation occurs in the uppermost part of the Weissliegend grey sandstones, with lesser abundance in the Boundary Dolomite, Kupferschiefer black shales and loamy dolomite of the Zechstein Limestone (Fig. 2). The Boundary Dolomite forms a discontinuous layer consisting of grey calcareous dolomite in this part of the Lubin mine (Piestrzyński and Salamon, 1986). The Kupferschiefer forms ~20–30 cm thick black shale layer, which is rich in ore minerali-

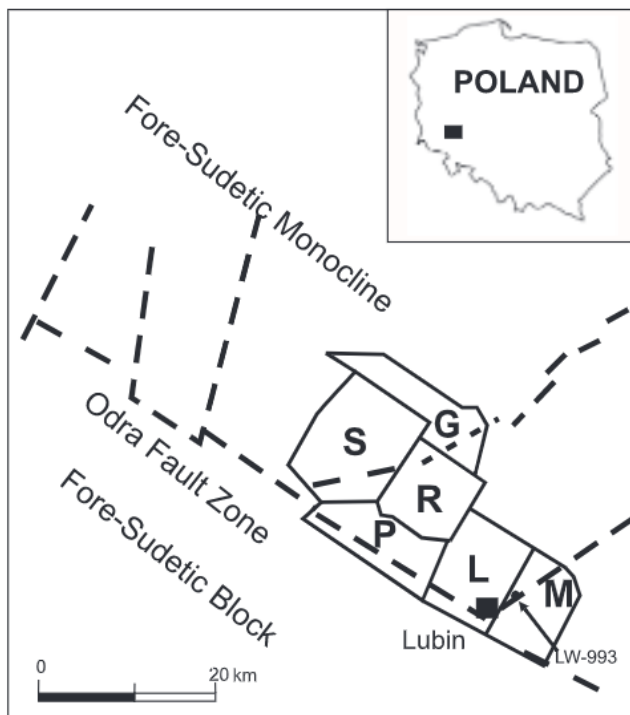


Fig. 1. Simplified map of the mining area of the Lubin-Sierszowice Kupferschiefer-type deposit, and location of the LW-993 section

Mining area: G – Głogów Głęboki Przemysłowy, P – Polkowice, S – Sierszowice, R – Rudna, L – Lubin, M – Małomice (modified from Pieczonka and Piestrzyński, 2011)

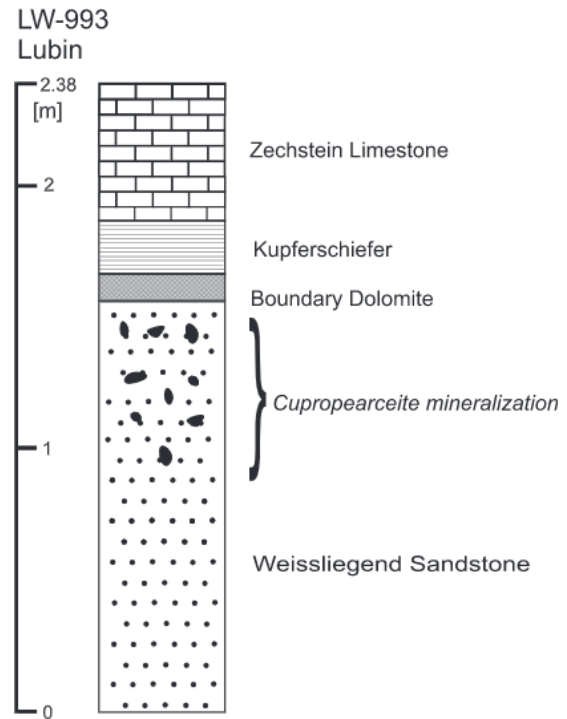


Fig. 2. Lithological sketch of the LW-993 profile

sation (Piestrzyński and Salamon, 1986). In this area, the loamy dolomite is a layer between the black shale and the upper Zechstein Limestone without ore mineralisation (Piestrzyński and Salamon, 1986).

SAMPLE COLLECTION AND ANALYTICAL METHODS

Thirteen samples (9–20 cm thick) were collected from the whole profile of the deposit in the eastern part of the Lubin mine (Figs. 1 and 2). The total profile sampled was 2.38 m long (Fig. 2). Whole-rock chemical analyses were carried out using the ASA method in the ACME Laboratory in Canada. Preliminary mineral identification was performed using an optical polarizing microscope in the reflected light mode. The textural observation and non-standardized chemical analyses of minerals were made using a FEI QUANTA 200 field emission gun scanning electron microscope equipped with an energy dispersive spectrometer (EDS) at the Faculty of Geology, Geophysics and Environmental Protection of the AGH-University of Science and Technology in Kraków, Poland.

The chemical analyses of the Cu and Ag minerals were performed using a JEOL JXA-8530F Hyperprobe field emission electron microprobe in the CEMPEG, Uppsala University, Sweden, and a JEOL Superprobe JXA-8230 electron microprobe in the Laboratory of Critical Elements AGH-KGHM, AGH-University of Science and Technology, Kraków, Poland. The electron probe microanalysis (EPMA) was operated in the wavelength-dispersion mode at an accelerating voltage of 20 kV, a probe current of 20 nA, focused beam with a diameter of 2 μm for bornite and chalcocite, and <1 μm for cupropearceite, native silver and silver amalgams. Counting times of 20 s on peak and 10 s on both (+) and (–) backgrounds were used. For

stromeyerite, mckinstryite and jalpaite, analytical conditions were 20 kV accelerating voltage, 10 nA probe current, and 5 µm beam size. Counting times for stromeyerite, mckinstryite and jalpaite were 10 s on peak and 5 s on both (+) and (–) backgrounds. The following standards and spectral lines were used: GaAs (AsLα), Se (SeLα), ZnS (SKα), Ag (AgLα), HgS (HgMα), Bi (BiMα), Fe or FeS₂ (on JXA-8230) (FeKα), Sb₂S₃ (SbLα), vanadinite or PbS (on JXA-8230) (PbMα), Au (AuLα), Cu (CuKα) and ZnS (ZnKα). Data were corrected to the ZAF procedure using JEOL software for electron microprobe.

RESULTS

Cupropearceite was reported in several samples collected from the upper part of the Weissliegend sandstone in the eastern part of the Lubin area (Figs. 1 and 2), where Ag-bearing minerals are highly abundant in the deposit (Piestrzyński and Salamon, 1986). The bulk Ag content in the studied LW-993 section varies from 30 ppm in the lower part of the sandstone to >100 ppm in dolomite, with >100 ppm values dominating in most of the profile. The bulk Cu content varies from 0.2 to >1 wt.% in the profile. Elevated concentrations of As (>750 ppm) and Hg (>50 ppm) are observed in the upper part of the sandstone. A Pb-bearing zone (>1 wt.% Pb) occurs in the dolomite level within this part of the deposit, which consists of not only Cu-rich minerals but also galena and sphalerite.

The main ore minerals in the upper part of the Weissliegend sandstone include chalcocite, bornite, stromeyerite, Hg-bearing stromeyerite, native silver, silver amalgams, mckinstryite, tennantite, pyrite, jalpaite, chalcopyrite and cupropearceite. These minerals show impregnation structure replacing the carbonate cement of the sandstone. The content of ore minerals is 1.7 vol.% in the sandstone, and most of these are Ag-bearing minerals (Tables 1–3).

Cupropearceite is present as grains up to 100 µm in size, forming intergrowths with bornite, stromeyerite, Hg-bearing stromeyerite, chalcocite, native silver, silver amalgams, mckinstryite, chalcopyrite and pyrite (Figs. 3 and 4). Occasionally, cupropearceite forms inclusions in bornite and chalcocite. In general, the ore minerals form xenomorphic grains and demonstrate partial replacement of Cu sulphides by Ag minerals (Fig. 4D).

Cupropearceite is characterized by grey colour with olive-green tint (Fig. 3), which is similar to the colour of tennantite and tetrahedrite. Tennantite and tetrahedrite are common in the Cu–Ag deposit of the Fore-Sudetic Monocline, making the identification of cupropearceite by optical microscopy difficult. Furthermore, reflectance and relief of cupropearceite are similar to those exhibiting by the minerals of tennantite-tetrahedrite group. Cupropearceite show neither internal reflections nor anisotropy, but has only poorly visible bireflectance.

The average composition of cupropearceite from the Cu–Ag deposit is 51.52 wt.% Ag, 23.69 wt.% Cu, 18.07 wt.% S, 7.34 wt.% As, 0.13 wt.% Fe, 0.04 wt.% Zn, 0.06 wt.% Bi and 0.02 wt.% Pb (Table 1). The average atomic proportions (in *apfu*) calculated for 29 atoms are 1.88 As, 10.79 S, 9.14 Ag, 0.04 Fe, 7.13 Cu, 0.01 Bi and 0.01 Zn (Table 1). Excess of Ag + Cu over 16 (i.e. 16.32 *apfu*) and S < 11 *apfu* (Table 3) can be related to analytical limitation due to small size of the grains and possible contamination from associated minerals.

The composition of the minerals accompanying cupropearceite is variable (Tables 2 and 3), with irregular distribution

of Ag in the intergrowths. For bornite, the Ag content ranges from 0.45–1.6 wt.%, whereas the Hg content is >0.3 wt.% (Table 2). The contents of Cu and Ag in chalcocite vary within a wide range of 72.12–77.44 wt.% and 1.71–7.31 wt.%, respectively. The lower Cu concentration in chalcocite is compensated by higher Ag content (up to 0.11 *apfu* of Cu; Table 2).

The samples contain also stromeyerite and an Hg-rich variety of stromeyerite. The Hg-rich stromeyerite is compositionally similar to balkanite (Cu₉Ag₅HgS₈) (Biagioni and Bindi, 2017; Kozub-Budzyń and Piestrzyński, 2017; Table 2). The stromeyerite, which is intergrown with cupropearceite, forms anhedral grains replacing Cu sulphides. It also forms oleander leaves structure in chalcocite (Fig. 4). The stromeyerite contains little admixture of Hg (<0.35 wt.%) and As (<0.13 wt.%; Table 2). It is commonly intergrown with Hg-bearing stromeyerite, which is brighter in high-contrast BSE images (Fig. 4D). The Hg-bearing stromeyerite contains 11.30–12.54 wt.% Hg, with little admixture of Au (<0.16 wt.%) and Se (<0.07 wt.%; Table 2). Mckinstryite forms intergrowths with stromeyerite. The mckinstryite contains up to 60.9 wt.% Ag, with admixtures of Hg and Au, which do not exceed 0.23 and 0.16 wt.%, respectively (Table 2).

The cupropearceite is commonly associated with native silver and silver amalgams. Native silver forms intergrowths with silver amalgams and contains up to 99.49 wt.% Ag, <3.48 wt.% Hg, <1.07 wt.% Cu and <0.14 wt.% Au (Table 3). The contents of Ag and Hg in silver amalgams are 77.57–94.08 wt.% and 6.79–22.10 wt.%, respectively (Table 3). The silver amalgams contain admixtures of Cu and Au, but they do not exceed 0.40 wt.% Cu and 0.07 wt.% Au (Table 3).

DISCUSSION AND CONCLUSIONS

Cupropearceite is a Cu-rich member of the pearceite-polybasite group of minerals (Bindi et al., 2007a, b, 2013). Ag atoms can be largely replaced by Cu in the structure (Bindi et al., 2007a, 2013, 2015a). Therefore, various Cu-rich minerals, such as cupropearceite and cupropolybasite, can be formed (Bindi et al., 2007a, b, 2013, 2015a). Until now, cupropearceite was documented only at the Sarbay mine (Bindi et al., 2007a, 2013; Bindi and Pekov, 2009 *vide* Bindi et al., 2015a), Pb–Zn–Cu Tsumeb deposit (Bindi et al., 2015a), Alexandr mine (Sejkora et al., 2010) and Madersbacher Köpfl (Kolitsch, 2017). Cupropearceite from the Sarbay mine is associated with tetrahedrite and forms anhedral and subhedral grains up to 300 µm in size (Bindi et al., 2007a). Pyrite, quartz and calcite are spatially related to cupropearceite in the Sarbay deposit (Bindi et al., 2007a). Chemical composition of cupropearceite from the Sarbay mine differs from that found in the Lubin mine: the Ag content is higher (~60 wt.% vs. 51.52 wt.%, respectively) and the Cu content is lower (~14 vs. 23 wt.%, respectively) (cf. Bindi et al., 2007a). An average formula calculated on the basis of 29 atoms is [(Cu_{3.51}Ag_{2.50}Fe_{0.01})Σ_{6.02}(As_{1.72}Sb_{0.24})Σ_{1.96}S₇][Ag₉CuS₄] (Bindi et al., 2007a). Cu-rich cupropearceite was also documented in the Sarbay deposit (Bindi and Pekov, 2009 *vide* Bindi et al., 2015a). In the polymetallic Vrančice deposit, both cupropearceite and Cu-rich cupropearceite were reported. They occur in a calcite vein with chalcocite, bornite, chalcopyrite and stromeyerite, and form an intergrowth of hexagonal crystals with cupropolybasite (Sejkora et al., 2010). In Vrančice, the formation of Ag mineralisation in the dominant part of Ag–Cu mineralisation is related to

Table 1

Representative results of the EPMA measurements of cupropearceite (in wt.% of elements) and atomic ratios

Analysis	As	S	Pb	Ag	Fe	Cu	Zn	Bi	Total
1	7.27	17.36	0.11	52.49	b.d.l.	23.61	b.d.l.	0.18	101.02
	<i>1.88</i>	<i>10.48</i>	<i>0.01</i>	<i>9.42</i>	<i>0.00</i>	<i>7.20</i>	<i>0.00</i>	<i>0.02</i>	
2	7.00	17.45	0.15	53.63	b.d.l.	21.76	b.d.l.	b.d.l.	100.00
	<i>1.83</i>	<i>10.68</i>	<i>0.01</i>	<i>9.75</i>	<i>0.00</i>	<i>6.72</i>	<i>0.00</i>	<i>0.00</i>	
3	7.21	18.13	b.d.l.	52.91	b.d.l.	23.53	b.d.l.	b.d.l.	101.79
	<i>1.83</i>	<i>10.77</i>	<i>0.00</i>	<i>9.34</i>	<i>0.00</i>	<i>7.05</i>	<i>0.00</i>	<i>0.00</i>	
4	7.18	17.84	b.d.l.	53.57	b.d.l.	22.98	b.d.l.	b.d.l.	101.57
	<i>1.84</i>	<i>10.68</i>	<i>0.00</i>	<i>9.53</i>	<i>0.00</i>	<i>6.95</i>	<i>0.00</i>	<i>0.00</i>	
5	6.79	18.54	b.d.l.	53.70	b.d.l.	22.27	b.d.l.	b.d.l.	101.29
	<i>1.73</i>	<i>11.05</i>	<i>0.00</i>	<i>9.51</i>	<i>0.00</i>	<i>6.70</i>	<i>0.00</i>	<i>0.00</i>	
6	7.22	18.63	b.d.l.	53.17	b.d.l.	22.35	b.d.l.	0.11	101.48
	<i>1.84</i>	<i>11.07</i>	<i>0.00</i>	<i>9.38</i>	<i>0.00</i>	<i>6.70</i>	<i>0.00</i>	<i>0.01</i>	
7	7.38	17.78	b.d.l.	51.18	0.19	24.86	b.d.l.	b.d.l.	101.38
	<i>1.88</i>	<i>10.57</i>	<i>0.00</i>	<i>9.03</i>	<i>0.07</i>	<i>7.46</i>	<i>0.00</i>	<i>0.00</i>	
8	7.35	18.46	b.d.l.	49.22	b.d.l.	26.72	b.d.l.	b.d.l.	101.75
	<i>1.84</i>	<i>10.77</i>	<i>0.00</i>	<i>8.53</i>	<i>0.00</i>	<i>7.87</i>	<i>0.00</i>	<i>0.00</i>	
9	6.95	17.98	b.d.l.	52.05	0.19	23.89	b.d.l.	0.15	101.22
	<i>1.78</i>	<i>10.73</i>	<i>0.00</i>	<i>9.22</i>	<i>0.07</i>	<i>7.19</i>	<i>0.00</i>	<i>0.01</i>	
10	7.49	19.54	b.d.l.	43.60	0.62	28.43	0.89	b.d.l.	100.58
	<i>1.83</i>	<i>11.15</i>	<i>0.00</i>	<i>7.39</i>	<i>0.20</i>	<i>8.18</i>	<i>0.25</i>	<i>0.00</i>	
11	7.48	17.45	b.d.l.	50.38	0.09	23.59	b.d.l.	0.10	99.08
	<i>1.95</i>	<i>10.63</i>	<i>0.00</i>	<i>9.12</i>	<i>0.03</i>	<i>7.25</i>	<i>0.00</i>	<i>0.01</i>	
12	7.47	18.08	b.d.l.	51.38	0.31	23.70	b.d.l.	b.d.l.	100.94
	<i>1.91</i>	<i>10.77</i>	<i>0.00</i>	<i>9.09</i>	<i>0.11</i>	<i>7.13</i>	<i>0.00</i>	<i>0.00</i>	
13	7.14	17.63	b.d.l.	51.99	0.12	22.41	b.d.l.	b.d.l.	99.27
	<i>1.87</i>	<i>10.76</i>	<i>0.00</i>	<i>9.43</i>	<i>0.04</i>	<i>6.90</i>	<i>0.00</i>	<i>0.00</i>	
14	7.30	18.63	b.d.l.	51.42	0.09	23.66	b.d.l.	0.20	101.30
	<i>1.85</i>	<i>11.01</i>	<i>0.00</i>	<i>9.03</i>	<i>0.03</i>	<i>7.06</i>	<i>0.00</i>	<i>0.02</i>	
15	7.30	17.88	b.d.l.	52.61	0.23	21.62	b.d.l.	b.d.l.	99.63
	<i>1.90</i>	<i>10.88</i>	<i>0.00</i>	<i>9.51</i>	<i>0.08</i>	<i>6.64</i>	<i>0.00</i>	<i>0.00</i>	
16	7.62	18.17	0.10	51.06	0.19	23.75	b.d.l.	0.17	101.07
	<i>1.94</i>	<i>10.82</i>	<i>0.00</i>	<i>9.03</i>	<i>0.07</i>	<i>7.13</i>	<i>0.00</i>	<i>0.02</i>	
17	7.56	18.20	b.d.l.	51.07	0.11	23.45	b.d.l.	b.d.l.	100.39
	<i>1.94</i>	<i>10.88</i>	<i>0.00</i>	<i>9.07</i>	<i>0.04</i>	<i>7.08</i>	<i>0.00</i>	<i>0.00</i>	
18	7.60	18.08	b.d.l.	51.80	0.16	23.41	0.09	b.d.l.	101.13
	<i>1.94</i>	<i>10.77</i>	<i>0.00</i>	<i>9.17</i>	<i>0.05</i>	<i>7.04</i>	<i>0.03</i>	<i>0.00</i>	
19	7.36	18.18	0.10	52.07	0.33	23.31	b.d.l.	0.10	101.44
	<i>1.87</i>	<i>10.81</i>	<i>0.00</i>	<i>9.20</i>	<i>0.11</i>	<i>7.00</i>	<i>0.00</i>	<i>0.01</i>	
20	7.44	18.18	b.d.l.	51.69	b.d.l.	23.52	b.d.l.	b.d.l.	100.83
	<i>1.90</i>	<i>10.85</i>	<i>0.00</i>	<i>9.16</i>	<i>0.00</i>	<i>7.08</i>	<i>0.00</i>	<i>0.00</i>	
21	7.53	17.51	b.d.l.	51.69	b.d.l.	23.73	b.d.l.	0.13	100.58
	<i>1.94</i>	<i>10.56</i>	<i>0.00</i>	<i>9.26</i>	<i>0.00</i>	<i>7.22</i>	<i>0.00</i>	<i>0.01</i>	
22	7.52	17.53	b.d.l.	51.22	0.07	24.52	b.d.l.	0.12	100.97
	<i>1.93</i>	<i>10.50</i>	<i>0.00</i>	<i>9.12</i>	<i>0.02</i>	<i>7.42</i>	<i>0.00</i>	<i>0.01</i>	
23	7.66	18.38	b.d.l.	51.83	0.30	23.43	b.d.l.	b.d.l.	101.60
	<i>1.94</i>	<i>10.87</i>	<i>0.00</i>	<i>9.10</i>	<i>0.10</i>	<i>6.99</i>	<i>0.00</i>	<i>0.00</i>	
24	7.46	18.00	b.d.l.	50.75	0.09	24.05	b.d.l.	0.10	100.45
	<i>1.91</i>	<i>10.77</i>	<i>0.00</i>	<i>9.02</i>	<i>0.03</i>	<i>7.26</i>	<i>0.00</i>	<i>0.01</i>	
Average	7.34	18.07	0.02	51.52	0.13	23.69	0.04	0.06	100.87
	<i>1.88</i>	<i>10.79</i>	<i>0.00</i>	<i>9.14</i>	<i>0.04</i>	<i>7.13</i>	<i>0.01</i>	<i>0.01</i>	

b.d.l. – below detection limits; atoms per formula unit (*apfu*) are given in italic. The number of ions for cupropearceite is calculated on the basis of (As + Sb + Ag + Fe + Cu + Zn + Pb + Bi + S) = 29 *apfu*. Analyses of Hg, Se and Sb are not presented in the table because the results are below detection limit of the EPMA

Table 2

Representative results of the EPMA measurements of stromeyerite, Hg-stromeyerite, mckinstryite, chalcocite and bornite (in wt.% of elements) and atomic ratios

Stromeyerite	Cu	S	Fe	Ag	Au	Hg	As	Se	Total
1	31.55	15.47	0.01	52.47	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.50
	<i>1.02</i>	<i>0.99</i>	<i>0.00</i>	<i>1.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
2	32.40	15.80	0.02	51.76	b.d.l.	0.35	b.d.l.	b.d.l.	100.33
	<i>1.03</i>	<i>1.00</i>	<i>0.00</i>	<i>0.97</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
3	31.92	15.86	0.03	52.39	b.d.l.	b.d.l.	0.13	b.d.l.	100.33
	<i>1.01</i>	<i>1.00</i>	<i>0.00</i>	<i>0.98</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
Hg-stromeyerite	Cu	S	Fe	Ag	Au	Hg	As	Se	Total
1	36.11	16.90	0.04	35.20	b.d.l.	12.54	b.d.l.	b.d.l.	100.78
	<i>8.80</i>	<i>8.16</i>	<i>0.01</i>	<i>5.06</i>	<i>0.00</i>	<i>0.97</i>	<i>0.00</i>	<i>0.00</i>	
2	33.86	17.48	0.03	35.62	b.d.l.	11.30	b.d.l.	b.d.l.	98.29
	<i>8.36</i>	<i>8.56</i>	<i>0.01</i>	<i>5.18</i>	<i>0.00</i>	<i>0.88</i>	<i>0.00</i>	<i>0.00</i>	
3	34.75	17.50	0.08	34.71	0.16	11.73	b.d.l.	0.07	99.00
	<i>8.52</i>	<i>8.50</i>	<i>0.02</i>	<i>5.01</i>	<i>0.01</i>	<i>0.91</i>	<i>0.00</i>	<i>0.01</i>	
Mckinstryite	Cu	S	Fe	Ag	Au	Hg	As	Se	Total
1	24.76	15.70	0.11	60.95	0.08	0.02	0.07	b.d.l.	101.67
	<i>0.81</i>	<i>1.01</i>	<i>0.00</i>	<i>1.17</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
2	23.19	15.81	b.d.l.	59.33	0.07	0.09	b.d.l.	b.d.l.	98.48
	<i>0.78</i>	<i>1.05</i>	<i>0.00</i>	<i>1.17</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
3	23.25	15.38	b.d.l.	60.21	0.16	0.23	b.d.l.	b.d.l.	99.23
	<i>0.78</i>	<i>1.02</i>	<i>0.00</i>	<i>1.19</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
Chalcocite	Cu	S	Fe	Ag	Au	Hg	As	Se	Total
1	77.44	19.49	0.01	2.45	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.39
	<i>1.98</i>	<i>0.99</i>	<i>0.00</i>	<i>0.04</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
2	72.12	19.13	0.13	7.31	b.d.l.	b.d.l.	b.d.l.	b.d.l.	98.68
	<i>1.89</i>	<i>0.99</i>	<i>0.00</i>	<i>0.11</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
3	76.98	19.83	0.40	1.71	b.d.l.	b.d.l.	b.d.l.	0.02	98.94
	<i>1.96</i>	<i>1.00</i>	<i>0.01</i>	<i>0.03</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
Bornite	Cu	S	Fe	Ag	Au	Hg	As	Se	Total
1	60.98	25.36	10.04	1.60	b.d.l.	0.03	b.d.l.	b.d.l.	98.02
	<i>4.93</i>	<i>4.07</i>	<i>0.92</i>	<i>0.08</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
2	62.27	25.87	11.15	0.45	0.04	0.03	b.d.l.	b.d.l.	99.81
	<i>4.92</i>	<i>4.05</i>	<i>1.00</i>	<i>0.02</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	
3	62.50	25.57	10.61	0.55	b.d.l.	b.d.l.	b.d.l.	b.d.l.	99.23
	<i>4.98</i>	<i>4.04</i>	<i>0.96</i>	<i>0.03</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	<i>0.00</i>	

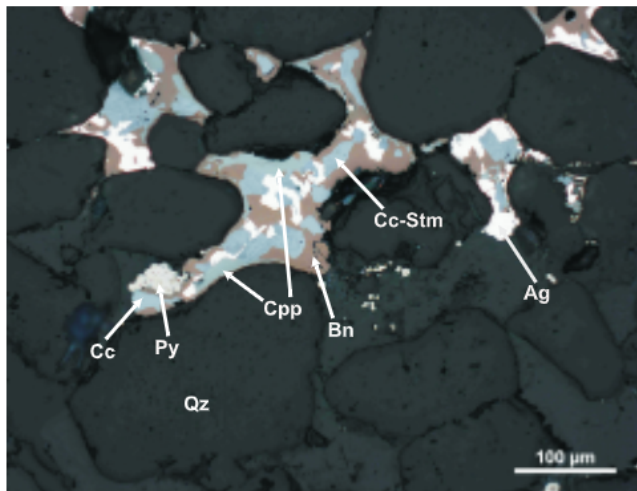
b.d.l. – below detection limits; atoms per formula unit (*apfu*) are given in italic. The number of ions for Cu-Ag sulphides is calculated on the basis of (As + Ag + Fe + Cu + Hg + Au + S + Se) = 3 *apfu* (for stromeyerite, mckinstryite and chalcocite); 23 *apfu* (for Hg-rich stromeyerite), 10 *apfu* (for bornite). Analyses of Sb are not presented in the table because the results are below detection limit of the EPMA

Table 3

Representative results of the EPMA measurements of native silver and silver amalgams (in wt.%)

Native silver	Hg	Au	Ag	Cu	Fe	Bi	Total
1	0.78	b.d.l.	99.49	0.28	0.02	b.d.l.	100.56
2	3.48	0.08	96.16	1.07	0.02	b.d.l.	100.80
3	2.13	0.14	98.15	0.72	b.d.l.	b.d.l.	101.13
Silver amalgams	Hg	Au	Ag	Cu	Fe	Bi	Total
1	22.10	0.07	77.57	0.40	b.d.l.	b.d.l.	100.14
2	14.19	b.d.l.	85.52	0.33	0.01	b.d.l.	100.04
3	6.79	b.d.l.	94.08	0.01	0.01	b.d.l.	100.89

b.d.l. – below detection limits; analyses of Sb and As are not presented in the table because the results are below detection limit of the EPMA



←
 Fig. 3. Intergrowth of cupropearceite (Cpp), bornite (Bn), stromeyerite (Stm), chalcocite (Cc), native silver (Ag) and pyrite (Py) replacing carbonate cement of sandstone; stromeyerite and chalcocite form oleander leaves structure (Cc-Stm); upper part of Weissliegend sandstone, Lubin mine; reflected light; Qz – quartz

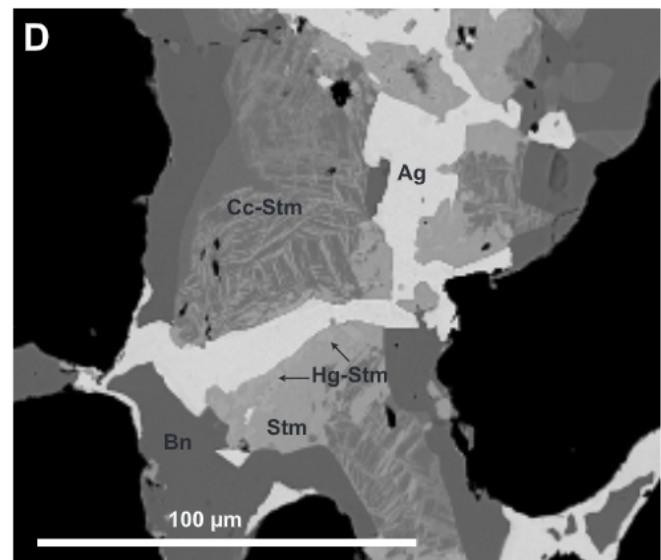
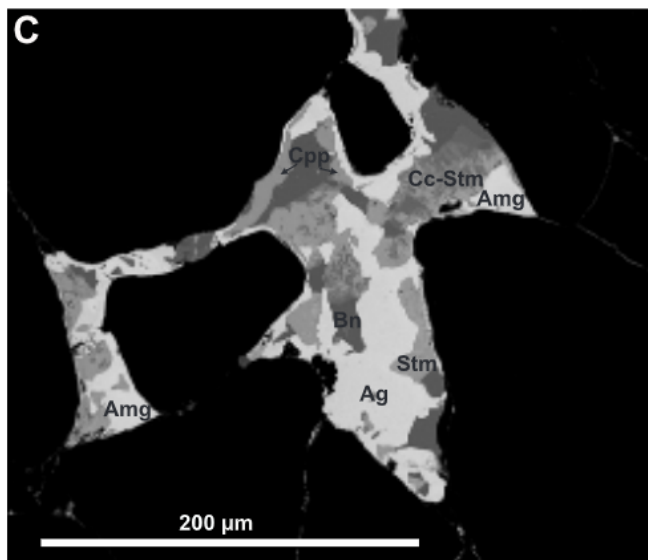
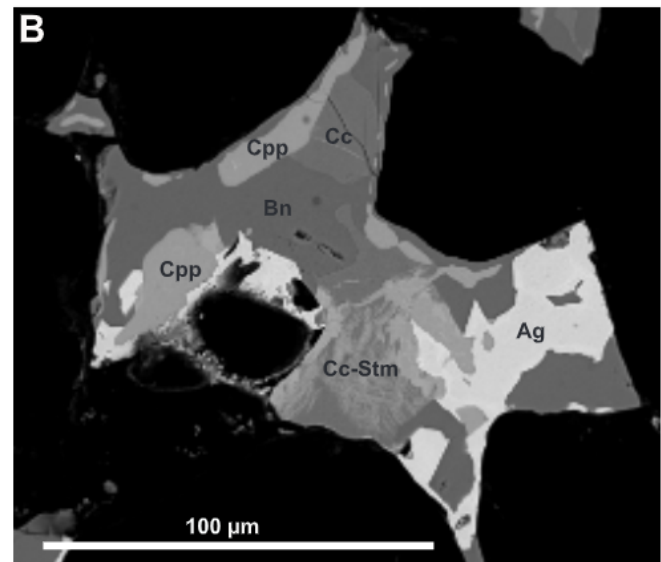
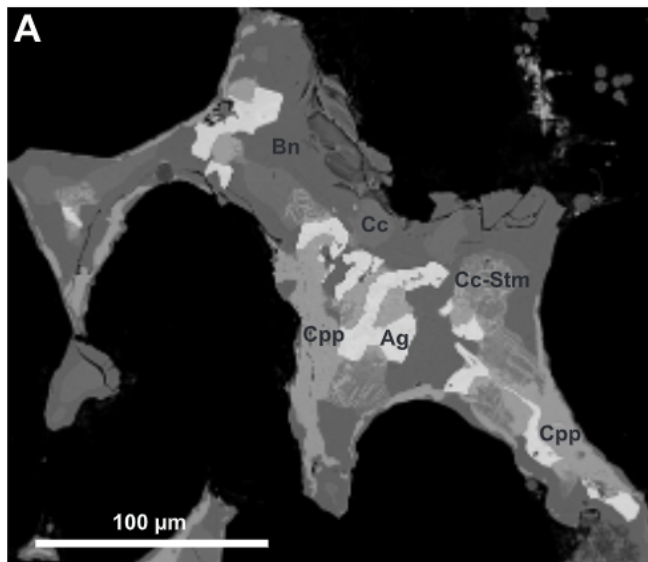


Fig. 4A–C – intergrowths of cupropearceite (Cpp), bornite (Bn), native silver (Ag), stromeyerite (Stm), chalcocite (Cc) and silver amalgams (Amg); stromeyerite and chalcocite form oleander leaves structure (Cc-Stm); D – intergrowth of Hg-bearing stromeyerite (Hg-Stm) with anhedral grains of stromeyerite (Stm) and native silver (Ag); stromeyerite and chalcocite form oleander leaves structure (Cc-Stm); upper part of Weissliegend sandstone, Lubin mine; BSE images

low-temperature processes (Sejkora et al., 2010). In Madersbacher Köpfl, cupropearceite forms grains 2–75 µm in size and occurs as fillings of cracks in tennantite and enargite or in dolomite (Kolitsch, 2017).

Cupropearceite from the Cu-Ag deposit in the Fore-Sudetic Monocline exhibits a composition similar to cupropearceite from Tsumeb. At the Tsumeb mine, cupropearceite occurs with enargite as inclusions in Zn-rich tennantite (Bindi et al., 2015a). The Tsumeb deposit contains rich and varying Cu-Zn-Pb-Ge multi-stage ore mineralisation that formed due to activity of hydrothermal fluids (Haynes, 1984; Kamona and Günzel, 2007). The fluid inclusions studies of quartz (closely related to deposition of chalcocite, bornite, tennantite and enargite) indicated that the homogenization temperature of quartz was 170–240°C, implying temperature conditions of ore mineralisation at ~250°C (Haynes, 1984). In contrast, a study of fluid inclusions by Kamona and Günzel (2007) suggests that homogenization temperature of quartz was lower, ranging from 115 to 173°C.

The temperature conditions of formation of the Cu-bearing zone in the Cu-Ag deposit in the Fore-Sudetic Monocline were estimated on the basis of vitrinite reflectance, and varies from 65 to 110°C (Kotarba et al., 2007; Speczik et al., 2007). On the other hand, the temperature conditions of formation of oxidative alteration by oxidizing fluids were up to 135°C (Oszczepalski, 1999; Oszczepalski et al., 2002; Kotarba et al., 2007; Speczik et al., 2007). The estimated maximum palaeotemperatures probably reflect the temperatures of hydrothermal fluids that induced both secondary oxidation and the Cu mineralisation (Kosakowski et al., 2007; Kotarba et al., 2007; Speczik et al., 2007). Furthermore, based on the assumption that monoclinic chalcocite is the main ore mineral in the deposit, Piestrzyński (2007b) suggested that Cu-bearing mineralisation formed at a temperature <103.5°C.

The laboratory experiments carried out by Harlov and Sack (1994) demonstrated that for constituents of pearceite-polybasite solid solutions, up to 29 wt.% Cu can be accommodated in pearceite forming, thus Cu-rich cupropearceite. The substitution of Cu may occur even at temperature conditions as low as 75°C and the maximum temperatures of Cu substitution (up to 24 wt.% Cu) do not exceed 150°C (Harlov and Sack, 1994).

The metasomatic replacement of chalcocite and bornite by native silver, silver amalgams and stromeyerite (Fig. 3) most likely indicates that the Ag-bearing mineralisation associated with cupropearceite postdated the main process of formation of Cu-bearing mineralization. Comparison of experimental data presented by Harlov and Sack (1994) with structural data from the Cu-Ag Lubin deposit strongly suggests that cupropearceite from the LW-993 section was formed simultaneously with the Cu-bearing mineralisation or during a later stage of crystallization of the Ag-bearing mineralization.

Despite the low abundance of cupropearceite in the Cu-Ag deposit in the Fore-Sudetic Monocline, its presence provides crucial insights to determine carriers of associated metals, particularly Ag and As. Discovery of cupropearceite in the Cu-Ag deposit of the Fore-Sudetic Monocline adds another occurrence of this rare mineral, which is furthermore present in a different paragenesis compared to what previously reported. The presence of cupropearceite also confirms low-temperature, hydrothermal origin of the Cu-Ag deposit.

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