

Mineralogy and geochemistry of the Kupferschiefer in the Nowa Sól, Mozów and Sulmierzyce North Cu-Ag deposits, Northern Copper Belt, SW Poland

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We describe the mineralogy and geochemistry of three deep (>1500 m BGL) Kupferschiefer-type deposits of the Fore-Sudetic Monocline: Nowa Sól, Mozów and Sulmierzyce North, which have been recently documented by the Canadian Miedzi Copper Corporation. Together with other known prospective areas, they form an extensive E-W-trending belt, referred to as the Northern Copper Belt. Samples from the 22 boreholes were examined, focusing on the Kupferschiefer-ore sensu stricto, since in each deposit the richest Cu-Ag mineralization occurs in shales. The ore minerals identified include chalcocite, digenite, djurleite, covellite, bornite, chalcopyrite, minerals from the tennantite-tetrahedrite group, native silver, silver amalgams, stromeyerite, minerals from the cobaltite-gersdorffite series, galena, sphalerite, pyrite and native bismuth. In the Nowa Sól and Mozów deposits, Cu-S-type minerals dominate the Cu-mineralization, while in the Sulmierzyce North deposit, apart from the Cu-S-type minerals, the ore mineral assemblage comprises also chalcopyrite and the tennantite-tetrahedrite group minerals. In the Nowa Sól deposit, Ag-bearing and Ag-barren chalcocite have been distinguished. Chalcocite from two other deposits is Ag-barren. Two types of Ag-amalgam have been identified: Hg-rich and Hg-poor. Other Ag minerals (stromeyerite and native Ag) also contain Hg admixtures. The chemical composition of bornite (which is the second most common ore mineral in each deposit) shows no significant variation. Only in the Nowa Sól deposit were minor amounts of Ag-bearing bornite identified. Co-Ni minerals from the Nowa Sól deposit are represented by middle members of the cobaltite-gersdorffite series. The newly documented deposits of the Northern Copper Belt belong to the same Kupferschiefer-type as well-known deposits of the Lubin-Sieroszowice area. However, some differences in distribution of ore mineralization and its chemical composition have been noted between these two areas. The results obtained support the generally accepted view, that the development of the Cu-Ag deposits of the Fore-Sudetic Monocline was a long-lasting, multiphase process.

Key words: Fore-Sudetic Monocline, Northern Copper Belt, Kupferschiefer, sediment-hosted stratiform copper deposits, mineralogy, geochemistry.

INTRODUCTION

The Northern Copper Belt (NCB) consists of three deep Cu-Ag deposits, documented recently in SW Poland: Nowa Sól, Mozów and Sulmierzyce North (Fig. 1). Apart from that, the NCB includes several areas prospective for Cu-Ag resources, as well as numerous smaller occurrences of high-grade Cu-Ag mineralization requiring further characterization (Oszczepalski et al., 2019; Zieliński et al., 2022).

We focus on thorough analyses of the mineralization in the shale ore of the Nowa Sól, Mozów and Sulmierzyce North deposits, detailing the mineralogical and geochemical characteristics of each deposit, determining the main differences between them, and comparing them with the better-known Cu-Ag deposits of the Lubin-Sieroszowice area (SW Poland).

The deposits of the NCB have been documented by the Canadian Miedzi Copper Corporation (MCC) in co-operation with the Polish Geological Institute - National Research Institute and the Faculty of Geology of the University of Warsaw. Details of the exploration program conducted by the MCC are described in Speczik et al. (2021). For each deposit, geological documentation was prepared and resources of Cu and Ag were calculated, together with the resources of several accompanying elements, such as Pb, Zn, Co, Ni, Mo and V. These documentations were approved by the Polish geological administration, confirming the feasibility of future development of the documented resources. Furthermore, technical reports and pre-feasibility studies were prepared, showing that mining operations in each of these deposits are economically justified. More information on the resources can be found in Speczik et al. (2022).

The deposits documented belong within sediment-hosted stratiform copper deposits (SSC), also referred to as *Kupferschiefer*-type. In Europe, deposits of this type are associated with the German and Polish parts of the Zechstein Basin. In Poland, *Kupferschiefer*-type deposits are related to the North-Sudetic

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Trough (the so-called Old Copper District) and the Fore-Sudetic Monocline (FSM). Deposits occurring in the southernmost part of the FSM, in the Lubin-Sieroszowice area (New Copper District; Fig. 1), are currently mined at depths between 700 and 1250 m BGL. Recently documented deposits occur in distal NW–NE parts of the FSM, at depths ranging between 1600 and 2500 m BGL. Together with other known occurrences of Cu-Ag mineralization, they form an extensive prospective area.

In recent years, detailed studies of ore mineralization in the deposits in question have been carried out. Oszczepalski et al. (2019) described the distribution of prospective areas with hypothetical and speculative Cu-Ag resources in SW Poland, as

well as preliminary descriptions of the Nowa Sól, Mozów and Sulmierzyce North deposits, including the results of petrographic studies of ores from these deposits. Bieńko and Pietrzela (2022) characterized the Nowa Sól deposit (which is the most accurately documented of the NCB deposits) and discussed the metal zonation in this deposit. Subsequently, Pietrzela and Bieńko (2023) described distribution patterns of the main and accompanying metals in the Nowa Sól, Mozów and Sulmierzyce North deposits and outlined the differences between them. The metal distribution in the NCB deposits have also been compared with other European *Kupferschiefer*-type deposits. Both studies included also petrographic data, to-



Fig. 2. Geology of the Kupferschiefer-type deposits of the FSM

A – stratigraphic position of the Zechstein Cu-bearing series and distribution of geochemical zones (modified after Oszczepalski et al., 2019); B – schematic cross-section of the Cu-Ag deposit with the position of epigenetic oxidized facies (*Rote Fäule*)

gether with photomicrographs. This article details microscopic observations and chemical microanalyses of the ore mineralization in the shale ore of the three NCB deposits. In the Kupferschiefer-type deposits of the FSM, ore mineralization may occur in three lithological units (carbonates, shales and sandstones). The Kupferschiefer-ore sensu stricto most commonly hosts mineralization of the highest grade, and is also the most representative as regards the mineralogy and geochemistry of the Cu-Ag mineralization. Carbonate ore from the Nowa Sól, Mozów and Sulmierzyce North deposits contains only minor proportion of the Cu-Ag mineralization (co-occurring with Pb-Zn mineralization), while sandstone ore does not occur in the Mozów and Sulmierzyce North deposits. Newly obtained data include many photomicrographs of the shale ore from each deposit, detailed descriptions of the sulphide mineralization and chemical compositions of the ore minerals identified, together with their empirical formulae. Comparison of the results from the three deposits investigated with the deposits of the Lubin-Sieroszowice area are also made.

GEOLOGICAL SETTING

The pre-Permian basement in the area of the FSM consists of Early Paleozoic metamorphic rocks and Carboniferous clastic rocks and granites, which were folded and consolidated during the Late Carboniferous Variscan orogeny (Kiersnowski and Petecki, 2017). The post-Variscan cover, comprising Permo-Mesozoic and Cenozoic strata, dips gently to the NE and unconformably overlies Paleozoic basement (Kłapciński, 1971; Fig. 2A).

The *Kupferschiefer*-type deposits of the FSM are associated with the contact zone between Permian continental red beds (*Rotliegend*) and upper Permian Zechstein marine rocks (Fig. 2A). Occurrences of ore mineralization are confined to the uppermost part of *Rotliegend* terrestrial sandstones and Zechstein marine sandstones, collectively referred to as *Weissliegend* and the shale-carbonate succession of the PZ1 cycle, comprising the *Kupferschiefer* and the Zechstein Limestone.

Lithostratigraphic descriptions of the Cu-bearing series can be found in many papers (e.g., Rydzewski, 1964; Kłapciński, 1971; Wyżykowski, 1971; Peryt, 1978, 1989; Nemec and Porębski, 1981; Tomaszewski, 1981; Oszczepalski and Rydzewski, 1987; Oszczepalski, 1989; Peryt and Oszczepalski, 2007; Poszytek and Suchan, 2016; Oszczepalski et al., 2019). The *Weissliegend* is composed of fine-grained, quartz sandstones. Their lower part represents aeolian-fluvial or dune sandstones, while the upper part consists of shallow marine sandstones. The *Kupferschiefer* is a typical black shale, deposited under reducing conditions of a stratified epicontinental sea. It can be represented also by laminated black mudstones, marls and carbonates, depending on the proportions between the main components, which are clay minerals (mainly illite with minor montmorillonite and kaolinite), carbonates (dolomite commonly prevails over calcite) and organic matter. The lithological profile of the Zechstein Limestone shows a regressive pattern. Its lower part is represented mainly by mudstones, while in the upper part wackestones, packstones and boundstones occur.

Occurrences of Cu-Ag mineralization in the Permian deposits, locally forming rich stratiform orebodies, are intimately related to the secondary, oxidative, Fe³⁺-bearing, red-coloured facies, referred to as *Rote Fäule* (Rydzewski, 1964, 1978; Oszczepalski, 1989, 1994, 1999; Püttmann et al., 1989; Speczik, 1995; Pieczonka, 2000; Bechtel et al., 2002; Oszczepalski et al., 2002). Widespread areas of extensive oxidation occur predominantly in the vicinity of palaeo-elevations (such as Fore-Sudetic Block and Wolsztyn elevation; Fig. 1). High-grade Cu-Ag mineralization is restricted to the areas proximal to the *Rote Fäule*. Orebodies occur at the closest vicinity of the redox boundary, on its reduced side.

The mineralization system is transgressive and usually steeply crosscuts stratification (Rydzewski, 1964; Oszczepalski, 1989, 1999; Speczik, 1995; Borg et al., 2012; Oszczepalski et al., 2019). The location of ore mineralization with respect to the distribution of oxidized and reduced facies within the lower Zechstein strata is shown in Figure 2B. Moving outwards from the central parts of the *Rote Fäule* areas, the redox boundary progressively cuts lower lithological units. Consequently, the sulphide mineralization also moves downwards in the lithological profile, from the Zechstein Limestone, through the *Kupferschiefer*, down to the *Weissliegend*

Apart from Fe-oxides (hematite), the oxidized rocks contain relicts of sulphide grains and pseudomorphs after pyrite framboids occurring originally in the lower Zechstein strata (Rydzewski, 1969; Oszczepalski, 1999). They commonly exhibit Au, Pt and Pd enrichment (Piestrzyński et al., 1996, 2002; Speczik et al., 1997; Piestrzyński and Pieczonka, 1997; Oszczepalski and Rydzewski, 1998; Pieczonka et al., 2008). A transition zone is distinguished at the contact between the oxidized and reduced facies (Oszczepalski, 1994, 1999).

The *Kupferschiefer*-type deposits of the FSM are characterized by a large-scale metal zonation pattern, both in the lateral and vertical distribution of metals (Rydzewski, 1976, 1978; Kucha, 1990; Speczik, 1995; Oszczepalski, 1999; Pieczonka et al., 2007; Pieczonka, 2011). It grades from an Fe³⁺ hematitic *Rote Fäule* zone, through a noble metal (Au, Pt, Pd) enrichment in the transition zone, a redox-proximal Cu zone with Ag enrichments, a widely overlapping Pb-Zn zone (with Pb being more proximal and Zn more distal), into a Fe²⁺ zone containing syndiagenetic pyrite.

Despite the ongoing debate on the genesis of the *Kupferschiefer* mineralization, it is generally agreed that its formation was a result of large-scale fluid migration (Rydzewski, 1976; Speczik et al., 1986; Jowett et al., 1987; Oszczepalski, 1989, 1999; Cathles et al., 1993; Wodzicki and Piestrzyński, 1994; Speczik, 1995; Bechtel et al., 2002; Borg et al., 2012). The main mineralizing event has been considered either early-to-late diagenetic (Rydzewski, 1976; Oszczepalski, 1989, 1999; Oszczepalski and Rydzewski, 1991; Wodzicki and Piestrzyński, 1994; Speczik et al., 1986) or late diagenetic-epigenetic (Jowett, 1986; Kucha and Pawlikowski, 1986; Blundell et al., 2003; Borg et al., 2012). The latter model was based mostly on various dating methods, indicating a Triassic age of mineralization (Jowett et al., 1987; Bechtel et al., 1999; Mikulski and Stein, 2017).

It is commonly agreed that there were several sources of metals in the mineralizing fluids responsible for the formation of European Kupferschiefer-type deposits, the main one being the Rotliegend strata, filling a fault-controlled basin that formed at the beginning of the Permian within the Variscan orogenic belt (Speczik et al., 1986; Kucha and Pawlikowski, 1986; Jowett, 1986; Jowett et al., 1987; Oszczepalski, 1989; Wodzicki and Piestrzyński, 1994; Blundell et al., 2003; Borg et al., 2012). The metals leached from the Rotliegend volcanic rocks were carried in solution as chloride complexes, through the redbeds, up the flanks of buried basement highs, to the reduced pyritic Kupferschiefer. Convective fluid circulation may have been generated by high post-Variscan heat flow and thermal events connected with intracontinental Permian rifting (Speczik et al., 1986; Oszczepalski, 1999) and/or by burial of the Permian strata and extensional rifting during the Triassic (Jowett et al., 1987; Blundell et al., 2003).

Generally, it seems plausible that the origin of the *Kupferschiefer* mineralization was a multiphase and long-lasting process, which continued for tens of millions of years after deposition of the *Kupferschiefer* shales (Cathles et al., 1993; Wodzicki and Piestrzyński, 1994; Speczik, 1995; Alderton et al., 2012).

MATERIALS AND METHODS

Borehole core samples obtained by the MCC were examined. During the exploration program, petrographic and mineralogical samples were collected from each core and thin sections were prepared (Speczik et al., 2021). In this study, only boreholes that encountered rich Cu-Ag mineralization in the shale ore were selected. In the Nowa Sól deposit, ore mineralization in the *Kupferschiefer* was documented in 16 boreholes drilled by the MCC. In the Mozów deposit, mineralized shales occur in 2, and in the Sulmierzyce North deposit in 4, boreholes drilled by the MCC.

Thin sections from the shale ore from the three deposits were observed in transmitted and reflected light, using a *NIKON ECLIPSE E600* polarizing microscope. Photomicrographs were taken and petrographic and mineralogical descriptions were made. On this basis, 10 samples from 8 boreholes of the Nowa Sól deposit, 3 samples from 1 borehole of the Mozów deposit and 4 samples from 3 boreholes of the Sulmierzyce North deposit were selected and examined.

Ore minerals were identified by scanning electron microscopy (SEM), using a ZEISS AURIGA 60 (CryoSEM), equipped with a focused ion beam (FIB) and a Bruker EDS XFlash 6|30 spectrometer. BSE (back-scattered electron) images of selected samples were acquired. EDS (energy dispersive spectroscopy) analyses were used to estimate the elemental composition of the mineral phases, by obtaining spectral images of the minerals investigated. Elemental distribution maps of selected elements were also prepared.

Subsequently, samples were examined using a *CAMECA SX-100* electron probe micro-analyser (EPMA). Elemental composition of minerals were acquired using WDS (wavelength dispersive spectroscopy) analyses. Results were used to calculate empirical formulas of identified ore minerals. The following parameters were used during the EPMA analyses: accelerating voltage of 25 kV, beam current ranging between 10 and 15 nA, beam size ranging between 1 and 5 µm, acquisition times of 20 s both at the peak position and the background position for

sulphur and acquisition times of 30 s both at the peak position and the background position for other elements. The spectral lines used included SK , ZnK (ZnS), FeK (Fe₂O₃), CoK (CoO), NiK (NiO), CuK (CuFeS₂), AsK (ZnAs₂), AgL (Ag₂Te), HgL (HgTe), BiM (Bi₂Te₃), AuL (native Au), CdL (CdS), and SbL (native Sb).

All analyses were made at the Faculty of Geology, University of Warsaw.

GENERAL CHARACTERISTICS OF THE DEPOSITS STUDIED

THE NOWA SÓL DEPOSIT

The Nowa Sól deposit is located in the NW part of the FSM, between the Fore-Sudetic Block and the Wolsztyn elevation. It covers an area of 119 km², with the depth of the ores ranging between 1770 and 2150 m BGL. Recently updated resources (calculated in the appendix to the geological documentation as of 31.12.2021) are 846 Mt of ore containing 10.96 Mt of Cu and 35.32 kt of Ag. The thickness of the ore deposit varies from 0.3 to 5 m (2.6 m on average), with average grades of 1.98% Cu and 90 ppm Ag (the threshold values of parameters that define the boundaries of each of the mineral deposits can be found in Speczik et al., 2020).

This deposit is located at the edge of the Zielona Góra oxidized field. Distribution of the oxidized and mineralized zones follows the general pattern characteristic of the Kupferschiefer-type deposits of the FSM. In the SW part of the deposit, closest to the oxidized field, the Rote Fäule facies reaches the base of the Kupferschiefer. Here, ore mineralization occurs in shales and carbonates, while sandstones are barren. Locally, even the Kupferschiefer is oxidized and ore mineralization covers only the upper part of the Zechstein Limestone. Towards the NE and SE, oxidation moves downwards in the lithological profile and the redox boundary is located below the top of the Weissliegend. Consequently, in the central and SE parts of the deposit, ore mineralization occurs within all three ore types, while at the northern and NE margins of the deposit, the ore series comprises only sandstones and shales. As a result, a proportion of 49% of the total Cu resources and 34% of the Ag resources of the deposit are hosted by sandstone ore. Carbonate ore contains 45% of Cu and 30% of the Ag resources. Shale ore hosts "only" 6% of the Cu resources and 36% of the Ag resources, but is characterized by high average grades: 6.42 wt.% Cu and 222 ppm Ag. Average grades of sandstone ore are 1.17 wt.% Cu and 63 ppm Ag, while average grades of carbonate ore are 1.03 wt.% Cu and 70 ppm Ag.

The thickness of the *Kupferschiefer* varies from 0.05 m to 0.59 m (on average 0.24 m). Its lowermost part is composed of black, clayey shales with a significant proportion of organic matter. Locally, it is represented by bituminous shales (southern part of the deposit). Laminae or lenses of detrital grains (quartz, rare feldspars, muscovite, lithoclasts and single heavy mineral grains) were also observed. Towards the upper part of the shales, the proportion of clayey minerals, organic matter and quartz grains decreases, and the content of carbonates increases (mainly dolomite, calcite is rare). The uppermost part of the *Kupferschiefer* consists of dark grey dolomitic shales.

THE MOZÓW DEPOSIT

The Mozów deposit is located in the NW part of the FSM, 22 km to the NE of the Nowa Sól deposit. Its area is 31 km², and the depth of the ores ranges from 2370 to 2540 m BGL. The deposit contains 223 Mt of ore, comprising 4.27 Mt of Cu and 5.72 kt of Ag, grading 2.40 % Cu and 46 ppm Ag. The ore deposit varies between 0.6 and 5.7 m thick (on average 2.56 m).

As with the Nowa Sól deposit, this deposit is located at the edge of the Zielona Góra oxidized field. Apart from that, the small Radoszyn oxidized field is located several km north of the Mozów deposit. The position of the redox boundary in the lithological profile is very consistent in the area discussed. Most commonly it is located at the base of the Kupferschiefer. Only locally, in the southern part of the deposit, are the lowermost several centimeters of shales oxidized. Thus, the ore series consists of the Kupferschiefer and Zechstein Limestone in various proportions, while the sandstones are barren. In the west, only the lowermost 0.3 m of the Zechstein Limestone contains Cu-sulphides. In the central and NE parts of the deposit it is 1-2.4 m, while in the north it is 5.5 m. 75% of the Cu and 58% of the Ag resources are hosted by carbonate ore, while 25% of the Cu and 42% of the Ag resources occur in shale ore. However, the shale ore is characterized by higher average Cu and Ag grades of 5.23 wt.% and 90 ppm, respectively, while in carbonate ore it is 1.76 wt.% Cu and 28 ppm Ag.

The thickness of the *Kupferschiefer* ranges from 0.20 m to 0.60 m (on average 0.32 m) and it is developed similarly as in the Nowa Sól deposit. In its lowermost part, clayey minerals and organic matter prevail over carbonate minerals. Admixtures of detrital grains are observed. Towards the upper part of the shales, the proportion of carbonates increases, while detrital grains are scarce.

THE SULMIERZYCE NORTH DEPOSIT

The Sulmierzyce North deposit is located in the NE part of the FSM, to the SE of the Wolsztyn elevation. It covers an area of 61 km², with the depth of the ores varying between 1400 and 2000 m BGL. The resources of the deposit are 267 Mt of ore containing 5.43 Mt of Cu and 6.87 kt of Ag. The thickness of the ore deposit ranges from 0.8 to 4.3 m (average 1.8 m), and grades 2.06 % Cu and 26 ppm Ag.

The deposit is located between two major oxidized fields: Ostrzeszów and Chwaliszew. Moreover, numerous minor oxidized areas have been recognised in the Sulmierzyce North area (Oszczepalski and Chmielewski, 2015). The redox boundary is generally located just above the Weissliegend, therefore the sandstones are barren. Only in one borehole in the SE part of the deposit was a 6 cm layer of mineralized Weissliegend observed. Locally, the lowest interval of the Kupferschiefer shows oxidation (up to several cm thick). The upper range of the ore series is more varied. At the northern and SE margins of the deposit, it comprises only Kupferschiefer. In the NE, SW and central parts of the deposit, the lowermost part of Zechstein Limestone also contains ore mineralization. In the northern/central part of the deposit, ore mineralization reaches to around 3 m above the Zechstein Limestone base. A characteristic feature of the Sulmierzyce North area comprises drastic changes of the oxidation range within a short distance. As a result, highly mineralized profiles may be directly adjacent to entirely oxidized ones. The exact extent of oxidized and reduced facies is difficult to trace in the Sulmierzyce North area, due to the close vicinity of several oxidized fields. The percentages by weight of both carbonate and shale ore in the deposit are almost equal (53% of carbonate and 47% of shale), but shale ore is characterized by high average grades: 3.24 wt.% Cu and 38 ppm Ag, while for carbonate ore it is 0.56 wt.% Cu and 4 ppm Ag. As a result, over 80% of Cu and 93% of Ag is hosted by shale ore.

A distinctive feature of this deposit is the thickness of the *Kupferschiefer*, which changes from 0.73 to 1.50 m (on average 1.14 m). Apart from the Sulmierzyce North deposit, such thick *Kupferschiefer* within the FSM has been documented only in the Polkowice deposit (Lubin-Sieroszowice area). Apart from typical clayey/carbonate shales (and minor bituminous shales), marly shales and laminated marls are also common in this deposit. Locally, in the northern part of the Sulmierzyce North area, typical black shales do not occur, and only laminated marls are observed.

RESULTS OF MINERALOGICAL AND GEOCHEMICAL STUDIES

THE NOWA SÓL DEPOSIT

MINERALOGY

Shale ore of the Nowa Sól deposit is mineralized mainly with chalcocite, commonly accompanied by digenite and/or djurleite. Chalcocite also co-occurs with bornite in various proportions. An accessory Cu-mineral is covellite. Among non-Cu minerals there are native Ag, Ag-amalgams, stromeyerite, Co-Ni sulph-arsenides, pyrite, galena, sphalerite and native bismuth.

Chalcocite occurs predominantly in the form of disseminated mineralization of various tenor (Fig. 3A, B). Chalcocite grains are either irregular or elongated concordantly with the shale lamination. Chalcocite replaces detrital grains, carbonate minerals and pyrite framboids. Disseminated mineralization is usually distributed evenly throughout the host rock. In the shale ore containing particularly rich sulphide mineralization, abundant accumulations of fine chalcocite grains were observed, in the shape of continuous layers or lenses.

Coarse-grained chalcocite is also common, mainly as aggregates, nests and lenses (Fig. 3C-E), accompanied by rich disseminated mineralization. These often consist of semi-massive chalcocite and remnants of gangue minerals (Fig. 3C). Less frequent is coarse-grained chalcocite replacing bioclasts. For example, short and thick chalcocite lenses were documented, which are most likely replacements of foraminifera (Fig. 3D). Chalcocite also replaces aggregates primarily composed of multiple pyrite framboids. Moreover, chalcocite occurs as lenses of various length and thickness (Fig. 3E). The least common style of mineralization forms regular, continuous chalcocite veinlets, usually concordant with shale lamination (Fig. 3F), in places vertical or diagonal. In highly mineralized samples, abundant accumulations of irregular, coarse-grained chalcocite aggregates were observed, forming semi-massive, continuous layers or lenses (Fig. 4A-D), always in association with rich disseminated mineralization.

In the Nowa Sól deposit, chalcocite commonly co-occurs with other Cu-S sulphides. In several samples chalcocite-digenite intergrowths have been documented (Figs. 3B and 4E). Digenite forming its own aggregates is less frequent. It also accompanies chalcocite in the disseminated mineralization, but in this case it is difficult to distinguish between the two minerals.

In some of the samples containing semi-massive, chalcocite-dominated mineralization, sulphide aggregates are composed of two, or even three, intergrowing mineral phases, differ-



Fig. 3. Photomicrographs of the ore mineralization in the shale ore of the Nowa Sól deposit, reflected light

A – disseminated chalcocite (cc) mineralization; B – chalcocite (cc) and digenite (dg) lenses in association with the disseminated mineralization; C – semi-massive chalcocite (cc) nest, cut by multiple chalcocite veinlets; D – chalcocite (cc) replacing bioclasts; E – numerous chalcocite (cc) lenses, accompanied by disseminated mineralization; F – horizontal chalcocite (cc) veinlet, in association with disseminated mineralization



Fig. 4. Photomicrographs of the ore mineralization in the Nowa Sól deposit, reflected light

A – semi-massive layer composed of chalcocite (cc) and most likely djurleite (dju?), with many exsolutions of minerals from the cobaltite (cbt) – gersdorffite (gdf) series; B – accumulation of chalcocite (cc)-djurleite (dju?) aggregates with numerous cobaltite (cbt) – gersdorffite (gdf) exsolutions; C – exsolutions of cobaltite (cbt) – gersdorffite (gdf) series minerals, aligned along the boundaries of a chalcocite (cc) – djurleite (dju?) composite; D – semi-massive aggregate of chalcocite (cc) and most likely djurleite (dju?), with cobaltite (cbt) – gersdorffite (gdf) exsolutions; E – chalcocite (cc) - digenite (dg) intergrowths; F – diagonal veinlet composed of chalcocite (cc) and Ag-amalgam (AgHg), accompanied by disseminated mineralization

ing only in the shade of their colour (Fig. 4A–D). In some cases, it is hard to determine whether they are composed of two slightly different varieties of chalcocite, or different minerals from the chalcocite-group, e.g. chalcocite and djurleite. In general, the physical and chemical similarities between some members of the chalcocite group make them difficult to identify by microscopic methods (cf. Piestrzyński, 2007).

Micro-analyses revealed only minor differences in the chemical composition of the observed Cu-S sulphides. The most common Cu-S mineral is chalcocite; however, the results were often inconclusive. In some of the samples, the presence of digenite was confirmed. Some of the chalcocite-group minerals revealed a chemical composition closer to stoichiometric djurleite. Interestingly, the chalcocite-djurleite composites (which may be accompanied by digenite) contain numerous exsolutions of Co-Ni sulpharsenides (Fig. 4C, D). They are also associated with Ag minerals (mainly Ag-amalgams and stromeyerite).

Bornite is the second most common sulphide in the shale ore of the Nowa Sól deposit. It usually accompanies chalcocite, both in fine-grained mineralization and in coarse-grained aggregates (Fig. 5A, B). Disseminated bornite occurs as its own individuals or as fine intergrowths with chalcocite and digenite. Bornite often replaces µm-size pyrite framboids. Aggregates of framboidal pyrite cemented by bornite were also observed.

Coarse-grained chalcocite-bornite composites may be irregular and contain bornite in their inner parts, surrounded by chalcocite (Fig. 5B). Bornite also co-occurs with chalcocite in abundant accumulations of coarse-grained aggregates in the form of semi-massive layers or veins (Fig. 5C–F).

In several samples, bornite was the dominant ore mineral, mainly in the form of fine disseminations (Fig. 6A). Locally in the bornite-dominate zones, shale ore contains numerous aggregates of various sizes, composed of densely packed pyrite framboids replaced by bornite (Fig. 6B, D). They may include μ m-size remnants of pyrite grains. Semi-massive layers composed of bornite replacements of pyrite framboids were also documented (Fig. 6C).

In the *Kupferschiefer*-type deposits of the FSM, several varieties of bornite have been distinguished, slightly differing in optical properties (e.g., Jarosz, 1966; Harańczyk, 1972; Kucha, 2007). In the samples studied, most bornite can be described as orange (bn1; Figs. 5A–D and 6A–C), while pink bornite (bn2) was occasionally observed (Fig. 5A, E, F). However, micro-analyses did not reveal any significant differences in their chemical composition. In some of the samples, bornite containing Ag admixtures was identified in minor amounts, characterized by an orange-brown colour (bn3; Fig. 6D). This variety can also replace pyrite framboids. Ag-rich bornite, co-occurring with Ag-amalgams, can be described as brown-grey (bn4; Fig. 6E). It was observed in those samples mineralized predominantly with bornite.

Covellite occurs in minor amounts in the samples analysed. It accompanies other sulphides, mainly in the disseminated mineralization. It was observed in the form of fine-grained intergrowths with digenite and/or bornite. Covellite may also cement pyrite framboids, together with bornite. It is an accessory mineral in the chalcocite-dominated mineralization. Slightly increased amounts of covellite were documented in the marginal parts of the deposit, where Cu-sulphides (bornite, chalcocite, digenite) are accompanied by pyrite, galena and sphalerite.



Fig. 5. Photomicrographs of the ore mineralization in the Nowa Sól deposit, reflected light

A – abundant disseminated mineralization composed of chalcocite (cc), orange bornite (bn1) and pink bornite (bn2); B – aggregates of orange bornite (bn1) surrounded by chalcocite (cc); C – semi-massive sulphide layer composed of chalcocite (cc) and orange bornite (bn1) in association with disseminated bornite; D – bornite (bn1)-dominated mineralization with chalcocite (cc) intergrowths; E – semi-massive sulphide layer composed of chalcocite (cc) and pink bornite (bn2); F – intergrowths of chalcocite (cc) with pink bornite (bn2) and minor galena (gn)



Fig. 6. Photomicrographs of the ore mineralization in the Nowa Sól deposit, reflected light

A – disseminated mineralization composed of orange bornite (bn1); **B** – orange bornite (bn1) with remnants of pyrite framboids (py); **C** – semi-massive layer composed of bornite (bn1) replacements of pyrite framboids (py); **D** – orange-brown Ag-bearing bornite (bn3) replacing pyrite framboids, with remnants of pyrite grains (py); **E** – overgrowths of Ag-amalgam (AgHg) on brown-grey Ag-rich bornite (bn4); **F** – chalcocite (cc) aggregate, with sphalerite (sp) intergrowths and native Ag inclusions; stromeyerite (smy) occurs at the contact between chalcocite and native Ag

Silver minerals include native Ag, Ag-amalgams and stromeyerite. Native Ag and Ag-amalgams occur primarily in the chalcocite-dominated mineralization. They form inclusions in coarse-grained chalcocite aggregates and chalcocite veinlets (Fig. 4F), as well as fine individuals dispersed in the host rock. Moreover, native Ag was observed in the bornite-chalcocite mineralization, mainly as fine grains and intergrowths with Cu-sulphides disseminated in the host rock. Ag-amalgams were recognised also in samples containing chalcocite-djurleite composites (accompanied by digenite) with exsolutions of Co-Ni sulpharsenides. Apart from that, overgrowths of Ag-amalgam on brown-grey bornite were noted in the samples mineralized predominantly with bornite (Fig. 6E). Stromeyerite occurs as rims around native Ag and Ag-amalgam inclusions in chalcocite aggregates and veinlets (Fig. 6D).

Co-Ni sulpharsenides occur commonly throughout the Nowa Sól deposit, but mainly in the form of very fine grains (usually several µm in size), dispersed in the shale ore, therefore they are difficult to document. However, locally, abundant accumulations of Co-Ni sulpharsenides were observed in the samples containing rich chalcocite-djurleite mineralization (Fig. 4A–D). They form numerous, µm-size exsolutions in coarse-grained aggregates of chalcocite group minerals. These exsolutions are often arranged in regular lines or concentrated along the boundaries of the sulphide composites (Fig. 4C). During chemical analyses, two members of the gersdorffite-cobaltite series were recognised, differing in proportions between Co and Ni. Apart from that, a mineral composed of Ni and As, with a low content of S and significant enrichment in Cu, was noted (nickeline?).

Pyrite in the shale ore occurs mainly as remnants of framboids, dispersed in the host rock, commonly cemented or replaced by Cu-sulphides (e.g. bornite, chalcocite, covellite). The most abundant concentrations of pseudomorphs after pyrite framboids, in the form of densely packed aggregates, were observed in the area where ore mineralization is dominated by bornite. Increased amounts of pyrite grains were noted in the marginal parts of the deposit, together with disseminated Cu-sulphides (bornite, chalcocite, digenite, covellite), accompanied by galena and sphalerite.

Galena was documented in the samples from the marginal parts of the deposit, similarly to pyrite. It forms fine disseminated grains or intergrowths with other sulphides (sphalerite, bornite, chalcocite, digenite, covellite). Galena may also cement pyrite framboids. Moreover, galena was observed as an accessory mineral in the bornite-chalcocite or bornite-dominated mineralization, as inclusions in coarse-grained aggregates (Fig. 5F) or as fine individuals dispersed in the host rock.

Sphalerite appears rarely in the studied samples. It was observed in the marginal parts of the deposit, together with galena. Scarce intergrowths of sphalerite in chalcocite aggregates are associated with chalcocite-bornite mineralization (Fig. 6F).

Native bismuth was recognised as minor inclusions in the mineralization comprising chalcocite-group minerals (both in semi-massive aggregates and in disseminated minerals).

MINERAL DISTRIBUTION

Shale ore in the Nowa Sól deposit is mineralized mainly with Cu-S sulphides, while Cu-Fe-S sulphides predominate only locally. A distinctive zonation in the distribution of Cu-sulphides, as well as other ore minerals, can be observed within the shale ore.

In the SW part of the deposit, the shale ore is mineralized with chalcocite (accompanied by digenite and covellite). In the central/western part of the deposit, chalcocite-dominated mineralization contains inclusions of Ag minerals. Shale ore from the central/eastern part of the deposit is mineralized with chalcocite-djurleite assemblage (with accessory digenite and covellite), hosting numerous exsolutions of Co-Ni sulpharsenides and co-occurring with Ag minerals. Inclusions of native Bi were documented in the Cu-S mineralization from the central part of the deposit. Towards the NE and SE, bornite becomes an accompanying sulphide. The proportion of bornite in the analysed samples varies. In some parts of the shale ore, bornite co-occurs with chalcocite in the disseminated mineralization. Rich mineralization consisting of both chalcocite and bornite in similar amounts was also observed. Accessory minerals are digenite and Ag minerals, with minor galena and covellite. In the central/northern part of the deposit, bornite can be the dominant mineral. At the NE and SE edges of the deposit, apart from chalcocite, bornite, digenite, covellite and Ag minerals, increased amounts of galena, sphalerite and pyrite were documented. Enrichment in galena is particularly characteristic of the NE-most part of the deposit.

Therefore, there is a zonation pattern, that in the vicinity of oxidized rocks, shale ore is mineralized almost entirely with Cu-S sulphides. Towards the NE and SE, as the distance from the oxidized field grows, the amount of Cu-Fe-S sulphides gradually increases. In the lowermost part of the shale ore Cu-S sulphides prevail, while moving upwards (towards the Zechstein Limestone), the proportion of Cu-Fe-S sulphides rises. Even farther from the oxidized field, at the NE and SE edges of the deposits, pyrite, galena and sphalerite are observed in the shale ore. Ag minerals occur in the entire deposit (both with Cu-S and Cu-Fe-S sulphides), but particularly rich concentrations were noted in the central/northern parts of the deposit.

In general, the lower, organic matter-rich part of the *Kupferschiefer* contains more veinlets and large aggregates than the uppermost part, in which disseminated mineralization prevails.

GEOCHEMISTRY

Chalcocite was observed in all samples studied (n = 212; n – number of analyses). Two main varieties of chalcocite were distinguished, differing in Ag content: Ag-barren and Ag-bearing. In some of the samples examined, both types of chalcocite were detected (they occur in different proportions but usually the Ag-barren variety prevails).

Ag-barren chalcocite was confirmed in all samples investigated. It was examined both in chalcocite-dominated mineralization (including chalcocite-group minerals containing abundant exsolutions of Co-Ni sulpharsenides) and in mineralization consisting of chalcocite and bornite. In the first case, Ag concentrations in chalcocite are negligible (on average 0.02 wt.% Ag), while in the second case, chalcocite reveals some minor Ag admixtures (on average 0.13 wt.% Ag). In general, the average Ag content in Ag-barren chalcocite is 0.05 wt.% (Table 1).

Ag-bearing chalcocite often accompanies the Ag-barren variety, both in samples mineralized predominantly with chalcocite and in samples mineralized with chalcocite and bornite. In some of the samples analysed it was the dominant variety. Veinlets, lenses or semi-massive aggregates and nests of Ag-bearing chalcocite usually contain microscopically visible inclusions of Ag minerals. The average Ag content in Ag-bearing chalcocite is 3.97 wt.% (Table 1). Aggregates and veinlets of particularly Ag-rich chalcocite, with Ag admixtures reaching up to 12.81 wt.% of Ag (the average value is 7.78 wt.% Ag) were observed in the samples mineralized mainly with semi-massive aggregates of Ag-barren chalcocite-group minerals with numerous exsolutions of Co-Ni sulpharsenides (Fig. 7).

S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
	Ag-b	barren c	halcocite	e (from	chalcoc	ite-don	ninated	minera	lization)		
18.76	75.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21.95	79.76	0.14	0.30	0.09	0.25	0.04	0.03	0.18	0.13	0.06	0.04	0.06
20.22	78.45	0.03	0.02	0.00	0.03	0.00	0.00	0.01	0.04	0.01	0.00	0.00
0.61	0.82	0.03	0.04	0.01	0.06	0.01	0.01	0.03	0.02	0.01	0.01	0.01
	Ag	j-barrer	chalcoc	ite (fror	n chalc	ocite-bo	ornite m	ineraliz	ation)			
19.94	74.59	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22.65	78.94	0.73	0.22	0.07	0.00	0.05	0.03	0.06	0.12	0.07	0.03	0.10
21.21	77.04	0.26	0.13	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01
0.80	1.03	0.22	0.06	0.02	0.00	0.01	0.01	0.02	0.03	0.02	0.01	0.03
			Ag-ba	arren cl	nalcocit	e (all sa	amples)					
18.76	74.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22.65	79.76	0.73	0.30	0.09	0.25	0.05	0.03	0.18	0.13	0.07	0.04	0.10
20.48	78.07	0.09	0.05	0.00	0.02	0.00	0.00	0.01	0.03	0.01	0.00	0.00
0.79	1.08	0.15	0.06	0.01	0.05	0.01	0.01	0.02	0.02	0.01	0.01	0.02
				Ag-be	aring ch	nalcocit	е					
18.25	66.54	0.00	1.03	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
20.24	78.38	0.21	12.81	1.06	0.39	0.14	0.02	0.20	0.06	0.05	0.07	0.00
19.44	75.50	0.02	3.97	0.04	0.01	0.00	0.00	0.01	0.03	0.00	0.01	0.00
0.37	2.66	0.04	2.66	0.13	0.05	0.02	0.00	0.03	0.02	0.01	0.02	0.00
	S 18.76 21.95 20.22 0.61 22.65 21.21 0.80 18.76 22.65 20.48 0.79 18.25 20.24 18.44 0.37	S Cu 18.76 75.59 21.95 79.76 20.22 78.45 0.61 0.82 0.61 0.82 19.94 74.59 22.65 78.94 21.21 77.04 0.80 1.03 22.65 79.76 22.65 79.76 22.65 79.76 20.48 78.07 0.79 1.08 18.25 66.54 20.24 78.38 19.44 75.50 0.37 2.66	S Cu Fe Ag-barren C 18.76 75.59 0.00 21.95 79.76 0.14 20.22 78.45 0.03 0.61 0.82 0.03 0.61 0.82 0.03 22.65 78.94 0.73 21.21 77.04 0.26 0.80 1.03 0.22 18.76 74.59 0.00 22.65 79.76 0.73 20.48 78.07 0.09 22.65 79.76 0.73 20.48 78.07 0.09 0.79 1.08 0.15 4 78.38 0.21 18.25 66.54 0.00 20.24 78.38 0.21 19.44 75.50 0.02	S Cu Fe Ag Ag-barren chalcocite 18.76 75.59 0.00 0.00 21.95 79.76 0.14 0.30 20.22 78.45 0.03 0.02 0.61 0.82 0.03 0.04 Ag-barren chalcoci 19.94 74.59 0.00 0.04 22.65 78.94 0.73 0.22 21.21 77.04 0.26 0.13 0.80 1.03 0.22 0.06 Lange 18.76 74.59 0.00 0.00 22.65 79.76 0.73 0.30 20.48 78.07 0.09 0.05 0.79 1.08 0.15 0.06 Use Use Use Use 18.25 66.54 0.00 1.03 20.24 78.38 0.21 12.81 19.44 75.50 0.02 3.97 0.37	S Cu Fe Ag Hg Ag-barren chalcocite (from 18.76 75.59 0.00 0.00 0.00 21.95 79.76 0.14 0.30 0.09 20.22 78.45 0.03 0.02 0.00 0.61 0.82 0.03 0.04 0.01 Ag-barren chalcocite (from 19.94 74.59 0.00 0.04 0.00 22.65 78.94 0.73 0.22 0.07 21.21 77.04 0.26 0.13 0.00 0.80 1.03 0.22 0.06 0.02 24.65 79.76 0.73 0.30 0.00 0.80 1.03 0.22 0.06 0.02 22.65 79.76 0.73 0.30 0.09 22.65 79.76 0.73 0.30 0.09 20.48 78.07 0.09 0.05 0.00 0.79 1.08 0.15 0.06 0.01	S Cu Fe Ag Hg Co Ag-barren chalcocite (from chalcocite) (from chalcocite) 18.76 75.59 0.00 0.00 0.00 21.95 79.76 0.14 0.30 0.09 0.25 20.22 78.45 0.03 0.02 0.00 0.03 0.61 0.82 0.03 0.04 0.01 0.06 Ag-barren chalcocite (from chalcocite) Ag.00 0.00 0.00 19.94 74.59 0.00 0.04 0.00 0.00 22.65 78.94 0.73 0.22 0.07 0.00 21.21 77.04 0.26 0.13 0.00 0.00 0.80 1.03 0.22 0.06 0.02 0.00 0.80 1.03 0.22 0.06 0.02 0.00 22.65 79.76 0.73 0.30 0.09 0.25 20.48 78.07 0.09 0.05 0.00 0.02	S Cu Fe Ag Hg Co Ni Ag-barren chalcocite (from chalcocite-dom 18.76 75.59 0.00 0.00 0.00 0.00 0.00 21.95 79.76 0.14 0.30 0.09 0.25 0.04 20.22 78.45 0.03 0.02 0.00 0.00 0.00 0.61 0.82 0.03 0.04 0.01 0.06 0.01 Ag-barren chalcocite (from chalcocite-bor 19.94 74.59 0.00 0.04 0.00 0.00 0.00 22.65 78.94 0.73 0.22 0.07 0.00 0.00 22.65 78.94 0.73 0.22 0.07 0.00 0.00 0.80 1.03 0.22 0.06 0.02 0.00 0.01 0.80 1.03 0.22 0.06 0.02 0.00 0.00 0.00 0.00 22.65 79.76 0.73 0.30	S Cu Fe Ag Hg Co Ni Sb Ag-barren chalcocite (from chalcocite-dominated 18.76 75.59 0.00 0.00 0.00 0.00 0.00 0.00 21.95 79.76 0.14 0.30 0.09 0.25 0.04 0.03 20.22 78.45 0.03 0.02 0.00 0.03 0.00 0.00 0.61 0.82 0.03 0.04 0.01 0.06 0.01 0.01 Ag-barren chalcocite (from chalcocite-bornite m 19.94 74.59 0.00 0.04 0.00 0.00 0.00 0.00 22.65 78.94 0.73 0.22 0.07 0.00 0.00 0.00 0.80 1.03 0.22 0.06 0.02 0.00 0.00 0.00 0.80 1.03 0.22 0.06 0.02 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00	S Cu Fe Ag Hg Co Ni Sb As Ag-barren chalcocite (from chalcocite-dominated minera 18.76 75.59 0.00 0.00 0.00 0.00 0.00 0.00 0.00 21.95 79.76 0.14 0.30 0.09 0.25 0.04 0.03 0.18 20.22 78.45 0.03 0.02 0.00 0.03 0.00 0.00 0.01 0.61 0.82 0.03 0.04 0.01 0.06 0.01 0.01 0.03 Ag-barren chalcocite (from chalcocite-bornite mineraliz 19.94 74.59 0.00 0.04 0.00 0.00 0.00 0.00 22.65 78.94 0.73 0.22 0.07 0.00 0.00 0.00 0.00 22.65 78.94 0.73 0.22 0.00 0.00 0.00 0.00 0.00 21.21 77.04 0.26 0.13 0.00 0.00 0.00 </td <td>S Cu Fe Ag Hg Co Ni Sb As Zn Ag-barren chalcocite (from chalcocite-dominated mineralization) 18.76 75.59 0.00 0.01 0.01 0.01 0.01 0.03 0.02 0.01 0.01 0.03 0.02 0.00</td> <td>S Cu Fe Ag Hg Co Ni Sb As Zn Bi Ag-barren chalcocite (from chalcocite-dominated mineralization) 18.76 75.59 0.00 0.01 0.01 0.04 0.01 0.00</td> <td>S Cu Fe Ag Hg Co Ni Sb As Zn Bi Cd Ag-barren chalcocite (from chalcocite-dominated mineralization) 75.59 0.00 0.01 0.01 0.04 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01</td>	S Cu Fe Ag Hg Co Ni Sb As Zn Ag-barren chalcocite (from chalcocite-dominated mineralization) 18.76 75.59 0.00 0.01 0.01 0.01 0.01 0.03 0.02 0.01 0.01 0.03 0.02 0.00	S Cu Fe Ag Hg Co Ni Sb As Zn Bi Ag-barren chalcocite (from chalcocite-dominated mineralization) 18.76 75.59 0.00 0.01 0.01 0.04 0.01 0.00	S Cu Fe Ag Hg Co Ni Sb As Zn Bi Cd Ag-barren chalcocite (from chalcocite-dominated mineralization) 75.59 0.00 0.01 0.01 0.04 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.01 0.01 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.01

Chemical composition of chalcocite from the shale ore of the Nowa Sól deposit

Concentrations of other metals in chalcocite are most often close to or below detection limits. An average of 0.26 wt.% Fe was observed in chalcocite co-occurring with bornite. Chalcocite containing abundant exsolutions of Co-Ni sulpharsenides revealed slightly increased content of Co (on average 0.14 wt.%).

The empirical formula of the Ag-bearing chalcocite, recalculated to 3 atoms per formula unit (apfu) is $Cu_{1.79-2.00}$, $Ag_{0.02-0.20}S_{0.97-1.03}$ (average formula is $Cu_{1.95}Ag_{0.06}S_{0.99}$). The empirical formula of the Ag-barren chalcocite recalculated to 3 apfu is $Cu_{1.87-2.04}S_{0.96-1.13}$ (on average $Cu_{1.97}S_{1.03}$). The empirical formula of the Ag-bearing chalcocite, recalculated to 1 atom of sulphur is $Cu_{1.78-2.03}Ag_{0.02-0.21}S$ (average formula is $Cu_{1.96}Ag_{0.06}S$). The empirical formula of the Ag-bearing chalcocite, recalculated to 1 atom of sulphur is $Cu_{1.78-2.03}Ag_{0.02-0.21}S$ (average formula is $Cu_{1.96}Ag_{0.06}S$). The empirical formula of the Ag-barren chalcocite recalculated to 1 atom of sulphur is $Cu_{1.66-2.14}S$ (on average $Cu_{1.93}S$).

In the calculations provided, data concerning all minerals from the chalcocite-group minerals have been included. The analyses reveal that some of the minerals studied are in fact closer to the empirical formula of djurleite or digenite. However, the results obtained were in some cases inconclusive. Therefore, in Table 1 all results were compiled as "chalcocite".

Bornite was studied in 4 samples (n = 89), containing three types of this mineral: bornite co-occurring with chalcocite (mainly orange variety; the pink variety was documented in minor amounts), bornite replacing aggregates of framboidal pyrite (orange or orange-brown), and bornite forming fine-grained intergrowths with Ag-amalgams (brown-grey).

The chemical composition of the orange bornite from each sample examined is similar (Table 2). Only some minor variations in proportions between Cu and Fe were observed. Moreover, there are no significant differences between the chemical composition of orange and pink bornite. In general, bornite co-occurring with chalcocite in semi-massive accumulations contains an average of 61.07 wt.% Cu and 11.11 wt.% Fe. Bornite forming intergrowths with chalcocite in the bornite-dominated mineralization reveals slightly different concentrations of both metals, namely on average 62.78 wt.% Cu and 10.79 wt.% Fe. In the orange bornite replacing pyrite framboids, the average contents of Cu and Fe are 61.59 wt.% and 11.20 wt.%, respectively.

Ag-bearing bornite contains on average 3.5 wt.% Ag; however, due to the very small size of its grains, obtaining highquality results of EPMA analyses was impossible. The average Ag content in orange/pink bornite is 0.06 wt.%. Admixtures of other metals were not detected.

The empirical formula of the orange/pink bornite (recalculated to 10 apfu) is $Cu_{4.82-5.08}Fe_{0.94-1.10}S_{3.96-4.14}$ (on average $Cu_{4.98}Fe_{0.99}S_{4.03}$). The empirical formula of the bornite recalculated to 4 atoms of sulphur is $Cu_{4.68-5.11}Fe_{0.95-1.08}S_4$ (on average $Cu_{4.95}Fe_{0.98}S_4$).

Native Ag, Ag-amalgams and stromeyerite were identified in the samples studied. Native Ag was investigated in 2 samples (n = 20). In the first sample, it forms relatively large inclusions in irregular aggregates of Ag-bearing chalcocite. It contains on average 95.86 wt.% Ag and 1.47 wt.% Hg. In the second sample, native Ag occurs as fine, disseminated grains (together with aggregates of bornite and Ag-barren chalcocite) or as inclusions in Ag-bearing chalcocite with intergrowths of sphalerite. In this sample, the average amount of Ag and Hg in the native Ag is 96.54 wt.% and 1.17 wt.%, respectively. The average chemical composition of the native Ag is 96.13 wt.% Ag and 1.35 wt.% Hg (Table 3).

Two types of Ag-amalgam were identified, differing in Hg content (Table 3). They were analysed in 3 samples (n = 54). Ag-amalgams poor in Hg were observed in the sample containing mainly chalcocite-djurleite mineralization with accessory digenite (which is in general Ag-barren), accompanied by Co-Ni

D





Fig. 7A – BSE image of a chalcocite (cc) aggregate containing numerous exsolutions of Co-Ni sulpharsenides (Co-rich member of the cobaltite-gersdorffite series), accompanied by Ag-amalgam (AgHg), with a stromeyerite (smy) rim around a chalcocite grain; B – elemental mapping showing distribution of Ag; C – elemental mapping showing distribution of Hg; D – elemental mapping showing distribution of Co; E – elemental mapping showing distribution of Ni; F – elemental mapping showing distribution of As; G – EDS spectrum of Hg-poor Ag-amalgam; H – EDS spectrum of Hg-bearing stromeyerite; I – EDS spectrum of Co-Ni sulpharsenide; J – EDS spectrum of Ag-barren chalcocite

S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
	Bornit	e co-occ	urring v	vith cha	Icocite	in semi	-massiv	e accu	mulatio	ns		
25.44	60.42	10.61	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26.12	61.95	12.24	0.11	0.00	0.05	0.08	0.03	0.08	0.12	0.09	0.05	0.10
25.86	61.07	11.11	0.06	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.00	0.02
0.17	0.42	0.35	0.03	0.00	0.01	0.02	0.01	0.03	0.03	0.02	0.01	0.03
Borni	te formin	ig intergr	owths w	vith cha	lcocite	in the b	ornite-o	lominat	ed mine	eralizati	on	
24.86	61.63	10.28	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
25.65	63.35	11.57	0.13	0.00	0.00	0.00	0.02	0.12	0.05	0.07	0.03	0.05
25.22	62.78	10.79	0.06	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.01	0.00
0.14	0.34	0.19	0.03	0.00	0.00	0.00	0.01	0.04	0.02	0.02	0.01	0.01
			Born	ite repla	acing p	rite fra	mboids					
25.28	60.71	11.03	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00
25.61	62.32	11.58	0.09	0.00	0.00	0.00	0.01	0.08	0.04	0.03	0.03	0.00
25.45	61.59	11.20	0.06	0.00	0.00	0.00	0.00	0.04	0.02	0.01	0.00	0.00
0.11	0.58	0.19	0.01	0.00	0.00	0.00	0.00	0.04	0.02	0.02	0.01	0.00
	Bornite (all samples)											
24.86	60.42	10.28	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26.12	63.35	12.24	0.13	0.00	0.05	0.08	0.03	0.12	0.12	0.09	0.05	0.10
25.40	62.27	10.89	0.06	0.00	0.00	0.00	0.00	0.03	0.02	0.01	0.00	0.00
0.32	0.84	0.27	0.03	0.00	0.01	0.01	0.01	0.04	0.02	0.02	0.01	0.02
	S 25.44 26.12 25.86 0.17 Borni 24.86 25.65 25.22 0.14 25.28 25.61 25.45 0.11 25.45 0.11 24.86 26.12 25.40 0.32	S Cu 25.44 60.42 26.12 61.95 25.86 61.07 0.17 0.42 Bornite formin 24.86 61.63 25.22 62.78 0.14 0.34 25.25 60.71 25.65 63.35 25.26 62.78 0.14 0.34 25.65 61.59 0.11 0.58 24.86 60.42 24.86 60.42 25.45 61.59 0.11 0.58 25.45 60.42 26.12 63.35 25.40 62.27 0.32 0.84	S Cu Fe Bornite co-occ 25.44 60.42 10.61 26.12 61.95 12.24 25.86 61.07 11.11 0.17 0.42 0.35 Bornite forming intergr 24.86 61.63 10.28 25.65 63.35 11.57 25.22 62.78 10.79 0.14 0.34 0.19 0.19 0.14 0.34 0.19 25.65 61.59 11.20 0.11 0.58 0.19 25.45 61.59 11.20 0.11 0.58 0.19 25.45 61.59 11.20 0.11 0.58 0.19 24.86 60.42 10.28 24.86 60.42 10.28 24.86 60.42 10.28 26.12 63.35 12.24 25.40 62.27 10.89 0.32 0.84 0.27	S Cu Fe Ag Bornite co-occurring v 25.44 60.42 10.61 0.03 26.12 61.95 12.24 0.11 25.86 61.07 11.11 0.06 0.17 0.42 0.35 0.03 Bornite forming intergrowths v 24.86 61.63 10.28 0.02 25.65 63.35 11.57 0.13 25.22 62.78 10.79 0.06 0.14 0.34 0.19 0.03 0.05 25.61 62.32 11.58 0.09 25.45 61.59 11.20 0.06 0.11 0.58 0.19 0.01 25.45 61.59 11.20 0.06 0.11 0.58 0.19 0.01 25.45 61.59 11.20 0.06 0.11 0.58 0.19 0.01 24.86 60.42 10.28 0.02 26.12 63.35 12.24 0.13 24.86 60.42 10.89 <td>S Cu Fe Ag Hg Bornite co-occurring with char 25.44 60.42 10.61 0.03 0.00 26.12 61.95 12.24 0.11 0.00 25.86 61.07 11.11 0.06 0.00 25.86 61.07 11.11 0.06 0.00 0.17 0.42 0.35 0.03 0.00 0.17 0.42 0.35 0.03 0.00 0.17 0.42 0.35 0.03 0.00 24.86 61.63 10.28 0.02 0.00 25.22 62.78 10.79 0.06 0.00 0.14 0.34 0.19 0.03 0.00 25.45 60.71 11.03 0.05 0.00 25.45 61.59 11.20 0.06 0.00 25.45 61.42 10.28 0.02 0.00</td> <td>S Cu Fe Ag Hg Co Bornite co-occurring with chalcocite 25.44 60.42 10.61 0.03 0.00 0.00 26.12 61.95 12.24 0.11 0.00 0.05 25.86 61.07 11.11 0.06 0.00 0.01 0.17 0.42 0.35 0.03 0.00 0.01 Bornite forming intergrowths with chalcocite 24.86 61.63 10.28 0.02 0.00 0.00 25.65 63.35 11.57 0.13 0.00 0.00 25.22 62.78 10.79 0.06 0.00 0.00 0.14 0.34 0.19 0.03 0.00 0.00 25.28 60.71 11.03 0.05 0.00 0.00 25.45 61.59 11.20 0.06 0.00 0.00 25.45 61.59 11.20 0.06 0.00 0.00 25.45 61.59 10.</td> <td>S Cu Fe Ag Hg Co Ni Bornite co-occurring with chalcocite in semi 25.44 60.42 10.61 0.03 0.00 0.00 0.00 26.12 61.95 12.24 0.11 0.00 0.00 0.00 25.86 61.07 11.11 0.06 0.00 0.00 0.00 0.17 0.42 0.35 0.03 0.00 0.01 0.02 Bornite forming intergrowths with chalcocite in the b 24.86 61.63 10.28 0.02 0.00 0.00 0.00 25.65 63.35 11.57 0.13 0.00 0.00 0.00 25.22 62.78 10.79 0.06 0.00 0.00 0.00 0.14 0.34 0.19 0.03 0.00 0.00 0.00 25.45 60.71 11.03 0.05 0.00 0.00 0.00 25.45 61.59 11.20 0.06 0.00 0.00</td> <td>S Cu Fe Ag Hg Co Ni Sb Bornite co-occurring with chalcocite in semi-massive 25.44 60.42 10.61 0.03 0.00 0.00 0.00 0.00 26.12 61.95 12.24 0.11 0.00 0.00 0.00 0.00 0.00 25.86 61.07 11.11 0.06 0.00 0.00 0.00 0.00 0.17 0.42 0.35 0.03 0.00 0.01 0.02 0.01 Bornite forming intergrowths with chalcocite in the bornite-or 24.86 61.63 10.28 0.02 0.00 0.00 0.00 0.00 25.65 63.35 11.57 0.13 0.00 0.00 0.00 0.02 25.22 62.78 10.79 0.06 0.00 0.00 0.00 0.00 0.14 0.34 0.19 0.03 0.00 0.00 0.00 0.00 25.28 60.71 11.03</td> <td>S Cu Fe Ag Hg Co Ni Sb As Bornite co-occurring with chalcocite in semi-massive accur 25.44 60.42 10.61 0.03 0.00 0.00 0.00 0.00 0.00 26.12 61.95 12.24 0.11 0.00 0.00 0.00 0.00 0.00 26.12 61.07 11.11 0.06 0.00 0.00 0.00 0.00 0.02 0.17 0.42 0.35 0.03 0.00 0.01 0.02 0.01 0.03 Bornite forming intergrowths with chalcocite in the bornite-dominat 24.86 61.63 10.28 0.02 0.00 0.00 0.00 0.00 0.00 25.65 63.35 11.57 0.13 0.00 0.00 0.00 0.01 0.04 25.22 62.78 10.79 0.06 0.00 0.00 0.00 0.01 0.04 Bornite replacing pyrite framboids 25.28</td> <td>S Cu Fe Ag Hg Co Ni Sb As Zn Bornite co-occurring with chalcocite in semi-massive accurulatio 25.44 60.42 10.61 0.03 0.00 0.01 0.02 0.01 0.03 0.03 0.03 0.03 0.00 0.00 0.00 0.00 0.00 0.02 0.01 0.02 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.01</td> <td>S Cu Fe Ag Hg Co Ni Sb As Zn Bi Bornite co-occurring with chalcocite in semi-massive accumulations 25.44 60.42 10.61 0.03 0.00 0.01</td> <td>S Cu Fe Ag Hg Co Ni Sb As Zn Bi Cd Bornite co-occurring with chalcocite in semi-massive accurulations 25.44 60.42 10.61 0.03 0.00 0.01<!--</td--></td>	S Cu Fe Ag Hg Bornite co-occurring with char 25.44 60.42 10.61 0.03 0.00 26.12 61.95 12.24 0.11 0.00 25.86 61.07 11.11 0.06 0.00 25.86 61.07 11.11 0.06 0.00 0.17 0.42 0.35 0.03 0.00 0.17 0.42 0.35 0.03 0.00 0.17 0.42 0.35 0.03 0.00 24.86 61.63 10.28 0.02 0.00 25.22 62.78 10.79 0.06 0.00 0.14 0.34 0.19 0.03 0.00 25.45 60.71 11.03 0.05 0.00 25.45 61.59 11.20 0.06 0.00 25.45 61.42 10.28 0.02 0.00	S Cu Fe Ag Hg Co Bornite co-occurring with chalcocite 25.44 60.42 10.61 0.03 0.00 0.00 26.12 61.95 12.24 0.11 0.00 0.05 25.86 61.07 11.11 0.06 0.00 0.01 0.17 0.42 0.35 0.03 0.00 0.01 Bornite forming intergrowths with chalcocite 24.86 61.63 10.28 0.02 0.00 0.00 25.65 63.35 11.57 0.13 0.00 0.00 25.22 62.78 10.79 0.06 0.00 0.00 0.14 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Chemical composition of bornite (orange/pink) from the shale ore of the Nowa Sól deposit

sulpharsenides. They occur as aggregates on their own or as intergrowths with Ag-bearing chalcocite (e.g. in the form of veinlets). They can be also associated with chalcocite-group minerals (Fig. 7). In this type of Ag-amalgam, on average 87.59 wt.% Ag and 10.23 wt.% Hg were detected. Apart from that, intergrowths of Hg-poor Ag-amalgams with brown-grey bornite were documented in bornite-dominated mineralization. Their average chemical composition is 90.04 wt.% Ag and 7.14 wt.% Hg. Hg-rich Ag-amalgams form inclusions in aggregates of Ag-bearing chalcocite, in the sample mineralized almost exclusively with chalcocite (both Ag-barren and Ag-bearing). The average amount of Ag and Hg in Hg-rich Ag-amalgams is 65.25 wt.% and 31.08 wt.%, respectively.

Stromeyerite is associated with native Ag and Ag-amalgams, commonly in the form of grains and rims surrounding Ag minerals inclusions in chalcocite (3 samples, n = 15). In two samples, it was observed together with native Ag inclusions in aggregates of Ag-bearing chalcocite. This variety of stromeverite contains average values of 49.06 wt.% Ag, 34.92 wt.% Cu and 14.33 wt.% S. Apart from that, Cu-Ag sulphide with chemical composition slightly differing from stoichiometric stromeyerite and revealing some Hg enrichment, was documented. It is associated with Hg-poor Ag-amalgams, occurring in the sample mineralized with Cu-S sulphides, accompanied by Co-Ni sulpharsenides (Fig. 7). It contains on average 41.52 wt.% Cu, 37.24 wt.% Ag, 15.12 wt.% S and 4.28 wt.% Hg, although its chemical composition is varied: Hg content ranges between 0.20 and 8.72 wt.%, while Ag content is between 23.50 and 52.81 wt.%.

The empirical formula of the stromeyerite (recalculated to 3 apfu) is $Cu_{0.99-1.29}Ag_{0.79-1.08}S_{0.83-1.02}$ (on average $Cu_{1.14}Ag_{0.94^-}S_{0.92}$). The average empirical formula of the Hg-bearing stromeyerite is $Cu_{1.30}Ag_{0.71}Hg_{0.04}S_{0.94}$. The empirical formula of the stromeyerite recalculated to 1 atom of sulphur is $Cu_{1.04-1.45^-}Ag_{0.79-1.27}S$ (on average $Cu_{1.24}Ag_{1.03}S$). The average empirical formula of the Hg-bearing stromeyerite is $Cu_{1.32}Ag_{0.78}Hg_{0.05}S$.

Co-Ni sulpharsenides have been studied in 2 samples (n = 35). They form numerous, round, several μ m-size exsolutions in chalcocite-djurleite composites. They always occur in Ag-barren chalcocite-group minerals, even in samples where both varieties of this mineral were observed.

Two of the Co-Ni sulpharsenides identified are members of the cobaltite-gersdorffite series. They contain similar amounts of Co and Ni and differ only slightly in the proportions between both metals (Table 4). In the first type, Ni slightly prevails. The average chemical composition of this variety is 16.68 wt.% Ni, 13.69 wt.% Co, 41.96 wt.% As, 17.85 wt.% S and 8.20 wt.% Cu. In the second type, Co prevails over Ni (Fig. 7). It contains an average of 19.45 wt.% Co, 10.72 wt.% Ni, 41.58 wt.% As, 18.98 wt.% S and 8.02 wt.% Cu.

One more Co-Ni mineral was identified. Its average chemical composition is 27.12 wt.% Ni, 39.94 wt.% As, 5.13 wt.% S and 19.23 wt.% Cu (Table 4). Moreover, on average 2.51 wt.% of Bi and 1.61 wt.% of Sb were observed. Low sulphur content (which may result from the surrounding chalcocite) indicates this mineral as a Ni-arsenide (nickeline?). The Ni content is lower than in typical nickeline and significant concentrations of Cu were detected instead. Co-Ni-rich sulpharsenides/arsenides from the Nowa Sól deposit are generally difficult objects to examine using EPMA, due to their small size. Therefore, significant amounts of Cu in their analyses may partially result from the surrounding chalcocite.

The empirical formula of the mineral from the cobaltitegersdorffite series in which Ni prevails (recalculated to 3 apfu) is (Ni_{0.44-0.52}Co_{0.35-0.45}Cu_{0.12-0.31})As_{0.90-1.00}S_{0.89-1.00} (on average (Ni_{0.48}Co_{0.40}Cu_{0.22})As_{0.95}S_{0.95}). The empirical formula of the mineral from the cobaltite-gersdorffite series in which Co prevails is (Co_{0.45-0.69}Ni_{0.21-0.40}Cu_{0.10-0.35})As_{0.88-0.97}S_{0.96-1.03} (on average (Co_{0.55}Ni_{0.31}Cu_{0.21})As_{0.93}S_{0.99}).

Galena was analysed in 3 samples (n = 19) mineralized with bornite and chalcocite. It occurs as inclusions in bornite and/or chalcocite aggregates or as fine grains disseminated in the

wt.%	S	Cu	Fe	Ag	Hg	Co	Ni	Sb	As	Zn	Bi	Cd	Au
					1	Native A	١g						
Min	0.02	0.29	0.00	93.24	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00
Max	0.36	4.41	0.08	97.69	4.44	0.05	0.00	0.03	0.07	0.28	0.06	0.88	0.00
Mean	0.10	1.29	0.01	96.13	1.35	0.00	0.00	0.01	0.00	0.03	0.01	0.50	0.00
S.D.	0.09	1.05	0.02	1.31	0.99	0.01	0.00	0.01	0.01	0.06	0.01	0.29	0.00
			Ag	g-amalga	m Hg-pc	or (co-	occurrin	g chalc	ocite)				
Min	0.03	0.13	0.00	82.49	3.09	0.00	0.00	0.00	0.00	0.03	0.00	0.17	0.00
Max	0.08	1.18	0.00	94.46	14.96	0.03	0.12	0.00	0.00	0.04	0.07	0.26	0.00
Mean	0.05	0.64	0.00	87.59	10.23	0.01	0.02	0.00	0.00	0.01	0.02	0.23	0.00
S.D.	0.02	0.31	0.00	4.07	4.15	0.01	0.04	0.00	0.00	0.01	0.02	0.03	0.00
			Ag	-amalgaı	n Hg-po	or (inter	growth	s with b	ornite)		-		
Min	0.02	0.31	0.09	87.24	4.63	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00
Max	1.41	2.87	1.41	93.08	9.39	0.01	0.00	0.02	0.00	0.10	0.00	0.84	0.05
Mean	0.32	1.02	0.32	90.04	7.14	0.00	0.00	0.00	0.00	0.01	0.00	0.41	0.00
S.D.	0.45	0.74	0.38	1.59	1.23	0.00	0.00	0.01	0.00	0.03	0.00	0.27	0.02
					Ag-am	nalgam	Hg-rich						
Min	0.07	0.47	0.00	60.75	28.06	0.01	0.00	0.00	0.00	0.00	0.00	0.09	0.00
Max	1.47	8.22	0.12	67.50	32.82	0.04	0.00	0.04	0.00	0.04	0.00	0.17	0.00
Mean	0.36	2.67	0.02	65.25	31.08	0.02	0.00	0.01	0.00	0.01	0.00	0.13	0.00
S.D.	0.39	2.01	0.03	1.65	0.98	0.01	0.00	0.01	0.00	0.02	0.00	0.02	0.00
				Strome	yerite (as	ssociate	d with	native A	\g)				
Min	12.46	29.49	0.04	42.85	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.04	0.00
Max	16.37	39.44	0.04	54.56	2.49	0.00	0.00	0.02	0.00	0.31	0.03	0.44	0.00
Mean	14.33	34.92	0.00	49.06	0.25	0.00	0.00	0.00	0.00	0.07	0.01	0.20	0.00
S.D.	1.41	3.06	0.01	3.75	0.75	0.00	0.00	0.01	0.00	0.09	0.01	0.15	0.00
		Stro	meyeri	te Hg-be	aring (as	sociate	d with I	-Ig-pooi	r Ag-am	algam)			
Min	11.64	28.55	0.02	23.50	0.20	0.02	0.02	0.00	0.00	0.03	0.00	0.07	0.00
Max	17.67	56.75	0.04	52.81	8.72	0.12	0.03	0.00	0.00	0.04	0.05	0.14	0.00
Mean	15.12	41.52	0.02	37.24	4.28	0.05	0.02	0.00	0.00	0.03	0.01	0.12	0.00
S.D.	2.20	10.24	0.02	11.45	3.75	0.05	0.02	0.01	0.00	0.02	0.02	0.03	0.00

Chemical composition of Ag minerals from the shale ore of the Nowa Sól deposit

Table 4

Chemical composition of Co-Ni minerals from the shale ore of the Nowa Sól deposit

wt.%	S	Cu	Fe	Ag	Hg	Co	Ni	Sb	As	Zn	Bi	Cd	Au
		Μ	ineral fi	rom the	cobalti	te-gersd	orffite se	ries witl	n Ni prev	ailing			
Min	16.36	4.39	0.02	0.00	0.00	12.05	15.15	0.00	39.54	0.00	0.07	0.00	0.00
Max	19.24	11.68	0.06	0.00	0.00	15.39	17.95	0.16	43.29	0.02	1.13	0.02	0.00
Mean	17.85	8.20	0.01	0.00	0.00	13.69	16.68	0.02	41.96	0.01	0.26	0.00	0.00
S.D	0.75	2.51	0.02	0.00	0.00	1.09	0.99	0.05	1.10	0.01	0.35	0.01	0.00
Mineral from the cobaltite-gersdorffite series with Co prevailing													
Min	18.47	3.82	0.00	0.00	0.00	15.94	7.20	0.00	39.08	0.00	0.07	0.00	0.00
Max	19.59	13.58	0.19	0.04	0.00	24.03	13.94	0.02	43.00	0.04	0.22	0.00	0.06
Mean	18.98	8.02	0.10	0.01	0.00	19.45	10.72	0.00	41.58	0.01	0.13	0.00	0.01
S.D	0.31	3.02	0.05	0.01	0.00	2.30	2.28	0.01	1.05	0.01	0.05	0.00	0.02
						Ni-arse	nide?						
Min	3.10	14.82	0.02	0.02	0.00	1.91	24.54	0.19	37.49	0.07	1.10	0.00	0.00
Max	6.01	22.83	0.08	0.03	0.00	4.54	29.65	3.21	45.29	0.07	8.05	0.00	0.00
Mean	5.13	19.23	0.03	0.01	0.00	3.11	27.12	1.61	39.94	0.01	2.51	0.00	0.00
S.D.	1.08	3.12	0.03	0.01	0.00	0.85	1.89	0.99	2.54	0.03	2.50	0.00	0.00

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Pb	Bi	Cd	Au	
							Galena								
Min	13.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.44	0.51	0.00	0.00	
Max	14.11	2.94	0.40	0.05	0.07	0.06	0.06	0.00	0.00	0.10	86.14	0.69	0.00	0.10	
Mean	13.78	1.45	0.12	0.00	0.00	0.01	0.01	0.00	0.00	0.01	85.05	0.57	0.00	0.02	
S.D.	0.27	0.88	0.14	0.01	0.02	0.02	0.02	0.00	0.00	0.03	0.54	0.04	0.00	0.03	
	Sphalerite														
Min	30.41	0.99	0.03	0.00	0.00	0.00	0.00	0.00	0.00	59.02	0.11	0.00	0.48	0.00	
Max	33.14	1.63	0.17	0.16	0.00	0.00	0.00	0.00	0.00	62.90	0.11	0.00	0.61	0.06	
Mean	32.21	1.29	0.07	0.06	0.00	0.00	0.00	0.00	0.00	61.39	0.11	0.00	0.57	0.02	
S.D.	1.56	0.32	0.09	0.08	0.00	0.00	0.00	0.00	0.00	2.08	0.00	0.00	0.08	0.04	

Chemical composition of galena and sphalerite from the shale ore of the Nowa Sól deposit

shales. The galena examined contains on average 85.05 wt.% Pb and 13.78 wt.% S (Table 5). An averages of 1.45 wt.% Cu and 0.57 wt.% Bi were also detected.

The empirical formula of galena from the samples analysed (recalculated to 2 apfu) is $Pb_{0.97-1.01}S_{0.99-1.03}$ (on average $Pb_{0.99}S_{1.01}$). The empirical formula of the galena (recalculated to 1 atom of sulphur) is $Pb_{0.94-1.02}S$ (on average $Pb_{0.98}S$).

Sphalerite was studied in one sample (n = 3), as intergrowths with chalcocite and native Ag. It contains on average 61.39 wt.% Zn, 32.21 wt.% S, 1.29 wt.% Cu and 0.57 wt.% Cd (Table 5).

The average empirical formula of the sphalerite analysed (recalculated to 2 apfu) is $Zn_{0.97}S_{1.03}$. The average empirical formula of the sphalerite (recalculated to 1 atom of sulphur) is $Zn_{0.93}S$.

THE MOZÓW DEPOSIT

MINERALOGY

The shale ore in this deposit contains rich chalcocite mineralization. Bornite mineralization was observed in the upper part of the shale ore. Small inclusions of Ag minerals are common. Other accompanying sulphides are digenite and covellite. Only minor amounts of galena were noted, while sphalerite is virtually absent. Pb and Zn contents are in general lower in the Mozów deposits than in the Nowa Sól and Sulmierzyce North deposits (Pietrzela and Bieńko, 2023). Co-Ni sulpharsenides are present in the shale ore, but they are difficult to document, as they occur in the form of fine and very fine disseminated grains.

Chalcocite occurs mainly as rich disseminated mineralization (Fig. 8A). Chalcocite grains and aggregates are often elongated concordantly with the shale lamination. In some parts of the shale ore, abundant, densely packed chalcocite aggregates and lenses replace carbonates, forming semi-massive, vein-like accumulations (Fig. 8B). Horizontal veinlets of massive chalcocite were also documented (Fig. 8C). The chalcocite mineralization is locally accompanied by fine grains and inclusions of Ag minerals (Fig. 8F), digenite, covellite and minor galena.

Bornite was recognised in the form of disseminated mineralization of low tenor (Fig. 8D). Similarly to chalcocite, bornite aggregates are often elongated concordantly with shale lamination (Fig. 8E). Dispersed bornite may be accompanied by digenite and/or covellite (in the form of fine individuals or intergrowths in bornite; Fig. 8E), as well as by numerous μ m-size pyrite framboids, partially replaced by bornite.

Digenite co-occurs with rich chalcocite disseminations. It was also observed as intergrowths with bornite grains, together with covellite (Fig. 8E).

Covellite was noted mainly in bornite-dominated mineralization, as fine intergrowths in bornite grains, together with digenite (Fig. 8E). In the chalcocite-dominated mineralization covellite may occur as fine individuals dispersed in the host rock.

Silver minerals were documented as fine and very fine grains disseminated in the host rock (Fig. 8F) or as fine inclusions in chalcocite. In the chemical analyses, stromeyerite was identified.

Galena was observed in minor amounts, as fine disseminations and inclusions in fine-grained chalcocite. Inclusions of galena in veinlets of massive chalcocite were also noted.

MINERAL DISTRIBUTION

In the shale ore of the Mozów deposit, Cu-S sulphides predominate over Cu-Fe-S phases. Chalcocite was documented in most of the samples investigated. The proportion of bornite increases in the uppermost part of the shale ore. Both the chalcocite and bornite mineralization may be accompanied by digenite and covellite. The Ag minerals and galena co-occur with chalcocite-dominated mineralization. Lateral zonation of minerals was not observed in this deposit; however, further boreholes would help determine whether any zonation pattern occurs in the adjacent area.

GEOCHEMISTRY

Chalcocite was studied in 2 samples (n = 17), mainly in the form of disseminated mineralization, and less often in veinlets. The average amount of Ag in the disseminated chalcocite is 0.17 wt.% (Table 6), while an average of 0.36 wt.% Ag was detected in the chalcocite veinlets. Therefore, the chalcocite in the Mozów deposit can be generally classified as Ag-barren.

The empirical formula of the chalcocite (recalculated to 3 apfu) is $Cu_{1.91-2.02}S_{0.98-1.08}$ (on average $Cu_{1.95}S_{1.04}$). The empirical formula of the chalcocite (recalculated to 1 atom of sulphur) is $Cu_{1.78-2.06}S$ (on average $Cu_{1.87}S$).



Fig. 8. Photomicrographs of ore mineralization in the Mozów deposit, reflected light

A – disseminated chalcocite (cc) mineralization; B – abundant chalcocite (cc) grains and lenses replacing carbonates; C – horizontal veinlet of massive chalcocite (cc); D – disseminated mineralization of low tenor, composed of pink bornite (bn2) with digenite (dg) and covellite (cv) intergrowths; E – elongated aggregates of pink bornite (bn2) with intergrowths of digenite (dg) and covellite (cv); F – Ag mineral (Ag) surrounded by disseminated chalcocite (cc)

Bornite was examined in one sample (n = 47), as finegrained, disseminated mineralization. It contains an average of 60.37 wt.% Cu and 11.42 wt.% Fe (Table 7). The average amount of Ag in the bornite is 0.29 wt.%. In most of the analyses, concentrations of Ag were from 0.03 to 0.81 wt.%; however, several analyses revealed Ag contents in the bornite exceeding 3.0 wt.%.

The empirical formula of the bornite (recalculated to 10 apfu) is $Cu_{4.53-4.87}Fe_{0.85-1.10}S_{4.11-4.49}$ (on average $Cu_{4.80}Fe_{1.03}S_{4.17}$). The empirical formula of the bornite recalculated to 4 atoms of sulphur is $Cu_{4.15-4.73}Fe_{0.76-1.03}S_4$ (on average $Cu_{4.60}Fe_{0.99}S_4$).

Ag minerals were analysed in one sample (n = 5), as fine grains, accompanying chalcocite-dominated disseminated mineralization (Fig. 9). Two Cu-Ag sulphides were identified. One is most likely stromeyerite (although its chemical composition slightly differs from stoichiometric stromeyerite), containing on average 44.53 wt.% Ag, 38.91 wt.% Cu and 16.25 wt.% S. The other is most likely Hg-bearing stromeyerite. It contains 36.05 wt.% Cu, 34.56 wt.% Ag, 16.29 wt.% S and 11.24 wt.% Hg.

The empirical formula of the stromeyerite (without Hg), recalculated to 3 apfu is $Cu_{1.06-1.29}Ag_{0.72-0.93}S_{0.98-1.00}$ (on average $Cu_{1.20}Ag_{0.81}S_{0.99}$). The average empirical formula of the

Table 6

Chemical composition of chalcocite from the shale ore of the Mozów deposit

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
				Chalcoo	cite (dis	semina	ted min	eralizat	ion)				
Min	19.59	76.59	0.06	0.13	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00
Max	20.73	79.99	0.13	0.22	0.00	0.00	0.00	0.03	0.00	0.09	0.00	0.00	0.08
Mean	20.15	78.39	0.08	0.17	0.00	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.02
S.D.	0.51	1.23	0.03	0.04	0.00	0.00	0.00	0.01	0.00	0.04	0.00	0.00	0.04

Table 7

Chemical composition of bornite from the shale ore of the Mozów deposit

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
						Bornit	е						
Min	25.94	55.95	9.58	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	28.99	61.50	12.09	3.67	0.24	0.06	0.00	0.03	0.05	0.11	0.08	0.06	0.11
Mean	26.47	60.37	11.42	0.29	0.01	0.00	0.00	0.00	0.01	0.02	0.01	0.00	0.02
S.D.	0.46	1.13	0.36	0.81	0.04	0.01	0.00	0.00	0.01	0.03	0.02	0.01	0.03



Fig. 9A – BSE image of disseminated chalcocite (cc), with inclusions of Hg-bearing stromeyerite (smy); B – elemental mapping showing distribution of Cu; D – elemental mapping showing distribution of Ag; E – EDS spectrum of Hg-bearing stromeyerite

Hg-bearing stromeyerite is $Cu_{1.17}Ag_{0.66}Hg_{0.12}S_{1.05}$. The empirical formula of the stromeyerite (without Hg), recalculated to 1 atom of sulphur is $Cu_{1.06-1.32}Ag_{0.74-0.93}S$ (on average $Cu_{1.21}-Ag_{0.82}S$). The average empirical formula of the Hg-bearing stromeyerite is $Cu_{1.12}Ag_{0.63}Hg_{0.11}S$.

Galena was examined as fine grains, accompanying chalcocite-dominated disseminated mineralization (only one analysis available). It contains 83.44 wt.% Pb, 13.48 wt.% S, and 0.60 wt.% Bi.

The empirical formula of the galena (recalculated to 2 apfu) is $Pb_{0.99}S_{1.01}$. The empirical formula of the galena (recalculated to 1 atom of sulphur) is $Pb_{0.98}S$.

THE SULMIERZYCE NORTH DEPOSIT

MINERALOGY

The shale ore in this deposit is mineralized predominantly with chalcocite and bornite in various proportions. Unlike in the Nowa Sól and Mozów deposits, mineralization composed almost exclusively of Cu-S sulphides is rare in the samples investigated, whereas chalcopyrite enrichments are characteristic of this deposit. Among accompanying minerals there are digenite, covellite, tennantite-tetrahedrite group minerals and pyrite. A distinctive feature of the Sulmierzyce North deposit is that sphalerite and galena are common minerals co-occurring with Cu-sulphides in the shale ore. Ag minerals, as well as Co-Ni sulpharsenides, are present, but due to the very fine size of their grains, they are difficult to observe. Ag concentrations in the shale ore are generally lower than in the Nowa Sól deposit (Pietrzela and Bieńko, 2023) and grains of Ag minerals are smaller and more dispersed than in the Nowa Sól deposit. Co-Ni sulpharsenides form µm-size exsolutions in the chalco-cite aggregates.

Chalcocite occurs mainly in the form of disseminated mineralization. Thin lenses concordant with shale lamination and replacements of pyrite framboids are common (Fig. 10A). Chalcocite can also replace bioclasts (mostly foraminifera). In the highly mineralized samples, accumulations of fine chalcocite grains were observed in the form of continuous layers or lenses. Semi-massive laminae, composed of chalcocite aggregates and pseudo-veins, were also documented in the samples containing particularly rich mineralization (Fig. 10B).



Fig. 10. Photomicrographs of the ore mineralization in the Sulmierzyce North deposit, reflected light

A – disseminated and streak chalcocite (cc) mineralization; B – semi-massive chalcocite (cc) mineralization; C – sulphide layer composed of chalcocite (cc) and orange bornite (bn1); D – intergrowths of chalcocite (cc) with orange bornite (bn1) forming disseminated mineralization; E – bornite-dominated (bn1) mineralization in the form of a semi-massive layer and bornite aggregates; F – abundant semi-massive mineralization, consisting exclusively of elongated chalcopyrite (ccp) aggregates

Chalcocite can be the dominant ore mineral, particularly in the lowermost parts of the shale ore. In such cases it is usually accompanied by digenite and covellite, with minor bornite. Chalcocite often co-occur with bornite in various proportions, both in disseminated mineralization (Fig. 10D) and in semi-massive laminae (Fig. 10C). Accessory minerals in the chalcocite-bornite mineralization are galena and sphalerite.

Bornite is the second most widespread ore mineral. Similarly to chalcocite, it occurs mainly as fine-grained, disseminated mineralization. Bornite commonly replaces pyrite framboids dispersed in the host rock. Coarse-grained aggregates and nests were observed, locally forming semi-massive layers (Fig. 10E). Irregular, vertical or diagonal bornite veinlets were also documented. Similarly to the Nowa Sól deposit, orange bornite predominates in the Sulmierzyce North deposit. Pink bornite is rare, mainly as fine individuals dispersed in the host rock.

In the bornite-dominated mineralization, chalcocite and digenite may occur, as well as minor sphalerite, galena and pyrite. Mineralization composed of both bornite and chalcocite (either dispersed or semi-massive) was also observed (Fig. 10C, D). Moreover, a characteristic paragenesis was recognised, consisting of bornite, chalcopyrite and sphalerite, accompanied by tennantite-tetrahedrite group minerals and galena. These sulphides occur as irregular intergrowths, dispersed in the shale ore (Fig. 11A, B) or concentrated in the form of rich accumulations (Fig. 11C, D). Coarse-grained nests consisting of bornite, chalcopyrite, tennantite-tetrahedrite group minerals and pyrite were also noted (Fig. 11E, F).

Chalcopyrite enrichments are commonly observed. In some of the samples studied, chalcopyrite is the dominant ore mineral. It occurs as fine disseminations, irregular aggregates, flat lenses and thin veinlets. The chalcopyrite-dominated mineralization

may be accompanied by galena, sphalerite and minor bornite. Locally, the shale ore contains abundant, semi-massive mineralization, consisting almost exclusively of elongated chalcopyrite aggregates (with only minor pyrite inclusions; Fig. 10F). Intergrowths of chalcopyrite with bornite, tennantite-tetrahedrite group minerals and sphalerite, with accessory galena and pyrite, were recognised either as disseminated mineralization (Fig. 11A–D), or as coarse-grained nests (Fig. 11E, F).

Digenite is an accompanying mineral in the chalcocite-dominated mineralization and, to a lesser extent, in the parts of the shale ore mineralized predominantly with bornite. It forms individuals and aggregates, or intergrowths with other sulphides.

Covellite is an accessory mineral, associated mainly with the chalcocite-digenite mineralization, containing minor bornite. It forms small grains or intergrowths with sulphide aggregates.

Tennantite-tetrahedrite group members are accompanying minerals in the Cu-dominated mineralization. They were observed as intergrowths with bornite, chalcopyrite, sphalerite and minor galena, dispersed in the host rock (Fig. 11A–D), or as coarse-grained nests together with chalcopyrite, bornite and pyrite (Fig. 11E, F).

Sphalerite commonly accompanies Cu-sulphides. Unlike in the Nowa Sól and Mozów deposits, Zn concentrations in the shale ore of the Sulmierzyce North deposit exceed Pb concentrations (Pietrzela and Bieńko, 2023) and sphalerite prevails over galena. Sphalerite was observed in the bornite-dominated mineralization (with minor chalcocite and digenite), as well as in chalcopyrite-dominated areas (with galena and minor bornite). Sphalerite occurs also in intergrowths with bornite, chalcopyrite, tennantite-tetrahedrite group minerals and galena (Fig. 11B–D). Sphalerite grains are also disseminated in the host rock.



Fig. 11. Photomicrographs of the ore mineralization in the Sulmierzyce North deposit, reflected light

A – aggregates composed of chalcopyrite (ccp), orange bornite (bn1), tennantite (tn) and galena (gn); B – aggregates of orange bornite (bn1) and sphalerite (sp) accompanied by chalcopyrite (ccp) and galena (gn); C – intergrowths of chalcopyrite (ccp) with orange bornite (bn1) and sphalerite (sp); D – disseminated mineralization consisting of sphalerite (sp) and orange bornite (bn1) aggregates, accompanied by tennantite (tn), chalcopyrite (ccp) and galena (gn); E – sulphide nest composed of chalcopyrite (ccp), orange bornite (bn1), pyrite (py) and sphalerite (sp); F – intergrowth of chalcopyrite (ccp) with tennantite (tn) in the form of a semi-massive sulphide nest

Galena usually forms small inclusions in aggregates of other minerals, mainly bornite, sphalerite and chalcopyrite (Fig. 11A, B, D). It is also an accompanying mineral in the chalcopyrite-dominated mineralization. Fine grains of galena can be dispersed in the host rock. Rarely it replaces bioclasts.

Pyrite commonly occurs as µm-size framboids, disseminated throughout almost the entire shale ore, particularly in areas of bornite-dominated mineralization. It also accompanies the chalcopyrite-dominated mineralization (in the form of small inclusions) and chalcopyrite-bornite-tennantite-tetrahedrite mineralization (Fig. 11E).

MINERALS DISTRIBUTION

The mineral assemblage in the Sulmierzyce North deposit consists of Cu-S and Cu-Fe-S sulphides in various proportions; however, no evident zonation in their distribution was recognised. At the NW and SE margin of the deposit Cu-S sulphides predominate (chalcocite and digenite), accompanied by covellite and bornite. In the northern/central and SW parts of the deposit, bornite and chalcocite are the main ore minerals (with accessory sphalerite, galena and digenite). In the central part of the deposit, bornite is the main Cu-sulphide, accompanied by sphalerite, galena, chalcopyrite, tennantite-tetrahedrite group minerals and pyrite. In the northern part of the deposit, apart from chalcocite and bornite, chalcopyrite enrichments were observed. The most abundant chalcopyrite mineralization was documented at the NE margin of the deposit, with accessory sphalerite, galena and bornite.

Development of the ore mineralization in this deposit is less regular than in the mineralization of the Nowa Sól deposit, both vertically and laterally. Laterally, an influence of the distance from the oxidized field on the proportion between Cu-S and Cu-Fe-S sulphides was not observed. Vertically, the typical zonation of minerals is also usually disrupted. In some boreholes, Cu-S sulphides (mainly chalcocite) prevail in the lowermost part of the shale ore, while Cu-Fe-S sulphides (bornite and chalcopyrite) occur in the uppermost part (particularly in the SW part of the deposit). However, there are also boreholes in which rich chalcocite mineralization was not documented at all. Moreover, in some boreholes chalcopyrite was the main ore mineral within the ore series. Apart from that, sphalerite and galena commonly co-occur with the rich Cu-mineralization. Distribution of ore mineralization in the Sulmierzyce North deposits depends mainly on the irregular range of the oxidized fields (Fig. 1), as well as on a significant thickness of shale ore. The patchy distribution of oxidized facies in the Sulmierzyce North area disrupts typical zonation of metals in this deposit (Pietrzela and Bieńko, 2023).

GEOCHEMISTRY

Chalcocite was examined in two samples (n = 38). In the first sample, it accompanies bornite-dominated mineralization and occurs as small aggregates with bornite or sphalerite, disseminated in the shale ore. Chalcocite from this sample contains from 0.03 to 0.19 wt.% Ag (on average 0.08 wt.% Ag). In the second sample, chalcocite is the dominant sulphide, with accessory bornite (mainly in semi-massive accumulations). It

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Table 8

Chemical composition of chalcocite from the shale ore of the Sulmierzyce North deposit

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
					Chalco	ocite (al	l sampl	es)					
Min	19.17	74.24	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	22.65	79.09	0.45	0.58	0.00	0.04	0.06	0.02	0.00	0.57	0.07	0.03	0.08
Mean	21.22	76.95	0.04	0.30	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.01
S.D.	0.78	1.19	0.08	0.17	0.00	0.01	0.01	0.00	0.00	0.14	0.01	0.01	0.02

contains from 0.27 to 0.58 wt.% Ag (on average 0.42 wt.% Ag). In general, the chalcocite can be classified as Ag-barren (Table 8).

Concentrations of other metals are mostly negligible. The chalcocite co-occurring with bornite contains an average of 0.08 wt.% Fe (otherwise it is 0.02 wt.%). In the chalcocite forming intergrowths with sphalerite, 0.17 wt.% Zn was detected.

The empirical formula of the chalcocite analysed (recalculated to 3 apfu) is $Cu_{1.87-2.02}S_{0.98-1.13}$ (on average $Cu_{1.94}S_{1.05}$). The empirical formula of the chalcocite recalculated to 1 atom of sulphur is $Cu_{1.66-2.06}S$ (on average $Cu_{1.84}S$).

Bornite was studied in 3 samples (n = 67). Two types of bornite were distinguished, slightly differing in chemical composition. The first variety was observed either as the main ore mineral, accompanied by minor chalcocite, sphalerite and galena or as intergrowths with chalcopyrite, sphalerite, tennantite-tetrahedrite group minerals and minor galena. It contains on average 60.45 wt.% Cu and 11.33 wt.% Fe (Table 9). The second variety is bornite accompanying semi-massive chalcocite. Its average Cu and Fe concentrations are 64.47 wt.% and 9.56 wt.% respectively. Both varieties of bornite reveal also different admixtures of Ag. In the first type only 0.03 w.% Ag was detected, while in the second it was 0.19 wt.% Ag (Table 9). Admixtures of other metals were not observed.

The empirical formula of the first variety of bornite (recalculated to 10 apfu) is $Cu_{4.60-5.00}Fe_{0.93-1.11}S_{4.06-4.35}$ (on average $Cu_{4.81}Fe_{1.03}S_{4.17}$) and for the second variety it is $Cu_{4.93-5.26}Fe_{0.78-0.99}S_{3.94-4.10}$ (on average $Cu_{5.13}Fe_{0.87}S_{4.00}$). The empirical formula of the first variety of bornite, recalculated to 4 atoms of sulphur, is $Cu_{4.23-4.90}Fe_{0.91-1.08}S_4$ (on average $Cu_{4.62}Fe_{0.98}S_4$) and for the second variety it is $Cu_{4.81-5.34}Fe_{0.78-0.97}S_4$ (on average $Cu_{5.13}Fe_{0.87}S_4$).

Chalcopyrite was examined in 2 samples (n = 40), either as the main ore mineral in the shale ore or as intergrowths with bornite, sphalerite and tennantite-tetrahedrite group minerals. In both cases, its chemical composition is similar. On average the chalcopyrite contains 33.18 wt.% Cu, 30.49 wt.% Fe and 34.67 wt.% S (Table 10). Admixtures of other elements were not detected.

The empirical formula of the chalcopyrite (recalculated to 4 apfu) is $Cu_{0.96-1.01}Fe_{0.98-1.03}S_{2.00-2.02}$ (on average $Cu_{0.97}Fe_{1.02}-S_{2.01}$). The empirical formula of the chalcopyrite recalculated to 2 atoms of sulphur is $Cu_{0.95-1.00}Fe_{0.97-1.03}S_2$ (on average $Cu_{0.97}-Fe_{1.01}S_2$).

Tennantite-tetrahedrite group minerals were analysed in one sample (n = 21). Two minerals from this group were distinguished, differing in the proportion between Sb and As (Table 11). The first occurs as intergrowths with bornite, chalcopyrite, sphalerite and minor galena. Its average chemical composition is close to stoichiometric tennantite: 41.83 wt.% Cu, 2.90 wt.% Fe, 17.56 wt.% As, 0.36 wt.% Sb and 28.55 wt.% S. An average of 5.72 wt.% Zn was also noted. The second mineral was observed in the form of intergrowths only with bornite (Fig. 12). It contains on average 40.46 wt.% Cu, 1.56 wt.% Fe, 6.50 wt.% Zn, 11.28 wt.% As and 11.04 wt.% Sb. Its chemical composition indicates that this is a middle member of the tennantite-tetrahedrite series.

The empirical formula of the tennantite (recalculated to 29 apfu) is $Cu_{9.75-10.01}Fe_{0.64-0.96}Zn_{1.18-1.68}As_{3.42-3.60}S_{13.37-13.51}$ (on average $Cu_{9.93}Fe_{0.78}Zn_{1.32}As_{3.54}S_{13.43}$). The empirical formula of the second mineral from the tennantite-tetrahedrite group (recalculated to 29 apfu) is $Cu_{9.86-10.18}Fe_{0.35-0.65}Zn_{1.49-1.63}As_{2.14-2.53}Sb_{1.30-1.55}S_{13.15-13.37}$ (on average $Cu_{9.95}Fe_{0.44}Zn_{1.55}As_{2.35}Sb_{1.42}S_{13.29}$). The empirical formula of the tennantite (recalculated to

Table 9

wt.%	S	Cu	Fe	Ag	Hg	Co	Ni	Sb	As	Zn	Bi	Cd	Au
					Bornit	e (the fi	irst type	e)					
Min	25.62	57.56	10.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	27.49	62.97	12.30	0.10	0.06	0.20	0.06	0.05	0.64	1.08	0.07	0.04	0.13
Mean	26.42	60.45	11.33	0.03	0.00	0.01	0.01	0.00	0.02	0.07	0.00	0.00	0.02
S.D.	0.41	1.00	0.45	0.03	0.01	0.04	0.02	0.01	0.10	0.19	0.01	0.01	0.03
	Bornite (the second type)												
Min	25.07	61.09	8.61	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	25.84	66.54	10.95	0.29	0.00	0.03	0.00	0.03	0.05	0.10	0.00	0.03	0.08
Mean	25.38	64.47	9.56	0.19	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
S.D.	0.22	1.66	0.77	0.05	0.00	0.01	0.00	0.01	0.01	0.03	0.00	0.01	0.02
					Borni	te (all s	amples)					
Min	25.07	57.56	8.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	27.49	66.54	12.30	0.29	0.06	0.20	0.06	0.05	0.64	1.08	0.07	0.04	0.13
Mean	26.13	61.59	10.83	0.08	0.00	0.01	0.00	0.00	0.02	0.05	0.00	0.00	0.01
S.D.	0.60	2.19	0.98	0.08	0.01	0.03	0.01	0.01	0.08	0.17	0.01	0.01	0.03

Chemical composition of bornite from the shale ore of the Sulmierzyce North deposit

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au
					С	halcop	rite						
Min	34.30	32.74	29.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	35.06	34.27	30.98	0.05	0.00	0.08	0.00	0.02	0.07	0.10	0.05	0.02	0.09
Mean	34.67	33.18	30.49	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.02
S.D.	0.15	0.36	0.38	0.01	0.00	0.01	0.00	0.00	0.02	0.02	0.01	0.00	0.03

Chemical composition of chalcopyrite from the shale ore of the Sulmierzyce North deposit

Table 11

Chemical composition of tennantite-tetrahedrite group minerals from the shale ore of the Sulmierzyce North deposit

wt.%	S	Cu	Fe	Ag	Hg	Со	Ni	Sb	As	Zn	Bi	Cd	Au		
	Tennantite (intergrowths with bornite/sphalerite/chalcopyrite)														
Min	28.40	41.20	2.38	0.00	0.00	0.00	0.00	0.04	16.93	5.11	0.00	0.02	0.00		
Max	28.72	42.26	3.56	0.07	0.00	0.05	0.07	1.07	17.98	7.31	0.00	0.06	0.10		
Mean	28.55	41.83	2.90	0.03	0.00	0.01	0.00	0.36	17.56	5.72	0.00	0.03	0.01		
S.D.	0.10	0.33	0.36	0.02	0.00	0.02	0.02	0.33	0.29	0.57	0.00	0.02	0.03		
	Middle member of the tennantite-tetrahedrite series (intergrowths with bornite)														
Min	26.59	40.15	1.23	0.05	0.00	0.04	0.00	10.19	10.12	6.15	0.00	0.02	0.00		
Max	27.61	40.83	2.30	0.07	0.09	0.04	0.00	12.02	12.23	6.77	0.00	0.08	0.05		
Mean	27.27	40.46	1.56	0.06	0.02	0.01	0.00	11.04	11.28	6.50	0.00	0.05	0.01		
S.D.	0.37	0.25	0.38	0.01	0.04	0.02	0.00	0.65	0.72	0.22	0.00	0.02	0.02		

Table 12

Chemical composition of (palena and sphalerite f	rom the shale ore of the	Sulmierzyce North deposit

wt.%	S	Cu	Fe	Ag	Hg	Co	Ni	Sb	As	Zn	Pb	Bi	Cd	Au
Galena														
Min	12.37	3.02	0.07	0.00	0.00	0.00	bdl	0.00	0.00	0.00	76.13	0.50	0.00	0.00
Max	14.56	8.43	0.49	0.08	0.00	0.00	bdl	0.00	0.00	3.80	82.88	0.65	0.00	0.06
Mean	13.92	5.38	0.24	0.04	0.00	0.00	bdl	0.00	0.00	1.01	79.44	0.57	0.00	0.02
S.D.	0.89	2.46	0.16	0.03	0.00	0.00	bdl	0.00	0.00	1.61	3.13	0.06	0.00	0.03
Sphalerite														
Min	32.62	0.17	0.12	0.02	0.00	0.00	0.05	0.00	0.00	56.62	0.05	0.00	0.14	0.00
Max	33.11	6.73	0.55	0.14	0.00	0.08	0.06	0.00	0.00	64.14	0.15	0.04	0.22	0.00
Mean	32.89	3.48	0.29	0.06	0.00	0.03	0.02	0.00	0.00	60.03	0.10	0.01	0.18	0.00
S.D.	0.20	2.62	0.15	0.06	0.00	0.04	0.03	0.00	0.00	2.91	0.03	0.02	0.03	0.00

bdl – below detection limit

13 atoms of sulphur) is $Cu_{9.46-9.71}Fe_{0.62-0.93}Zn_{1.14-1.63}As_{3.29-3.51}S_{13}$ (on average $Cu_{9.61}Fe_{0.76}Zn_{1.28}As_{3.42}S_{13}$). The empirical formula of the second mineral from the tennantite-tetrahedrite group (recalculated to 13 atoms of sulphur) is $Cu_{9.60-10.07}Fe_{0.34-0.65}Zn_{1.47-1.59}As_{2.12-2.46}Sb_{1.26-1.52}S_{13}$ (on average $Cu_{9.73}Fe_{0.43}Zn_{1.52}As_{2.30}Sb_{1.39}S_{13}$).

Galena was studied in one sample (n = 5), where it occurs as inclusions in aggregates composed of bornite, chalcopyrite and tennantite-tetrahedrite group minerals. Its average chemical composition is 79.44 wt.% Pb and 13.92 wt.% S (Table 12). Also, on average 5.38 wt.% Cu, 1.01 wt.% Zn and 0.57 wt.% Bi were detected. Empirical formula of galena from the sample analysed (recalculated to 2 apfu) is $Pb_{0.91-0.99}S_{1.01-1.09}$ (on average $Pb_{0.95}S_{1.05}$). The empirical formula of the galena recalculated to 1 atom of sulphur is $Pb_{0.83-0.98}S$ (on average $Pb_{0.91}S$).

Sphalerite was examined in one sample (n = 6), where it occurs in aggregates with bornite, chalcopyrite and tennantite-tetrahedrite group minerals. It contains typically 60.03 wt.% Zn, 32.89 wt.% S and 3.48 wt.% Cu (Table 12). Minor concentrations of Fe (0.29 wt.%) and Cd (0.18 wt.%) were observed.

The empirical formula of the sphalerite (recalculated to 2 apfu) is $Zn_{0.92-0.97}S_{1.03-1.08}$ (on average $Zn_{0.94}S_{1.06}$). The empirical formula of the sphalerite recalculated to 1 atom of sulphur is $Zn_{0.85-0.95}S$ (on average $Zn_{0.90}S$).



Fig. 12A – photomicrograph of a mineral from the tennantite-tetrahedrite group (ttr) forming an intergrowth with bornite (bn), with minor inclusions of galena (gn); B – BSE image of a mineral from the tennantite-tetrahedrite group forming an intergrowth with bornite; C – elemental mapping showing distribution of Cu; D – elemental mapping showing distribution of Fe; E – elemental mapping showing distribution of Pb; G – EDS spectrum of a mineral from the tennantite-tetrahedrite group

SUMMARY OF THE RESULTS

In the samples of the shale ore studied from the Nowa Sól, Mozów and Sulmierzyce North deposits, disseminated mineralization is the most widespread mineralization style. Coarse-grained nests and aggregates (which may form semi-massive veins and lenses) were observed mainly in the Nowa Sól deposit. In the Sulmierzyce North deposit they are slightly less frequent, while in the Mozów deposit, disseminated mineralization is accompanied by sulphide veinlets.

In the deposits investigated, chalcocite is the dominant ore mineral and the second most common mineral is bornite. In the Nowa Sól deposit chalcocite may contain Ag admixtures, while in the Mozów and Sulmierzyce North deposits the chalcocite is Ag-barren. In the Nowa Sól deposit, parts of the shale ore are mineralized almost exclusively with chalcocite (disseminated and/or coarse grained). Intergrowths of chalcocite and bornite are less common. Bornite-dominated mineralization was documented only locally and it replaces primary pyrite mineralization. In the Mozów deposit, chalcocite (disseminated or in veinlets) strongly prevails over bornite (mainly disseminated). In the Sulmierzyce North deposit both minerals may occur separately as well as in intergrowths (either chalcocite or bornite may prevail). In the three deposits, orange bornite predominates and pink bornite was recognised in minor amounts. Apart from that, fine grains of Ag-bearing orange-brown and brown-grey varieties of bornite were distinguished in the Nowa Sól deposit.

Other Cu-S minerals, such as digenite, djurleite and covellite, are also present in the shale ore from the three studied deposits. In the Nowa Sól deposit, semi-massive intergrowths of chalcocite with djurleite and/or digenite were noted. Covellite is an accompanying mineral in the Nowa Sól deposit. In the Mozów and Sulmierzyce North deposits, both digenite and covellite are accompanying minerals.

Chalcopyrite was observed only in the Sulmierzyce North deposit, as were minerals from the tennantite-tetrahedrite group. They occur together, in a paragenesis with bornite, sphalerite and minor galena. Apart from that, in some of the samples, shale ore was mineralized almost exclusively with chalcopyrite, which does not contain any significant admixtures.

Ag minerals are present in all the deposits investigated. In the Nowa Sól deposit, native Ag, Ag-amalgams and stromeyerite were documented. Native Ag and Ag-amalgams mainly form inclusions in chalcocite (rarely in bornite), or as disseminated individuals. In the native Ag, admixtures of Hg were consistently detected. The Ag-amalgams vary in Hg content (Hg-rich and Hg-poor varieties were recognised). Stromeyerite forms rims around native Ag and Ag-amalgams. In the Mozów deposit, stromeyerite occurs as very fine grains disseminated in the host rock or small inclusions in chalcocite. Both in the Nowa Sól and Mozów deposits, two types of stromeyerite were distinguished. The first is close to stoichiometric stromeyerite and the second contains some Hg enrichments. In the Sulmierzyce North deposit, Ag minerals were difficult to examine as their grains are smaller and more dispersed than in the other two deposits.

Co-Ni sulpharsenides occur in the shale ore from the three deposits documented, but only in the Nowa Sól deposit was grain size appropriate for chemical analyses. They are represented mainly by middle members of the cobaltite-gersdorffite series, differing in proportions between Co and Ni. In the first type identified, Ni prevails over Co, while in the second Co predominates. Cu-bearing Ni-arsenide was also distinguished. The Co-Ni minerals form abundant accumulations in the samples containing rich chalcocite-djurleite mineralization accompanied by digenite.

In the Nowa Sól deposit, galena and sphalerite form disseminated individuals or intergrowths with Cu-sulphides (galena prevails over sphalerite). In the Sulmierzyce North deposit, both minerals co-occur with Cu mineralization in the shale ore, either with chalcocite and/or bornite or in a chalcopyrite/tennantite-tetrahedrite/bornite paragenesis (sphalerite prevails over galena). In the Mozów deposit, only minor inclusions of galena in chalcocite were noted. In all deposits discussed, galena contains minor admixtures of Bi. In the sphalerite from the Nowa Sól and the Sulmierzyce North deposits, minor Cd concentrations were detected.

Pyrite is common in the Nowa Sól and Sulmierzyce North deposits, mainly in the form of framboids dispersed in the host rock (usually replaced by other sulphides) or together with galena and sphalerite. In the Nowa Sól deposit, aggregates composed of densely packed framboids replaced by bornite were observed. In the Sulmierzyce North deposit, pyrite forms inclusions in chalcopyrite.

Native bismuth was recognised only in the Nowa Sól deposit, as fine inclusions in chalcocite-group minerals.

In the Nowa Sól deposit, the horizontal distribution of ore minerals is strongly influenced by the distance from the oxidized field. Cu-S phases prevail in the close vicinity of the *Rote Fäule* facies. Moving outwards (towards the NE and SE), Cu-Fe-S phases appear in the shale ore. The most abundant Ag minerals were documented slightly farther from the oxidized field than the highest grade Cu mineralization. In the most redox-distant parts of the deposit, Pb-Zn mineralization (accompanied by pyrite) co-occur with Cu-sulphides, which is in accordance with the general pattern of metals distribution in the FSM. Enrichments in Pb and Zn are characteristic also of the SE part of the deposit. In general, the northern margins of the Nowa Sól deposit can be described as a polymetallic zone, where rich Cu-Ag-Zn-Pb mineralization is present in the shale ore. In the Mozów deposit, lateral zonation of metals was not recognised. In the Sulmierzyce North deposit, zonation of minerals typical of the FSM deposits is barely observed. Cu-S and Cu-Fe-S minerals occur in similar proportions, and a distinctive Pb-Zn zone is not developed here. Sphalerite and galena were noted mainly in the samples from the central part of the deposit.

The vertical distribution of the mineralization in the Nowa Sól deposit is influenced by the oxidized zone. Chalcocite is concentrated mainly in the lowermost part of the shale ore, while bornite predominates in its upper part. In the vertical profile of the ore deposit, Ag minerals are usually observed together with the richest Cu mineralization. In the Mozów deposit, the vertical distribution of Cu sulphides is also consistent with the general pattern. Cu-S minerals prevail directly above the redox boundary, while Cu-Fe-S phases predominate in the uppermost part of the shale ore. Chalcocite mineralization is particularly rich in the shale ore. Ag minerals are common in the shale ore, but generally there is no correlation between Cu and Ag in this deposit and the highest Ag concentrations occur higher in the lithological profile than do the richest Cu enrichments (Pietrzela and Bieńko, 2023). The Pb-Zn zone was not detected in the Mozów deposit. In the shale ore, minor amounts of galena were documented and sphalerite is virtually absent. In the vertical distribution of mineralization in the Sulmierzyce North deposit, Cu-S sulphides usually prevail in the lowermost part of the shale ore, while Cu-Fe-S sulphides were noted in the uppermost part, but this typical zonation of minerals can be disrupted. Galena and sphalerite appear in the shale ore as accompanying minerals, together with Cu mineralization. Ag minerals are rare and are always present in the same zone as the richest Cu mineralization. There is a strong correlation between Cu and Ag in the Sulmierzyce North deposit (Pietrzela and Bieńko, 2023).

DISCUSSION

The deposits of the NCB, as well as the deposits of the Lubin-Sieroszowice area (such as Rudna, Polkowice, Sieroszowice, Lubin-Małomice, and Radwanice-Gaworzyce deposits), are *Kupferschiefer*-type deposits; therefore, their geological structure, mineralogy and geochemistry are to some extent similar. However, at a more detailed level, the distribution of ore mineralization and its chemical composition vary across all these deposits.

The Nowa Sól deposit shows some resemblance to the Polkowice, Sieroszowice and Rudna deposits. In all these areas, the ore deposit may consist of sandstones, shales as well as carbonates, while mineralization in the shale ore is strongly dominated by chalcocite (the distribution of ore minerals in the deposits of the Lubin-Sieroszowice area has been described in detail by Pieczonka et al., 2007). Locally, chalcocite concentrations decrease and bornite mineralization occurs instead. However, in the Nowa Sól deposit no chalcopyrite was observed in the shale ore, as opposed to the previously mentioned deposits. Amounts of galena and sphalerite in the shale ore are generally low in the Nowa Sól deposit, similarly to the Polkowice and Sieroszowice deposits. Occurrences of Ni-Co sulpharsenides are characteristic of the Nowa Sól deposit, which were also noted in the SW part of the Polkowice-Sieroszowice area (Pieczonka et al., 2007).

The Mozów deposit can be compared with Radwanice-Gaworzyce deposit, as the ore mineralization in both areas occurs predominantly in shales and carbonates. In the shale ore of the Mozów deposit chalcocite is the main Cu sulphide, similarly to other deposits in the Lubin-Sieroszowice area; however, no chalcopyrite or sphalerite were observed. Bornite mineralization is concentrated in the uppermost part of the *Kupferschiefer*.

In the Sulmierzyce North deposit, the mineralization occurs mainly in shales and to a lesser extent in carbonates, so there is limited similarity with the Polkowice deposit. A characteristic feature of the Sulmierzyce North deposit is chalcopyrite enrichments in the shale ore, which were also documented in most of the other deposits of the Lubin-Sieroszowice area (Polkowice, Sieroszowice, Rudna and Lubin-Małomice deposit). The Sulmierzyce North deposit reveals some galena and sphalerite co-occurring with rich Cu-Ag mineralization, therefore it shows some resemblance to the Rudna and Lubin-Małomice deposits. However, typical Pb-Zn bearing shales, containing only galena and sphalerite mineralization (with no Cu-sulphides), known from Rudna and Lubin-Małomice deposits, were not observed in any of the NCB deposits. A distinctive feature of the Sulmierzyce North deposit is also the presence of a chalcopyrite-bornite-sphalerite-tennantite paragenesis. In the northern part of the Rudna deposit, as well as the eastern part of the Lubin-Małomice deposit, bornite co-occurs with tennantite and chalcopyrite in the uppermost part of the sandstone ore and in the shale ore (Piestrzyński, 2007). Elevated concentrations of tennantite are also known from the Polkowice deposit (Pieczonka et al., 2007).

As in the Lubin-Sieroszowice deposits, the most common Cu-sulphides in all the NCB deposits are sulphides from the Cu-S group, primarily chalcocite. In the Kupferschiefer-type deposits of the FSM, chalcocite-dominated mineralization usually co-occurs with digenite and djurleite (Kucha, 2007: Piestrzyński, 2007; Pieczonka, 2011). Moreover, some authors have distinguished two varieties of chalcocite (Mayer and Piestrzyński, 1985). In several samples from the Nowa Sól deposit, rich mineralization consisting of two or three chalcocite group minerals was observed. It may be composed of two varieties of chalcocite, or different minerals from the chalcocitegroup, such as chalcocite and djurleite, but due to physical and chemical similarities between all members of the chalcocite group minerals, their precise identification using microscopic methods, as well as EMPA analyses, was difficult. It has been suggested that Ag-rich djurleite may often be mistaken for Ag-rich chalcocite in the Kupferschiefer-type deposits of the FSM (Szopa et al., 2021).

In all Kupferschiefer deposits, Cu-S group minerals commonly show admixtures of Ag. The most significant Ag-bearing Cu-sulphide is chalcocite. It was noted by several authors that in the Lubin-Sieroszowice area, the Ag content in chalcocite is the highest when chalcocite co-occurs with Ag minerals. When Ag minerals are not present in the shale ore, Ag concentrates mainly in chalcocite (Kucha, 2007; Piestrzyński, 2007; Kozub-Budzyń and Piestrzyński, 2017). Similarly, in the Nowa Sól deposit, Ag-bearing chalcocite commonly co-occurs with Ag minerals. In some of the samples studied, both varieties of chalcocite were observed: Ag-bearing, with inclusions of Ag minerals, and Ag-barren, lacking inclusions. In the Mozów deposit, this pattern was not documented. The chalcocite analysed can be classified as Ag-barren, but it contains inclusions of Ag minerals nevertheless. However, only few samples from this deposit were studied, so more analyses are required in order to confirm these results. In the Sulmierzyce North deposit the Ag content is the lowest: the chalcocite is Ag-barren and Ag minerals are rare.

Kozub-Budzyń and Piestrzyński (2017) reported, that in the Lubin-Sieroszowice area, chalcocite occurring in paragenesis with native Ag contains an average of 5.51 wt.% Ag, while in chalcocite from samples in which no Ag minerals were present, Ag admixtures are generally lower, on average 2.21 wt.% Ag. According to Mikulski et al. (2020), the average Ag content in chalcocite from the Lubin-Sieroszowice area is 4.59 wt.% Ag. In chalcocite from the shale ore on the Polkowice-Sieroszowice area, analysed by Foltyn et al. (2022), it is 0.37 wt.% Ag. Up to 1.78 wt.% Ag were noted in the chalcocite from the Radwanice-Gaworzyce deposit by Chmielewski et al. (2021). Ag admixtures in other Cu-S minerals have also been documented, but they are in general less than 1.0 wt.% (Kozub-Budzyń and Piestrzyński, 2017; Mikulski et al., 2020; Chmielewski et al., 2021; Foltyn et al., 2022). In the samples from the Nowa Sól deposit, the average Ag content in Ag-bearing chalcocite is 3.97 wt.%, while in Ag-barren chalcocite it is 0.05 wt.%. Particularly Ag-rich chalcocite, with Ag concentrations reaching up to 12.81 wt.% (on average 7.78 wt.% Ag), was also observed. Therefore, the average Ag content in the chalcocite from the Nowa Sól deposit is generally as in the Lubin-Sieroszowice area. Contrary to the results published by Kozub-Budzyń and Piestrzyński (2017), in the Mozów deposit, Ag admixtures in chalcocite are low (typically 0.17 wt.% in the disseminated chalcocite and 0.36 wt.% in chalcocite veinlets), yet it still contains inclusions of Ag minerals. In turn, Ag concentrations in chalcocite from the Sulmierzyce North deposit are as in the Mozów deposit (the average value is 0.30 wt.%) but it does not co-occur with Ag minerals.

Both in the deposit of the Sieroszowice-Lubin area and the NCB, the most important Ag minerals are native Ag, Ag-amalgams and stromeyerite. Ag-bearing minerals usually exhibit Hg enrichments. Kozub-Budzyń and Piestrzyński (2017) detected an average of 96.53 wt.% Ag and 2.92 wt.% Hg in native Ag from the Lubin-Sieroszowice area (the Hg content varies in the range from 0.10 to 6.38 wt.%). The average chemical composition of native Ag from the Nowa Sól deposit is generally similar: 96.13 wt.% Ag and 1.35 wt.% Hg (the Hg content varies from 0.26 to 4.44 wt.%).

In Ag-amalgams from the Lubin-Sieroszowice area, Hg concentrations may reach up to 30 wt.% (Piestrzyński, 2007). For example, 73.17-94.08 wt.% Ag (average 83.58 wt.%) and 6.43-23.90 wt.% Hg (average 14.90 wt.%) was noted in the Ag-amalgams examined by Kozub-Budzyń and Piestrzyński (2017). Ag alloys investigated by Mikulski et al. (2020) contain from 39.68 to 76.71 wt.% Ag (with an average value of 64.22 wt.%) and from 19.56 to 34.46 wt.% Hg (an average value is 22.74 wt.%). In the Nowa Sól deposit, Ag-amalgams poor in Hg, co-occurring with chalcocite-group minerals, contain an average of 87.59 wt.% Ag and 10.23 wt.% Hg, while in Hg-poor Ag-amalgams co-occurring with bornite (brown-grey variety) it is on average 90.04 wt.% Ag and 7.14 wt.% Hg. In the Hg-rich Ag-amalgam forming inclusions in Ag-bearing chalcocite, average Ag and Hg amounts are 65.25 wt.% and 31.08 wt.% respectively. Thus, the chemical composition of Ag-amalgams from the Nowa Sól deposit is slightly more varied than in the Lubin-Sieroszowice area.

In the deposits of the Lubin-Sieroszowice area, it is commonly observed, that at the contact between Cu-sulphides and Ag minerals (mainly native Ag and Ag-amalgams) there are reaction rims, associated with metasomatic replacements of Cu-sulphides by Ag, composed of Cu-Ag sulphides (Salamon, 1979; Kozub-Budzyń and Piestrzyński, 2017; Chmielewski et al., 2021). Kozub-Budzyń and Piestrzyński (2017) reported that reaction rims between Cu-sulphides and native-Ag contain 55.79–68.83 wt.% Cu and 12.38–25.29 wt.% Ag, while reaction rims between Cu-sulphides and Ag-amalgams are composed of Cu-Ag sulphides with Hg admixtures (<1.92 wt.%). Furthermore, reaction rims between Cu-sulphides and native Ag/Ag-amalgams are often composed of stromeyerite. In general, the chemical composition of the minerals from the stromeyerite group is varied in the deposits of the Lubin-Sieroszowice area. According to Piestrzyński (2007), stromeyerite forming intergrowths with Ag-Hg minerals, or co-occurring with rich Ag-Hg mineralization, exhibits significant Hg enrichments, reaching up to 11.02 wt.%. The average chemical composition of stromeyerite, given by Kozub-Budzyń and Piestrzyński (2017) is 50.23 wt.% Ag, 33.99 wt.% Cu and 15.91 wt.% S. The stromeyerite forming intergrowths with Ag-amalgams also contains up to 3.06 wt.% Hg. In the samples from the Lubin deposit, Hg-rich stromeyerite was distinguished, with Hg enrichments reaching up to 12.57 wt.% (Kozub-Budzyń and Piestrzyński, 2017).

In the samples from the NCB deposits, reaction rims composed of Cu-Ag sulphides were also observed, mainly in the Nowa Sól deposit. Their chemical composition is close to stoichiometric stromeyerite, but the proportion between Cu and Ag can vary. Stromeyerite co-occurring with inclusions of native Ag in chalcocite aggregates contains an average of 49.06 wt.% Ag, 34.92 wt.% Cu and 14.44 wt.% S. The average chemical composition of Cu-Ag sulphide associated with inclusions of Hg-poor Ag-amalgam in chalcocite, slightly differs from stoichiometric stromeyerite and reveals some Hg enrichments: 41.52 wt.% Cu, 37.24 wt.% Ag, 15.12 wt.% S and 4.28 wt.% Hg (Hg content ranges between 0.20 and 8.72 wt.%, while Ag content is between 23.50 and 52.81 wt.%). In the Mozów deposit, two Cu-Ag sulphides were identified, accompanying chalcocite-dominated disseminated mineralization. The average chemical composition of the first is also similar to stromeyerite: 44.35 wt.% Ag, 38.91 wt.% Cu and 16.25 wt.% S. The second, presumably Hg-bearing stromeyerite, contains on average 36.05 wt.% Cu, 34.56 wt.% Ag, 16.29 wt.% S and 11.24 wt.% Hg.

As can be seen, the chemical composition of Ag minerals from the NCB deposits, is more less in line with the earlier studies of Ag minerals from the Lubin-Sieroszowice area. It has been noted that development of Ag own minerals in the Kupferschiefer-type deposits was probably different than in the case of Ag admixtures in Cu-minerals (Chmielewski et al., 2021). This observation also applies to the NCB deposits. According to most of the previous studies, the origin of Ag ore minerals is associated with secondary processes (Salamon, 1979; Piestrzyński and Salamon, 1986; Pieczonka, 2011; Kozub-Budzyń and Piestrzyński, 2017). Ag minerals replacing outer parts of Cu-sulphide grains and aggregates, as well as reaction rims at the contact between ore minerals and Ag minerals, indicate that the development of Ag mineralization post-dated the Cu mineralization (Pieczonka, 2011; Kozub-Budzyń and Piestrzyński, 2017; Chmielewski et al., 2021). The occurrences of Cu-Ag minerals around the native Ag and Ag-amalgams in the samples from the NCB corroborate these observations.

Several varieties of bornite have been distinguished in the deposits of the Lubin-Sieroszowice area (Jarosz, 1966; Harańczyk, 1972; Salamon, 1976; Kucha, 2007). Two most common varieties are described as orange and pinkish-purple (Jarosz, 1966; Harańczyk, 1972). The formula of the orange bornite is $Cu_{5-x}Fe_{1+x}S_4$, where x = 0.15. The orange bornite is poor in Ag, as opposed to the pinkish-purple bornite, which always contains some Ag admixtures. In general, Ag admixtures in the bornite may reach up to 30 wt.% (Ag is substituted for Cu). Such Ag-rich bornite (often with Hg enrichments) is characterized by pink-grey and grey-brown colours. Another variety of bornite, described by Kucha (2007) is characterized by Fe deficiency, compensated by higher Cu content (so-called $1/_2$ bornite $Cu_{5.5}Fe_{0.5}S_4$). In the samples from the deposits of the

NCB, bornite is significantly less diverse. In the samples from the Nowa Sól deposit, orange bornite predominates. Pink bornite was also observed in several samples, but it was much less frequent. Both types of bornite show very similar chemical composition. Two Ag-bearing varieties of bornite have also been identified (orange-brown and brow-grey), forming intergrowths with Ag-amalgams; however, they occur in minor amounts. In the Mozów deposit pink bornite occurs, while in the Sulmierzyce North deposit orange bornite predominates.

Ag admixtures can be observed in bornite. According to Kozub-Budzyń and Piestrzyński (2017), Ag admixtures in bornite co-occurring with Ag minerals (in the Lubin-Sieroszowice area) reach from 0.20 to 7.00 wt.% Ag (while the Cu and Fe contents are respectively lower). Bornite from samples in which no Ag minerals are present contains from 0.03 to 1.00 wt.% Ag. Particularly Ag-rich, pink-grey bornite, hosting up to 8.66 wt.% Ag was also documented by these authors. Up to 0.09 wt.% Hg was detected in bornite with significant Ag enrichments, co-occurring with Ag-amalgams. Bornite analysed by Mikulski et al. (2020) is Ag-barren, while in bornite from the shale ore studied by Foltyn et al. (2022) only 0.04 wt.% Ag was reported. Ag concentrations in bornite from the Radwanice-Gaworzyce deposit reach up to 1.16 wt.% (Chmielewski et al., 2021). In the deposits of the NCB, minor amounts of Ag-bearing bornite (containing on average 3.5 wt.% Ag) were documented, only in the Nowa Sól deposit, in the form of fine intergrowths with Ag-amalgams.

Chalcopyrite is common in the deposits from the Lubin-Sieroszowice area. Its chemical composition corresponds to the formula (Fe,Ag)CuS₂ and (Ag,Fe)(Cu,Ag)S₂ (Kucha and Głuszek, 1983). In the deposits of the NCB, chalcopyrite in the shale ore was rarely observed (only in several samples from the Sulmierzyce North deposit). Chalcopyrite in the Lubin-Sieroszowice area, investigated by Kozub-Budzyń and Piestrzyński (2017) does not reveal significant Ag admixtures (up to 0.14 wt.%, on average 0.06 wt.%), while the chalcopyrite studied by Mikulski et al. (2020) is Ag-barren. Numerous samples of chalcopyrite were analysed by Foltyn et al. (2022), but in general Ag concentrations in chalcopyrite from the shale ore do not exceed 0.10 wt.%. In chalcopyrite examined by Chmielewski et al. (2021) up to 0.21 wt.% Ag occurs. Chalcopyrite from the Sulmierzyce North deposit can also be classified as Aq-barren.

Minerals from the tennantite-tetrahedrite group are distributed very irregularly in the Lubin-Sieroszowice area (tennantite is much more frequent than tetrahedrite). Elevated contents of both minerals are associated with epigenetic ore veins (Piestrzyński, 2007). In the Sulmierzyce North deposit, tennantite also prevails over tetrahedrite, but epigenetic veins were not detected.

Both in the deposits of the Lubin-Sieroszowice area and the NCB, minerals from the cobaltite-gersdorffite series occur in the form of very fine grains; therefore, their analyses and comparisons are difficult. Cobaltite reported from the Lubin-Sieroszowice area by Harańczyk (1972) and Kucha (1976) contains up to do 18.4 wt.% Ni, 4.58 wt.% Cu and 0.87 wt.% Fe, which is similar to the results obtained in this study.

Pb-Zn mineralization varies across the FSM deposits. In general, galena concentrates mainly in the uppermost part of the ore series, while sphalerite mineralization predominates slightly above the Cu zone and Pb zone. However, disruptions of the typical zonation are commonly observed (Piestrzyński, 2007). In the deposits of the NCB, the development of the Pb-Zn zone also varies. Only in the Nowa Sól deposit does distribution of both metals follow a typical pattern, as they occur in the distal parts of the mineralized zone. In the Sulmierzyce North deposit the content of galena and sphalerite is lower, but they overlap with Cu-Ag mineralization. In the Mozów deposit, a Pb-Zn zone was not detected.

Differences in Pb and Zn concentrations in all three deposits may indicate different compositions of basement rocks, which were the source of metals carried by mineralizing fluids responsible for the formation of each deposit. It is generally agreed that the main source of metals in the mineralizing fluids were the Rotliegend strata, particularly the Lower Permian volcanics and pre-Permian basement rocks (composed of lower Paleozoic metamorphic rocks and Carboniferous clastic rocks and granite) containing some amounts of hydrothermal sulphide mineralization (Speczik, 1979, 1985; Jowett, 1986; Jowett et al., 1987; Oszczepalski, 1989, 1999; Speczik, 1995). It has been suggested that volcanic and sedimentary basement rocks and Lower Permian volcanics served as the main sources of Cu while acid intrusive rocks of Late Carboniferous age were responsible for elevated Pb concentrations in some occurrences (Speczik and Rydzewski, 1983; Speczik et al., 1986). In the Nowa Sól deposit, a relatively well-developed Pb-Zn zone may result from the presence of Carboniferous granites in the basement rocks (Speczik, 1979, 1985; Jowett, 1986; Jowett et al., 1987; Oszczepalski, 1989, 1999; Speczik, 1995). Significantly lower contents of Pb and Zn in the Mozów and Sulmierzyce North deposits may result from the considerable distance from the Fore-Sudetic Block and lack of Variscan granites in the feeder area during the Rotliegend period, when palaeo-depressions were being filled with deposit.

CONCLUSIONS

Ore mineralization in the shale ore from the deep Cu-Ag deposits documented in the Northern Copper Belt shows pronounced differences. This may indicate varied ore-forming processes and different compositions of mineralizing brines responsible for development of each deposit, perhaps resulting from distinct compositions of the source rocks.

In all three deposits, chalcocite is the dominant ore mineral and the second most common mineral is bornite. In the shale ore of the Nowa Sól deposit, the proportion of bornite increases with increasing distance from the oxidized facies. In the shale ore of the Mozów deposit, chalcocite strongly prevails over bornite. In the Sulmierzyce North deposit, chalcocite and bornite occur in similar amounts, but they are distributed less regularly. Moreover, Sulmierzyce North is the only deposit with significant amounts of chalcopyrite and minerals from the tennantite-tetrahedrite group in the shale ore.

The main difference in the chemical composition of chalcocite in the three deposits is Ag content, which is the highest in the Nowa Sól deposit. By contrast, in the Mozów deposit, the chalcocite is Ag-barren. However, only 2 boreholes from this deposit have been investigated, therefore, it is possible that in the outer parts of this deposit chalcocite contains more Ag. In the Sulmierzyce North deposit, chalcocite exhibits only minor admixtures of Ag and can also be classified as Ag-barren. The proportion between Cu and S in the chalcocite varies slightly, indicating that some of the results obtained are closer to stoichiometric djurleite (particularly in the Nowa Sól deposit). Minor amounts of bornite enriched in Ag were documented only in the Nowa Sól deposit.

Ag minerals are most common in the Nowa Sól deposit, where they usually co-occur with high-grade chalcocite mineralization. Ag minerals were also noted in the Mozów deposit, but they are not directly related to the richest Cu-mineralization. In the Sulmierzyce North deposit, the Ag content in the shale ore is the lowest and Ag minerals were scarcely observed.

Pb-Zn mineralization is developed to a different extent in each deposit. In the Nowa Sól deposit, Pb and Zn contents increase towards the NE, with increasing distance from the oxidized field. The most significant part of the Pb-Zn mineralization occurs above the Cu-series. Shale ore from the northern margins of the deposit contains rich polymetallic Cu-Ag-Pb-Zn mineralization. In the boreholes from the Mozów deposit, Pb and Zn minerals are virtually absent from the shale ore. In the Sulmierzyce North deposit, Pb and Zn minerals are much less frequent than in the Nowa Sól deposit, but they tend to occur with the high-grade Cu mineralization.

Co-Ni sulpharsenides were found only in samples from the Nowa Sól deposit, as the contents of both Co and Ni are the highest in the Nowa Sól deposit. Co-Ni minerals co-occur with high-grade Cu-S mineralization.

Each of the deposits from the Northern Copper Belt is characterized by a different distribution of the ore mineralization. The differences demonstrated result mainly from the distinct spatial range of the oxidized facies in each deposit. In the Nowa Sól deposit, the ore mineralization covers three lithological units (sandstones, shales and carbonates), but its position in the vertical profile varies and depends on the distance from the oxidized field. In the Mozów deposit, the distribution of the ore mineralization is very regular around the oxidized facies, as it covers the *Kupferschiefer* and lowermost part of the Zechstein Limestone, while the sandstones are entirely barren. In the Sulmierzyce North deposit, oxidation usually reaches the lowermost parts of the *Kupferschiefer* while the ore is present within either shales and carbonates or only shales.

In the Nowa Sól deposit, mineral zonation is strongly developed, similarly to the Lubin-Sieroszowice deposits. Reaction rims occurring at the contact between Cu-sulphides and Ag minerals indicate that Ag mineralization post-dated Cu mineralization. In the Sulmierzyce North deposit, mineral zonation typical of the *Kupferschiefer*-type deposits of the FSM is disrupted by the vicinity of several oxidized fields. As for the Mozów deposit, more boreholes should be examined, in order to determine the presence of mineral zonation. Taking into account all the patterns in the distribution and formation of ore minerals, it can be inferred that the deposits in question were formed as a result of a long-lasting, multiphase process.

The deposits of the NCB show some resemblance to the deposits of the Lubin-Sieroszowice area, in terms of geological structure, mineralogy and geochemistry. At a more detailed level, the distribution of ore mineralization and its chemical composition vary to some extent across these two areas.

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REFERENCES

https://doi.org/10.1016/j.oregeorev.2016.05.007

- Bechtel, A., Elliott, W.C., Wampler, J.M., Oszczepalski, S., 1999. Clay mineralogy, crystallinity, and K-Ar ages of illites within the Polish Zechstein basin: Implications of the age of Kupferschiefer mineralization. Economic Geology, 94: 261–272; https://doi.org/10.2113/gsecongeo.94.2.261
- Bechtel, A., Gratzer, R., Püttmann, W., Oszczepalski, S., 2002. Geochemical characteristics across the oxic/anoxic interface (Rote Fäule front) within the Kupferschiefer of the Lubin-Sieroszowice mining district (SW Poland). Chemical Geology, 185: 9–31;

https://doi.org/10.1016/S0009-2541(01)00395-3

- Bieńko, T., Pietrzela, A., 2022. Trace element distribution and geochemical zonation in the world-class Nowa Sól sediment-hosted Cu-Ag deposit, SW Poland. Mineralium Deposita, 57: 827–851; https://doi.org/10.1007/s00126-022-01110-6
- Blundell, D.J., Karnkowski, P.H., Alderton, D.H.M., Oszczepalski, S., Kucha, H., 2003. Copper mineralization of the Polish Kupferschiefer: a proposed basement fault-fracture system of fluid flow. Economic Geology, 98: 1487–1495; http://doi.org/10.2113/gsecongeo.98.7.1487
- Borg, G., Piestrzyński, A., Bachmann, G.H., Püttmann, W., Walther, S., Fiedler, M., 2012. An overview of the European Kupferschiefer deposits. SEG Special Publications, 16: 455–486.
- Cathles, L.M., Oszczepalski, S., Jowett, E.C., 1993. Mass balance evaluation of the late diagenetic hypothesis for Kupferschiefer Cu mineralization in the Lubin basin of southwestern Poland. Economic Geology, 88: 948–956; https://doi.org/10.2113/gsecongeo.88.4.948
- Chmielewski, A., Oszczepalski, S., Głuszyński, A., Kuczak, A., 2021. Spatial distribution of silver at the contact zone of reduced rocks with oxidized rocks (Rote Fäule) in the Cu-Ag Radwanice-Gaworzyce deposit (in Polish with English summary). Przegląd Geologiczny, 69: 411–426; https://doi.org/10.7306/2021.25
- Foltyn, K., Bertrandsson Erlandsson, V., Zygo, W., Melcher, F., Pieczonka, J., 2022. New perspective on trace element (Re, Ge, Ag) hosts in the Cu-Ag Kupferschiefer deposit, Poland: insight from a LA-ICP-MS trace element study. Ore Geology Reviews, 143; https://doi.org/10.1016/j.oregeorev.2022.104768
- Harańczyk, C., 1972. Ore mineralization of the Lower Zechstein euxenic sediments of the Fore-Sudetic monocline (in Polish with English summary). Archiwum Mineralogiczne, 30: 13–144.
- Jarosz, J., 1966. Minerals of the stromeyerite group in copper-bearing sandstones (in Polish). Rudy i Metale Nieżelazne, 11: 464–465.
- Jowett, E.C., 1986. Genesis of Kupferschiefer Cu-Ag deposits by convective flow of Rotliegendes brines during Triassic rifting. Economic Geology, 81: 1823–1837; https://doi.org/10.2113/gsecongeo.81.8.1823
- Jowett, E.C., Rydzewski, A., Jowett, R.J., 1987. The Kupferschiefer Cu-Ag ore deposits in Poland: a re-appraisal of the evidence of their origin and presentation of a new genetic model. Canadian Journal of Earth Sciences, 24: 2016–2037; https://doi.org/10.1139/e87-192
- Kiersnowski, H., Petecki, Z., 2017. Geology of the Zechstein basement of the Legnica-Głogów Copper District (LGOM) and its surroundings: A critical overview (in Polish with English summary). Biuletyn Państwowego Instytutu Geologicznego, 468: 175–198; https://doi.org/10.5604/01.3001.0010.0111
- Kłapciński, J., 1971. Lithology, fauna, stratigraphy and palaeogeography of the Permian in the fore-Sudetic monocline (in Polish with English summary). Geologia Sudetica, 5: 1–135.

- Kozub-Budzyń, G., Piestrzyński, A., 2017. Geochemical characteristic of Ag-bearing minerals occurring in copper ore deposit at the Fore-Sudetic Monocline (in Polish with English summary). Biuletyn Państwowego Instytutu Geologicznego, 468: 49–60; https://doi.org/10.5604/01.3001.0010.0103
- Kucha, H., 1976. Organic matter, Au, Ni and Co in Zechstein rocks of the Fore Sudetic Monocline (Western Poland) (in Polish with English summary). Annales Societatis Geologorum Poloniae, 46: 369–417.
- Kucha, H., 1990. Geochemistry of the Kupferschiefer, Poland. Geologische Rundschau, 79: 387–399; https://doi.org/10.1007/BF01830634
- Kucha, H., 2007. Mineralogy and geochemistry of the Lubin-Sieroszowice orebody (in Polish with English summary). Biuletyn Państwowego Instytutu Geologicznego, 423: 77–94.
- Kucha, H., Głuszek A., 1983. Variation of Cu, Zn, Pb, Ag mineralization in the deposit of the Lubin Mine (in Polish with English summary). Annales Societatis Geologorum Poloniae, 53: 143–168.
- Kucha, H., Pawlikowski, M., 1986. Two-brine model of the genesis of strata-bound Zechstein deposits (Kupferschiefer type), Poland. Mineralium Deposita, 21: 70–80; https://doi.org/10.1007/BF00204365
- Mayer, W., Piestrzyński, A., 1985. Ore minerals from lower Zechstein sediments at Rudna mine, Fore-Sudetic Monocline, SW Poland. Prace Mineralogiczne, 75: 1–80.
- Mikulski, S.Z., Stein, H.J., 2017. Re-Os isotopic age of the Cu-Ag sulfide ore and its mineralogical and geochemical characteristic from the Lubin-Polkowice mining area (SW Poland) (in Polish with English summary). Biuletyn Państwowego Instytutu Geologicznego, 468: 79–96;
- https://doi.org/10.5604/01.3001.0010.0105
- Mikulski, S.Z., Oszczepalski, S., Sadłowska, K., Chmielewski, A., Małek, R., 2020. Trace element distributions in the Zn-Pb (Mississippi Valley-Type) and Cu-Ag (Kupferschiefer) sediment-hosted deposits in Poland. Minerals, 10: 75; https://doi.org/10.3390/min10010075
- Nemec, W., Porębski, S., 1981. Sedimentary environment of the Weissliegendes sandstones in Fore-Sudetic Monocline. In: Proceedings of International Symposium Central European Permian, Jabłonna, 27–29 April 1978 (ed. Z. Pakulska): 281–293. Geological Institute, Warsaw, Poland.
- **Oszczepalski, S., 1989.** Kupferschiefer in southwestern Poland: Sedimentary environments, metal zoning, and ore controls. Geological Association of Canada Special Paper, **36**: 571–600.
- **Oszczepalski, S., 1994.** Oxidative alteration of the Kupferschiefer in Poland: Oxide-sulfide parageneses and implications for ore-forming models. Geological Quarterly, **38** (4): 651–672.
- Oszczepalski, S., 1999. Origin of the Kupferschiefer polymetallic mineralization in Poland. Mineralium Deposita, 34: 599–613; https://doi.org/10.1007/s001260050222
- Oszczepalski, S., Chmielewski, A., 2015. Predicted metallic resources in Poland presented on the prospective maps at scale 1:200 000 – copper, silver, gold, platinum and palladium in the Kupferschiefer ore series (in Polish with English summary). Przegląd Geologiczny, 63: 534–545.
- Oszczepalski, S., Rydzewski A., 1987. Palaeogeography and sedimentary model of the Kupferschiefer in Poland. Lecture Notes in Earth Sciences, 10: 189–205; https://doi.org/10.1007/BFb0011379
- Oszczepalski, S., Rydzewski, A., 1991. The Kupferschiefer mineralization in Poland. Zentralblatt für Geologie und Paläontologie, Teil I, 4: 975–999.
- Oszczepalski, S., Rydzewski, A., 1998. Gold, platinum and palladium in Lubin-Sieroszowice deposit based on borehole data (in Polish). PTMin - Prace Specjalne, 10: 51–70.

- Oszczepalski, S., Nowak, G.J., Bechtel, A., Zák, K., 2002. Evidence of oxidation of the Kupferschiefer at Lubin-Sieroszowice deposit. Implications for Cu-Ag and Au-Pt-Pd mineralization. Geological Quarterly, 46 (1): 1–23.
- Oszczepalski, S., Speczik, S., Zieliński, K., Chmielewski, A., 2019. The Kupferschiefer deposits and prospects in SW Poland: past, present and future. Minerals, 9: 592–633; https://doi.org/10.3390/min9100592
- Peryt, T.M., 1978. Sedimentology and paleoecology of the Zechstein Limestone (Upper Permian) in the Fore-Sudetic area (Western Poland). Sedimentary Geology, 20: 217–243; https://doi.org/10.1016/0037-0738(78)90055-6
- Peryt, T.M., 1989. Basal Zechstein in southwestern Poland: sedimentation, diagenesis, and gas accumulations. Geological Association of Canada Special Paper, 36: 601–625.
- Peryt, T.M., Oszczepalski, S., 2007. Stratigraphy of the ore series (in Polish). In: Monografia KGHM Polska Miedź S.A. (eds. A. Piestrzyński, A. Banaszak and M. Zaleska-Kuczmierczyk): 108–111. KGHM Cuprum Sp. z o.o., Lubin.
- Pieczonka, J., 2000. Oxidation zones in a copper ore deposit on the Fore-Sudetic Monocline (in Polish). PTMin – Prace Specjalne, 16: 9–54.
- Pieczonka, J., 2011. Factors controlling distribution of ore minerals within copper deposit, Fore-Sudetic Monocline, SW Poland (in Polish with English summary). Wydawnictwo AGH, Kraków.
- Pieczonka, J., Piestrzyński, A., Lenik, P., Czerw, H., 2007. Distribution of ore minerals in the copper deposit, Fore-Sudetic Monocline, SW Poland (in Polish with English summary). Biuletyn Państwowego Instytutu Geologicznego, 423: 95–108.
- Pieczonka, J., Piestrzyński, A., Mucha, J., Głuszek, A., Kotarba, M., Więcław D., 2008. The red-bed-type precious metal deposit in the Sieroszowice-Polkowice copper mining district, SW Poland. Annales Societatis Geologorum Poloniae, 78: 151–280.
- Piestrzyński, A., 2007. Ore mineralization (in Polish). In: Monografia KGHM Polska Miedź S.A. (eds. A. Piestrzyński, A. Banaszak and M. Zaleska-Kuczmierczyk): 98–128. KGHM Cuprum Sp. z o.o., Lubin.
- Piestrzyński, A., Pieczonka, J., 1997. Gold and PGE on an oxide-reducing interface in Lower Zechstein sediments of the Fore-Sudetic Monocline, SW Poland. In: Mineral Deposits: Resources and Exploration – Where do They Meet? (ed. H. Papunen): 99–102. Proceedings of the 4th Biennial SGA Meeting, Turku, Finland, 11–13 August 1997. A.A. Balkema, Rotterdam, Netherlands.
- Piestrzyński, A., Salamon, W., 1986. Perspectives of silver bearing capacity of the eastern part of copper deposits in the Fore-Sudetic Monocline (in Polish with English summary). Gospodarka Surowcami Mineralnymi, 2: 469–481.
- Piestrzyński, A., Wodzicki, A., Banaszak, A., 1996. Gold in the copper deposits of the Fore-Sudetic Monocline (SW Poland) (in Polish with English summary). Przegląd Geologiczny, 44: 1098–1102.
- Piestrzyński, A., Pieczonka, J., Głuszek, A., 2002. Redbed-type gold mineralisation, Kupferschiefer, south-west Poland. Mineralium Deposita, **37**: 512–528; https://doi.org/10.1007/s00126-002-0256-9
- Pietrzela A., Bieńko, T., 2023. Comparison of main and accompanying metals distribution patterns in newly documented deposits of the Northern Copper Belt in Poland. Geochemistry: Exploration, Environment, Analysis, 23: 1–23; https://doi.org/10.1144/geochem2022-046
- Poszytek, A., Suchan, J., 2016. A tight-gas reservoir in the basinal facies of the Upper Permian Ca1 in the southwestern Zechstein Basin, Poland. Facies, 62: 3; https://doi.org/10.1007/s10347-015-0453-5

Püttmann, W., Merz, C. and Speczik, S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. Applied Geochemistry, 4: 151–161; https://doi.org/10.1016/0883-2927(89)90046-2

- **Rydzewski, A., 1964.** Petrography and mineralization of the Zechstein deposits in the areas of Fore-Fudetic Monocline and of Pericline of Żary (in Polish with English summary). Przegląd Geologiczny, **12**: 476–479.
- **Rydzewski A., 1969.** Occurrence and genesis of pyrite in the Zechstein rocks of the Fore-Sudetic monocline (in Polish with English summary). Geological Quarterly, **13** (4): 811–820.
- Rydzewski, A., 1976. Origin of Lower Zechstein polymetallic mineralization (in Polish with English summary). Przegląd Geologiczny, 24: 176–181.
- **Rydzewski, A., 1978.** Oxidated facies of the Zechstein copper-bearing shale in the Fore-Sudetic Monocline (in Polish with English summary). Przegląd Geologiczny, **26**: 102–107.
- Salamon, W., 1976. Precious metals in Zechstein black shales in the Fore-Sudetic Monocline (in Polish). Rudy i Metale Nieżelazne, 12: 472–477.
- Salamon, W., 1979. Ag and Mo in Zechstein sediments of the Fore-Sudetic Monocline (in Polish with English summary). Prace Mineralogiczne, 62: 1–59.
- Speczik, S., 1979. Ore mineralization in the basement Carboniferous rocks of the Fore-Sudetic Monocline (SW Poland) (in Polish with English summary). Geologia Sudetica, 14: 77–122.
- Speczik, S., 1995. The Kupferschiefer mineralization of Central Europe: New aspects and major areas of future research. Ore Geology Reviews, 9: 411–426; https://doi.org/10.1016/0169-1368(94)00022-G
- Speczik, S., Skowronek, C., Friedrich, G., Diedel, R., Schumacher, C. and Schmidt, F.P., 1986. The environment of
- generation of some base metal Zechstein occurrences in central Europe. Acta Geologica Polonica, **36**: 1–35.
- Speczik, S., Piestrzyński, A., Rydzewski, A., Oszczepalski, S., 1997. Exploration for Cu-Ag and Au-Pt-Pd Kupferschiefer-type deposits in SW Poland. In: Mineral Deposits: Resources and Exploration – Where do They Meet? (ed. H. Papunen): 119–122. Proceedings of the 4th Biennial SGA Meeting, Turku, Finland, 11–13 August 1997. A.A. Balkema, Rotterdam, Netherlands.
- Speczik, S., Zieliński, K., Bieńko, T., Pietrzela, A., 2020. Documenting deep copper and silver deposits investor's criteria (in Polish with English summary). Górnictwo Odkrywkowe, 61: 43–54.
- Speczik, S., Zieliński, K., Bieńko, T., Pietrzela, A., 2021. The prospecting strategy for a deep Cu-Ag ore deposit in Poland – An anatomy of success. Ore Geology Reviews, 131; https://doi.org/10.1016/j.oregeorev.2021.104053
- Speczik, S., Szamałek, K., Zieliński, K., Pietrzela, A., Bieńko, T., 2022. The new Northern Copper Belt of south-western Poland: a summary. Acta Geologica Polonica, 72: 469–477.
- Szopa, K., Krzykawski, T., Banasik, K., Król, P., Skreczko, S., Mounteanou, S.A., Koziarska, M., 2021. EMPA, XRD, and Raman characterization of Ag-bearing djurleite from the Lubin Mine, Lower Silesia, Poland. Minerals, 11: 454; https://doi.org/10.3390/min11050454
- Tomaszewski, J.B., 1981. Development of Zechstein deposits in the vicinity of Lubin and Sieroszowice. In: Proceedings of International Symposium Central European Permian, Jabłonna, April 27–29, 1978 (ed. Z. Pakulska): 341–355. Geological Institute, Warsaw, Poland.
- Wodzicki, A., Piestrzyński, A., 1994. An ore genetic model for the Lubin-Sieroszowice mining district, Poland. Mineralium Deposita, 29: 30–43; https://doi.org/10.1007/BF03326394
- Wyżykowski, J., 1971. Zechstein copper-bearing formation in Poland (in Polish with English summary). Przegląd Geologiczny, 19: 117–122.
- Zieliński, K., Speczik, S., Pietrzela, A., Bieńko, T., 2022. Possibilities of documenting new copper deposits in the Northern Copper Belt of the Fore-Sudetic Monocline (in Polish with English summary). Górnictwo Odkrywkowe, 63: 26–32.