

Mineralogy and geochemistry of Cu-Zn-Pb-As-Sn±Bi±Ag ores from the Miedzianka-Ciechanowice deposit, Sudetes, Poland

Kacper Muszyński¹, Jaroslav Pršek², Jiří Sejkora³, Zdeněk Dolníček⁴,
Tomaš Mikuš⁵, Bożena Gołębiowska⁶

¹ AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland, e-mail: kmuszyn@agh.edu.pl (corresponding author), ORCID ID: 0000-0003-3059-4594

² AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland, ORCID ID: 0000-0003-4331-8273

³ National Museum, Department of Mineralogy and Petrology, Prague, Czech Republic, ORCID ID: 0000-0003-2763-2043

⁴ National Museum, Department of Mineralogy and Petrology, Prague, Czech Republic, ORCID ID: 0000-0002-4033-9207

⁵ Slovak Academy of Sciences, Geological Institute, Banská Bystrica, Slovak Republic, ORCID ID: 0000-0002-7173-9852

⁶ AGH University of Krakow, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland, ORCID ID: 0000-0002-4103-1124

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Abstract: Miedzianka-Ciechanowice is a hydrothermal vein-type quartz, quartz-carbonate, and baryte-sulfide deposit in the eastern metamorphic cover of the Karkonosze granite of the Sudetes. A polymetallic Cu-Zn-Pb-As-Sn±Bi±Ag mineralization has been identified. The main ore minerals include chalcopyrite, bornite, sphalerite, members of the tetrahedrite group, galena, chalcocite, pyrite, arsenopyrite, mawsonite, and stannoidite. Several previously unknown mineral phases from this deposit have also been discovered. Miedzianka-Ciechanowice is the second location in Poland where the presence of Bi-rich tennantite-(Zn) has been confirmed. Furthermore, a few analyses of Bi-dominated tetrahedrite group minerals have indicated the presence of *annivite* (not officially approved by the Commission on New Minerals, Nomenclature and Classification). Various silver minerals are also found in the study area, including hessite, cervelleite, native silver, stromeyerite, acanthite, mckinstryite, proustite, selenojalpaite, and naumannite within baryte veins. The association of both Bi-rich tetrahedrite-group minerals and silver minerals hosted by baryte veins is very rare in the Sudetes. The aim of this study is to provide compositional data on the dominant mineral paragenesis in the deposit, represented by the Cu-Zn-Pb-Sn±Bi±Ag assemblage.

Keywords: Miedzianka-Ciechanowice, Bi-rich tetrahedrite group minerals, silver assemblages, tin-bearing sulfides, hydrothermal mineralization

INTRODUCTION

The Miedzianka-Ciechanowice deposit is one of many hydrothermal polymetallic deposits in the Sudetes (Zimnoch 1978, Piestrzyński et al. 1992,

Mikulski 2005, 2010, Madziarz 2009a, Mochnacka et al. 2009, 2012, Pršek et al. 2019). The main object of mining was hydrothermal polymetallic veins which have been exploited for hundreds of years (Dziekoński 1972, Madziarz 2009a, 2009b, 2010)

similarly to other locations in the Karkonosze-Izera Massif: Rędziny – disseminated mineralization in amphibolites and phyllites (Pieczka et al. 2006, Gołębiewska et al. 2012), Chełmiec – hydrothermal vein-type carbonate-sulfide deposit (Paulo 1973, Muszyński et al. 2023), Radzimowice – vein-type deposit (Mikulski 2005, 2007), Czarnów – quartz-sulfide vein-type deposit (Mikulski 2010), and Grudno – hydrothermal quartz (Paulo & Salamon 1972). Many of these deposits have not been sufficiently mineralogically studied by modern methods due to the cessation of mining and lack of economic importance. In the Miedzianka-Ciechanowice area of the Rudawy Janowickie Mountains, several dozen Cu-, Pb-, and Zn-bearing hydrothermal polymetallic veins, locally enriched in Ag, associated with late-Variscan granite magmatism have been documented (Mochnacka et al. 2012). The polymetallic mineralization in this deposit is associated with a hydrothermal quartz-carbonate-baryte-vein (Siuda & Gołębiewska 2011, Mochnacka et al. 2012), which contains various mineralizations, including base metal sulfides, tin, bismuth, silver, uranium, and rare earth elements (Zimnoch 1978, Siuda & Gołębiewska 2011, Mochnacka et al. 2012, Siuda 2012).

This paper presents new data on the mineralogy, geochemistry, and mineral associations of the Miedzianka-Ciechanowice hydrothermal polymetallic vein deposit. Its aim is to provide compositional data on the dominant mineral paragenesis in the deposit, represented by the Cu-Zn-Pb-Sn±Bi±Ag assemblage.

LOCALITY AND GEOLOGICAL SETTING

The research area is located in southwestern Poland, between the villages of Miedzianka and Ciechanowice in the eastern part of the Karkonosze-Izera Massif (Mochnacka et al. 2012). This area is situated in the northern part of the Rudawy Janowickie Mountains, which form the eastern metamorphic cover of the Karkonosze Granite (Siuda & Gołębiewska 2011). This mountain range is divided into three units: metasedimentary-volcanic Kowary-Czarnów unit with Kowary gneisses, the Leszczyniec volcanic unit, and the phyllite

Przybkowice unit (Kozdrój 2003). The Miedzianka-Ciechanowice area is composed mainly of amphibolites and amphibolite schists, with small inserts of mica schists and quartz-sericite schists, greenstones and skarns (Siuda & Gołębiewska 2011) from the Kowary-Czarnów unit (Kozdrój 2003) (Fig. 1). Subsequently emplaced dyke rocks, including rhyolites, intersect amphibolite, greenstones, amphibole schists and quartz-sericite schists. These dyke rocks are associated with the Karkonosze Granite intrusion (Siuda & Gołębiewska 2011). The metamorphic rocks of the entire region were metamorphosed during the Variscan orogeny prior to the emplacement of the Karkonosze granite (Mazur et al. 2010). The Miedzianka-Ciechanowice deposit is associated with the Intra-Sudetic fault located in the northeastern part of the area (Teisseyre 1968). There is a system of parallel NW-SE faults within the deposit that are connected with the accommodated tectonic movements during a late stage of the Variscan orogeny (Teisseyre 1968).

Two types of ore mineralization have been recognized in the Miedzianka-Ciechanowice area (Zimnoch 1978, Mochnacka 1982). The first is skarn type: magnetite-sphalerite-pyrite mineralization occurring in the western and southwestern parts of the village of Miedzianka. Its formation is related to the metamorphism and metasomatism of lenses of carbonate rocks in contact with the Karkonosze granite intrusion. This type of ore includes magnetite, sphalerite, pyrite, and pyrrhotite (Mochnacka 1982).

The second, hydrothermal type, which is the subject of this work, is associated with polymetallic vein-type mineralization and is more widespread than the first type. Quartz, quartz-calcite, calcite, dolomite, and baryte veins are found throughout the area. Mainly quartz and quartz-calcite veins are ore-mineralized. The ore veins trend W-E and dip to the N or S (Zimnoch 1961). Forty-one veins have been discovered in the Miedzianka-Ciechanowice deposit, whose thicknesses range from 0.01 to 3 meters (Madziarz 2010). In the western field, Cu-bearing hydrothermal quartz and quartz-calcite veins with uranium and tin minerals are found along with skarns (Mochnacka et al. 2012).

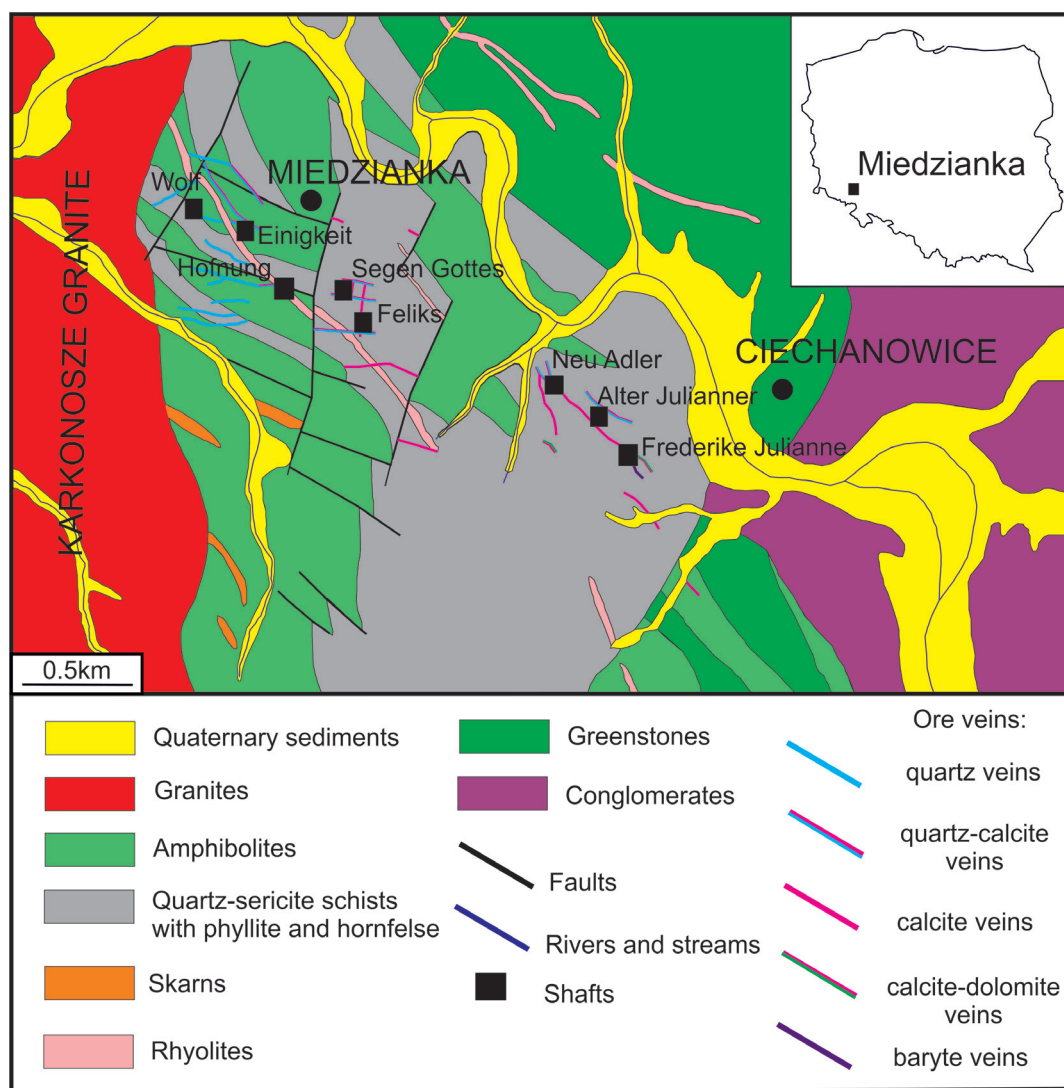


Fig. 1. Geological structure of the Miedzianka-Ciechanowice area (modified from Siuda & Gołębiewska 2011)

The eastern field, near the village of Ciechanowice, is known for its diverse mineral associations, including copper, silver, bismuth, cobalt, and tin minerals (Mochnacka et al. 2012). These minerals are hosted in quartz, quartz-calcite, calcite, dolomite, and baryte veins. Rare pink baryte veins were reported in the southeastern part of the Miedzianka deposit (this study). The northern part of the Miedzianka ore field, located on the opposite side of the Bóbr River, is characterized by Pb-Zn mineralization (Mochnacka et al. 2012). Ore mineralization forms irregular, massive accumulations in quartz, quartz-calcite, or calcite veins, rarely veinlets or disseminations in the host rocks (primarily amphibolite or amphibolite

schists). The main ore minerals in the Miedzianka-Ciechanowice area are chalcopyrite and bornite (Mochnacka et al. 2012).

MATERIALS AND METHODS

Samples of quartz, quartz-calcite, calcite, calcite-dolomite, and baryte veins containing ore mineralization with Cu-Zn-Pb-Sn-Bi±Ag paragenesis were collected from old dumps of the Einigkeit, Hoffnung, Segen Gottes, Friederike-Juliane, Feliks, Alter Julianer, and Neu Adler shafts (Fig. 1) in the Miedzianka ore field. Various textures of ores from the Miedzianka-Ciechanowice deposit are observed: massive, nested, veinlet, and

disseminations. Sixty-five samples were selected for microscopic reflected light observations, while 21 representative samples were selected for microprobe studies.

Microprobe analyses were performed in the laboratories of the Slovak Academy of Sciences in Banská Bystrica and at the National Museum in Prague, using a JEOL Super Probe JXA-8230 and a Cameca SX-100 microanalyzer, respectively. The analyses were performed using the WDS method under the following conditions: accelerating voltage of 20 kV (Banská Bystrica) and 25 kV (Prague), beam current of 20 nA, and beam diameter of 1 μm . The following standards and analytical lines were used: PbM α , AgL α , SbL α , InL α , TeL α , SnL α , ClK α , CuK α , SK α , ZnK α , FeK α , CoK α , NiK α , BiM β , CdL α , AuM α , BaM α , CaM α , CrK α , AsL β , SeL β , GaL α , GeL α , NaK α , PK α , MnK α , HgL α , and TlL α . The following analytical conditions were applied for the oxygen-bearing phases: 15 kV accelerating voltage, 10–20 nA beam current, and 2–10 μm beam diameter.

The following standards and analytical lines were used:

- for carbonates: AlK α , BaL α , CaK α , CoK α , FeK α , CuK α , MnK α , NaK α , NiK α , PK α , PbM α , SK α , SiK α , and ZnK α ;
- for baryte: CaK α , PbM α , SrL β , MgK α , SiK α , NaK α , AlK α , FeK α , BaL α , and SK α ;
- for monazite: ZrL α , PK α , YL α , NaK α , SiK α , AsL α , AlK α , SrL β , CeL α , LaL α , CaK α , ThM α , SK α , UM α , BaL α , BiM α , MnK α , TiK α , PbM α , KK α , ClK α , NdL β , SmL α , FK α , PrL β , GdL α , YbL α , ErL α , DyL β , EuL α , TbL α , TmL α , MgK α , LuM β , HoM β , FeK α , CuK α , ScK α , VK α , and HfM α ;
- for uraninite: CaK α , ThM α , SK α , UM α , PbM α , PK α , YL α , NaK α , SiK α , AlK α , LuM β , HoM β , YbL α , ErL α , DyL β , EuL α , TbL α , TmL α , GdL α , SmL α , NdL β , CeL α , LaL α , MnK α , TiK α , and BaL α .

RESULTS

The studied ore mineralization, which contains a Cu–Zn–Pb–Sn $\pm$ Bi $\pm$ Ag paragenesis, is primarily dominated by massive aggregates of chalcopyrite in quartz, quartz-calcite veins (Fig. 2A), or

massive bornite in quartz-calcite, calcite-dolomite (Fig. 2B), and baryte veins. Two types of baryte, including white (baryte I) and pink (baryte II), were discovered (Fig. 2C). The most common ore minerals are chalcopyrite and bornite, which form macroscopically visible, usually irregular aggregates up to 4 cm and 1 cm in size, respectively. Massive bornite-chalcocite accumulations up to 0.5 cm were also observed. Chalcopyrite and bornite form intergrowths with sphalerite, members of the tetrahedrite-tennantite series, chalcocite, galena, arsenopyrite, and löllingite. During the laboratory research (microscope studies and EMP analyses), mawsonite, stannoidite, bismuth, wittichenite, betekhtinite, cubanite, clausthalite, monazite, hesite, cervelleite, native silver, stromeyerite, acanthite, naumannite, mckinstryite, selenojalpaite, proustite, very rare Bi-rich TGM (tetrahedrite group minerals), and *annivite* were also discovered. Silver minerals and native silver are mainly associated with massive bornite-chalcocite ore and form irregular aggregates, veinlets, intergrowths with other silver phases, and elongated or irregular inclusions. The Bi-rich TGM form brighter zones within tennantite-(Zn). The paragenetic sequence resulting from this study is shown in Figure 3, and the minerals will be described in the following sections of the paper according to this sequence. The chemical analyses are included in Appendix 1, and the chemical formulas of the minerals are provided in Appendix 2 (the appendices are available online as a supplementary file to the article). The mineral abbreviations used in this study follow the IMA–CNMNC-approved mineral symbols proposed by Warr (2021).

Carbonates

Carbonates are very common in the Miedzianka-Ciechanowice deposit, where calcite, dolomite, and ankerite are observed. Calcite, which is the most abundant, forms veins and veinlets within amphibolite, greenstones, amphibolite, and quartz-sericite schists. It sometimes creates coarse-grained aggregates that intergrow with white baryte and rare ankerite. Calcite is usually associated with quartz or dolomite, forming quartz-calcite veins in the western part of the deposit, while calcite-dolomite veins predominate in the eastern part.

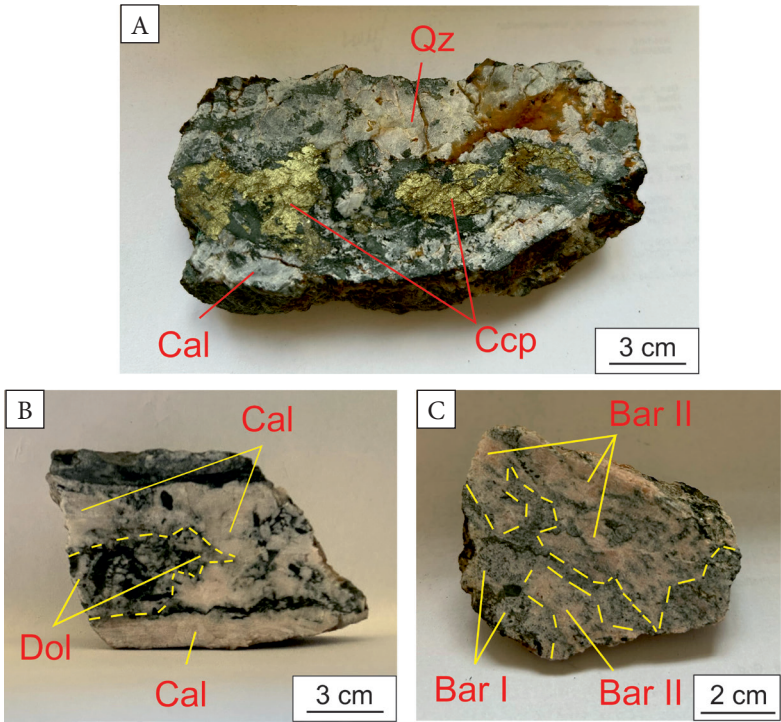


Fig. 2. Types of hydrothermal ore veins in Miedzianka-Ciechanowice deposit: A) massive chalcopyrite aggregates in quartz-calcite vein; B) calcite-dolomite vein; C) two types of baryte: white (Bar I) and pink (Bar II)

Mineral	Type of vein		Quartz		Calcite		Dolomite		Baryte	
			Py I	Py II	Py I	Py II	Py I	Py II	Py I	Py II
Pyr										
Ar										
Sph										
Ccp										
Ann										
Tet										
Bor										
Chal										
Bet										
Nat										
Wit										
Gal										
Ura										
Maw										
Sta										
Hes										
Cer										
Str										
Nat										
Aca										
Mck										
Pro										
Sel										
Na										
Löl										
Cub										
Cla										
Mon										

Fig. 3. Mineral succession of Cu-Zn-Pb-As-Sn±Bi±Ag mineralization from Miedzianka-Ciechanowice deposit based on results of this study (thicker lines refer to the main minerals; thinner lines indicate less widespread and rare minerals)

Calcite contains low concentrations of Mn (up to 0.03 apfu), Fe (up to 0.01 apfu), and Mg (up to 0.01 apfu). Other admixtures occur in very low concentrations of less than 0.01 apfu.

Dolomite is usually coarse-grained and occurs with calcite, forming calcite-dolomite veins and veinlets. Pure dolomite is very rare and occurs as thin veinlets that do not contain any mineralization. Additionally, the coarse-grained dolomite also forms intergrowths with white baryte and ankerite and contains significant admixtures of Fe (up to 0.12 apfu) and Mn (up to 0.08 apfu). The concentrations of Al, Zn, Na, Si and Ba are very low and do not exceed 0.01 apfu.

Ankerite is very rare and occurs as fine-grained intergrowths with coarse-grained calcite and dolomite. It rarely forms tiny veinlets within bigger calcite-dolomite veins, which contain only low contents of Na (up to 0.01 apfu). Concentrations of the other admixtures are below 0.01 apfu.

Baryte

Two types of baryte were discovered in the studied location. The most widespread is white baryte (baryte I) which occurs as veins and veinlets up

to several cm thick. Coarse-grained baryte sometimes intergrows with calcite and less abundant dolomite or encloses them. The baryte I veins are nearly pure with a simple texture, rarely showing macroscopically visible base-metal mineralization. It generally shows no deformation features. Occasionally, it hosts base-metal sulfides, especially bornite II and tin sulfides, bismuth or wittichenite. White baryte from Miedzianka-Ciechanowice exhibits low admixtures of Sr (up to 0.03 apfu), Na and Ca (up to 0.01 apfu). The contents of Al, Mg, Mn, and Pb are very low, less than 0.01 apfu.

Pink baryte (baryte II) is very rare and usually occurs as tiny veinlets and generally shows no deformation features. Similarly to baryte I, it does not create complex textures and occasionally contains macroscopically visible ore mineralization; mainly bornite II and chalcocite, rarely wittichenite and mawsonite II. Baryte II hosts separate subhedral grains of native silver up to 80 μm and various other Ag-rich minerals. It contains higher contents of Sr up to 0.06 apfu (Fig. 4) and lower contents of Ca and Na (up to 0.01 apfu). The other admixtures occur in very low concentrations, similarly to baryte I.

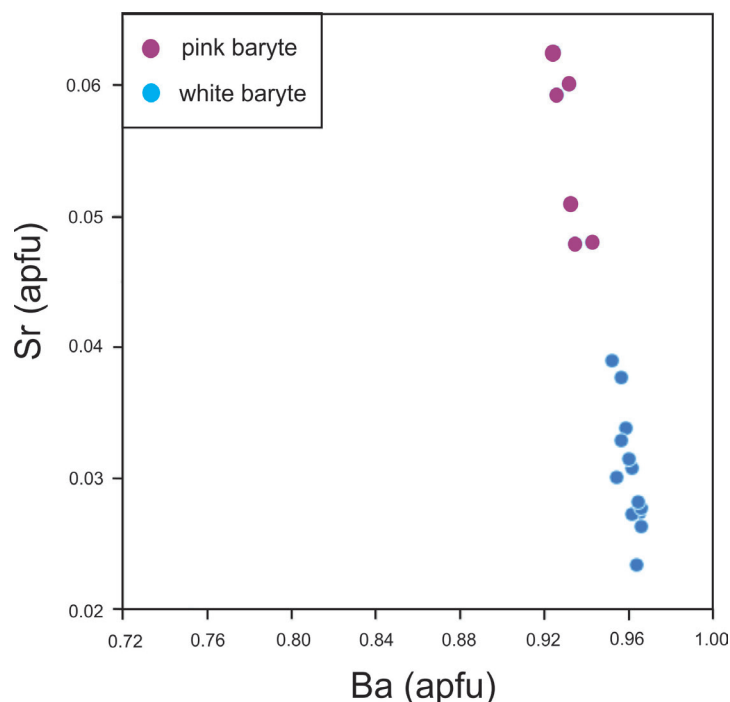


Fig. 4. Diagram of Ba vs. Sr substitution in baryte I and II from Miedzianka-Ciechanowice

Pyrite

Pyrite is one of the main sulfide minerals in the deposit. Two generations of pyrite have been discovered. The first generation forms separate, subhedral grains up to 200 µm disseminated in chalcopyrite I in quartz, quartz-calcite veins. These grains are usually cracked, and the cracks are sometimes filled with chalcopyrite I. Pyrite I is occasionally associated with sphalerite I and II, members of tetrahedrite group minerals, and galena I and II in calcite-dolomite gangue. Crystals of pyrite I up to 150 µm have also been found in arsenopyrite. The second generation occurs in every type of ore vein. It forms tiny, idiomorphic grains up to 50 µm in bornite II. Pyrite II is accompanied by members of tetrahedrite-tennantite series, chalcopyrite II. Both generations of pyrite are chemically pure.

Arsenopyrite

Arsenopyrite is a common mineral and occurs in quartz and quartz-calcite veins. It usually forms massive aggregates up to 300 µm in size as well as separate idiomorphic grains. The grain size of arsenopyrite varies significantly, ranging from 20 to 200 µm. The arsenopyrite aggregates contain grains of pyrite up to 150 µm and tiny crystals of chalcopyrite I, tennantite and cubanite. Arsenopyrite grains are sometimes overgrown by younger löllingite (Fig. 5A). It is usually chemically pure, although some grains contain small contents of Cu (up to 0.01 apfu) without any zoning visible in BSE (Backscattered Electrons) images. The empirical formula of arsenopyrite, based on 1 cation, could be written as $(\text{Fe}_{0.99-1.00}\text{Cu}_{0.00-0.01})_{\Sigma=1.00}\text{As}_{0.97-0.99}\text{S}_{0.99-1.01}$.

Sphalerite

Sphalerite is a widespread mineral in the Miedzianka-Ciechanowice deposit. Two generations of sphalerite (Fe-rich and Fe-poor) have been distinguished. The older, Fe-rich sphalerite I occurs as intergrowths with chalcopyrite I, reaching up to 800 µm in quartz and quartz-calcite veins. Intergrowths of both generations of sphalerite are very rare and occur in calcite-dolomite veins. These intergrowths contain tiny, usually elongated inclusions and veinlets of chalcopyrite I (Fig. 5B). Grains of older sphalerite I are

sometimes surrounded by chalcopyrite I and show the presence of cracks and voids. Sphalerite I is accompanied by bornite I, galena I, members of tetrahedrite group minerals (especially Bi-enriched tetrahedrite group minerals), mawsonite, and stannoidite. It contains significant contents of Fe (up to 0.08 apfu), Cu (up to 0.08 apfu) and Co (up to 0.01 apfu). The empirical formula of sphalerite I, based on 1 cation, could be written as $(\text{Zn}_{0.83-0.96}\text{Fe}_{0.02-0.08}\text{Cu}_{0.02-0.08})_{\Sigma=0.99-1.00}\text{S}_{0.98-1.03}$.

The Fe-poor sphalerite II occurs mainly as veinlets in quartz and calcite veins and intergrowths with bornite II up to 500 µm, and rarely chalcocite in calcite-dolomite veins. It is associated with chalcocite, arsenopyrite, löllingite and wittichenite. The Fe-free sphalerite II occurs with members of tetrahedrite group minerals, especially Bi-free tennantite-(Zn), tetrahedrite-(Zn) and tetrahedrite-(Fe). Cracks in sphalerite II are filled with younger chalcocite and galena II veinlets (Fig. 5C). Sphalerite II contains low contents of Cd (up to 0.03 apfu), Fe (up to 0.02 apfu) and Cu (up to 0.01 apfu). The empirical formula of sphalerite II, based on 1 cation, could be written as $(\text{Zn}_{0.94-1.00}\text{Cd}_{0.00-0.03}\text{Fe}_{0.00-0.02}\text{Cu}_{0.00-0.01})_{\Sigma=1.00}\text{S}_{0.96-1.02}$.

Chalcopyrite

Chalcopyrite is the most widespread mineral in the Miedzianka-Ciechanowice deposit. Two generations of chalcopyrite have been discovered. Chalcopyrite I forms nest-like, massive, and irregular aggregates up to 2 mm in quartz, quartz-calcite, and calcite-dolomite veins. It usually creates intergrowths with sphalerite I (Fig. 5B), II, bornite I, tetrahedrite-tennantite series, pyrite and galena I. It contains tiny inclusions of pyrite, members of tetrahedrite group minerals, bismuth, mawsonite, stannoidite and löllingite. This mineral also creates tiny veinlets in pyrite and sphalerite I. Chalcopyrite I is sometimes accompanied by monazite and contains low contents of Co (up to 0.01 apfu). The empirical formula (based on the sum of two cations) of chalcopyrite I is $(\text{Cu}_{0.98-1.04}\text{Fe}_{0.96-1.01}\text{Co}_{0.00-0.01})_{\Sigma=2.00}\text{S}_{1.95-2.03}$.

Younger chalcopyrite II usually occurs as scattered euhedral and subhedral grains in bornite II aggregates, mostly in calcite-dolomite and baryte veins; however, it is also present in minor amounts in quartz-calcite veins.

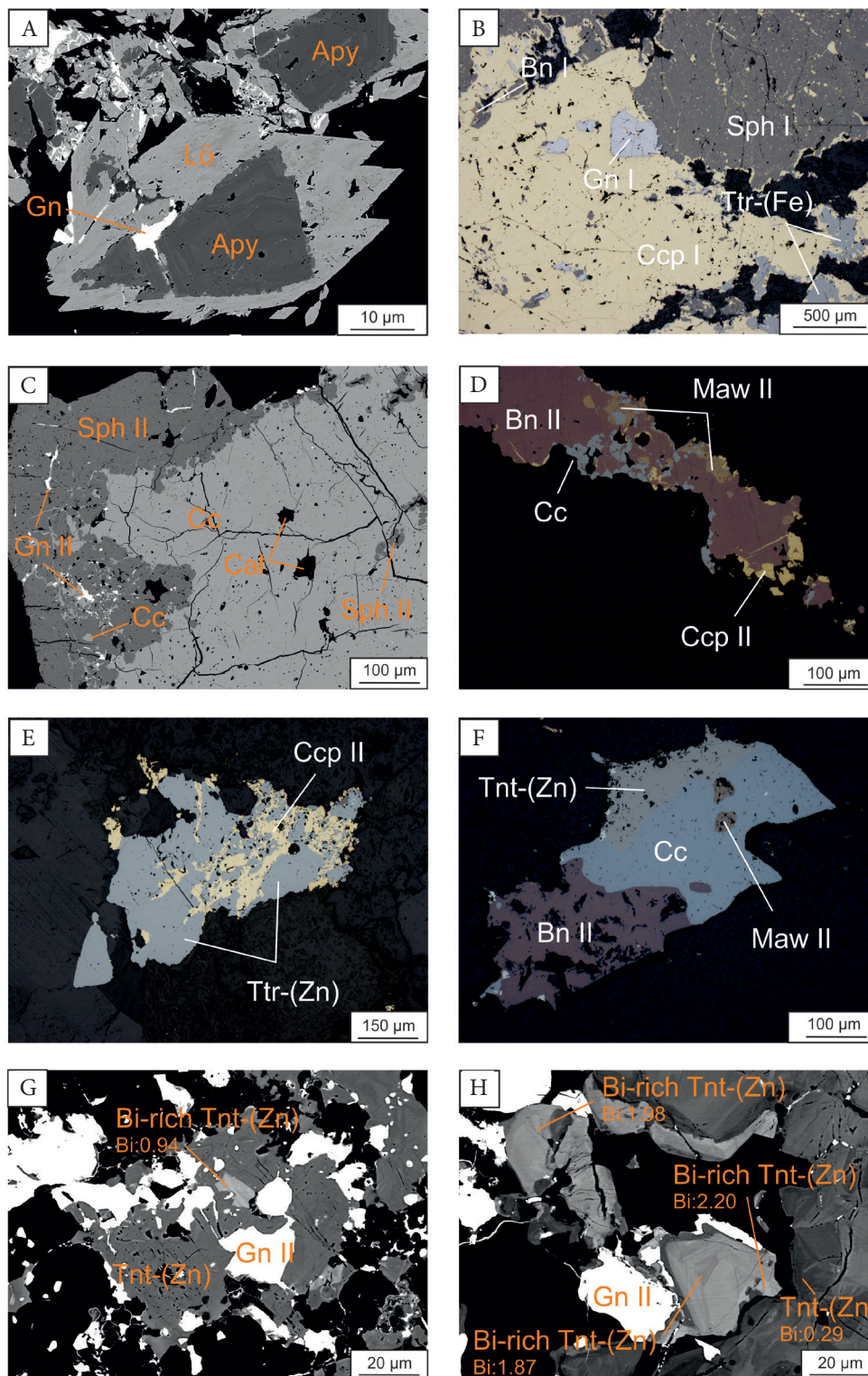


Fig. 5. Back-scattered electron (A, C, G, H) and reflected-light (B, D–F) images illustrating the main features of mineral assemblages: A) löllingite surrounding arsenopyrite crystals with galena II in calcite-dolomite vein; B) intergrowths of chalcopyrite I with sphalerite I and tetrahedrite-(Fe), crystals of galena I and inclusions of bornite I in quartz vein; C) intergrowths of chalcocite with sphalerite II and galena II veinlets in calcite vein; D) aggregate of bornite II with accumulation of chalcocite and mawsonite II with tiny crystals of chalcopyrite II in calcite vein; E) chalcopyrite II cutting tetrahedrite-(Zn) aggregate in quartz-calcite vein; F) intergrowths of bornite II with chalcocite, tennantite-(Zn) with mawsonite II in calcite-dolomite vein; G) Bi-rich tennantite-(Zn) in the central part of intergrowth of tennantite-(Zn) with galena II in calcite vein; H) zonal Bi-rich tennantite-(Zn) with Bi-poor tennantite-(Zn) and galena II in calcite vein

It forms fine intergrowths with bornite II (Fig. 5D), and subhedral grains up to 300 µm, which form streaks in bornite II aggregates. It also forms tiny veinlets in bornite II, members of tetrahedrite group minerals (Fig. 5E) and chalcocite. Chalcopyrite II is accompanied by chalcocite, members of tetrahedrite group minerals and tin sulfides. It sometimes replaces bornite II and arsenopyrite grains. Chalcopyrite II also contains inclusions of chalcocite and galena II and is chemically pure. The empirical formula (based on the sum of two cations) of chalcopyrite II is $(\text{Cu}_{1.00-1.01}\text{Fe}_{0.99-1.00})_{\Sigma=2.00}\text{S}_{1.98-1.99}$.

Tetrahedrite group minerals

Members of tetrahedrite group minerals (TGM) were found in quartz and quartz-calcite-dolomite veins. They occur as subhedral grains varying in size 50–300 µm and aggregates up to 600 µm, usually overgrown with chalcopyrite I and bornite II. They are accompanied by sphalerite I and II, galena I and II, chalcocite, mawsonite, löllingite, and bismuth. Tiny inclusions of TGM up to 40 µm were discovered in chalcopyrite I aggregates. Two compositional sub-groups were distinguished: Bi-poor and Bi-rich TGM. Four minerals represent Bi-poor TGM: tetrahedrite-(Zn), tetrahedrite-(Fe), tennantite-(Zn), and tennantite-(Fe) (Fig. 6A). Microprobe analyses revealed a predominance of Zn members over Fe ones (Fig. 6B) and that tennantite is more abundant than tetrahedrite. The EPM analyses also indicate a wide range of Zn ↔ Fe substitution (Fig. 6B). Tetrahedrite-(Zn) and tetrahedrite-(Fe) are rare and form intergrowths with tennantite-(Zn), chalcopyrite I, and sphalerite I (Fig. 5B) and II, or are cross-cut by younger chalcopyrite II (Fig. 5E). They rarely create tiny inclusions within mawsonite II. The amount of Zn ranges from 1.57 apfu to 2.20 apfu in tetrahedrite-(Zn) and from 0.82 apfu to 0.96 apfu in tetrahedrite-(Fe). The content of Fe ranges from 0.15 apfu to 0.62 apfu in tetrahedrite-(Zn) and from 1.16 apfu to 1.21 apfu in tetrahedrite-(Fe). Tetrahedrite-(Zn) and tetrahedrite-(Fe) contain some small amounts of Ag (up to 0.03 apfu) and Pb (up to 0.01 apfu). Moreover, tetrahedrite-(Zn), which forms tiny inclusions in mawsonite II, has a significant content of Bi (up to 0.42 apfu). Oscillatory zonation caused by Bi enrichment is clearly visible in BSE images,

with brighter zones containing higher amounts of Bi than darker zones. Tennantite-(Zn) is the most common member of tetrahedrite group minerals. It forms intergrowths with chalcopyrite I, bornite II and chalcocite (Fig. 5F), and subhedral grains. It is accompanied by mawsonite II, sphalerite I and II, löllingite, galena I and II, wittichenite or stromeyerite, and native silver. The amount of Zn ranges from 0.94 apfu to 2.17 apfu, while the content of Fe ranges from 0.11 apfu to 1.06 apfu. Tennantite-(Zn) is enriched with Bi (content of Bi reaches up to 0.98 apfu) and contains admixtures of Pb (up to 0.06 apfu) and Ag (up to 0.03 apfu). Moreover, a wide range of As ↔ Bi substitution is clearly visible (Fig. 6C). Tennantite-(Fe) is rare and occurs as inner zones that are surrounded by tennantite-(Zn). In addition, it is usually accompanied by Fe-free sphalerite II. The content of Zn ranges from 0.46 apfu to 1.21 apfu, while the amount of Fe ranges from 0.90 apfu to 1.44 apfu. It contains high contents of Bi (up to 0.61 apfu) and low amounts of Ag (up to 0.02 apfu). The average empirical formula based on 16 cations for tetrahedrite-(Zn) is $(\text{Cu}_{10.01}\text{Ag}_{0.02}\text{Zn}_{1.70}\text{Fe}_{0.27})_{\Sigma=12.00}(\text{Sb}_{3.25}\text{As}_{0.66}\text{Bi}_{0.09})_{\Sigma=4.00}\text{S}_{12.66}$, for tetrahedrite-(Fe) is $(\text{Cu}_{9.91}\text{Ag}_{0.02}\text{Fe}_{1.19}\text{Zn}_{0.88})_{\Sigma=12.00}(\text{Sb}_{2.15}\text{As}_{1.85})_{\Sigma=4.00}\text{S}_{13.94}$, for tennantite-(Zn) is $(\text{Cu}_{10.04}\text{Ag}_{0.01}\text{Zn}_{1.34}\text{Fe}_{0.61})_{\Sigma=12.00}(\text{Sb}_{0.18}\text{As}_{3.45}\text{Bi}_{0.37})_{\Sigma=4.00}\text{S}_{12.86}$, and for tennantite-(Fe) is $(\text{Cu}_{10.06}\text{Ag}_{0.01}\text{Fe}_{1.15}\text{Zn}_{0.78})_{\Sigma=12.00}(\text{Sb}_{0.17}\text{As}_{3.77}\text{Bi}_{0.06})_{\Sigma=4.00}\text{S}_{12.91}$. According to the classification of the tetrahedrite group (Biagioni et al. 2020), tetrahedrite-group compositions with an S content not exceeding 12.50 apfu (27 analyses) are classified as keno-members (Fig. 6D). The EMP analyses indicated the presence of keno-tetrahedrite-(Fe), keno-tennantite-(Zn) and keno-tennantite-(Fe).

Within tennantite-(Zn) in the calcite vein, very rare Bi-rich tennantite-(Zn) with a Bi content greater than 1.00 apfu was discovered. It is accompanied by tennantite-(Zn), Se-enriched galena II (Fig. 5G), Fe-rich sphalerite I, chalcopyrite I, bismuth, and wittichenite. It usually occurs as brighter zones up to 25 µm thick, enriched in bismuth within tennantite-(Zn), and rarely forms tiny zonal grains up to 20 µm. Zonation in Bi-rich tennantite-(Zn) is related to the Bi content, which reaches up to 26.44 wt.% (2.20 apfu) (Figs. 5H, 6C). These zones occasionally exhibit Bi contents surpassing those of As, classifying these domains as *annivite*-(Zn).

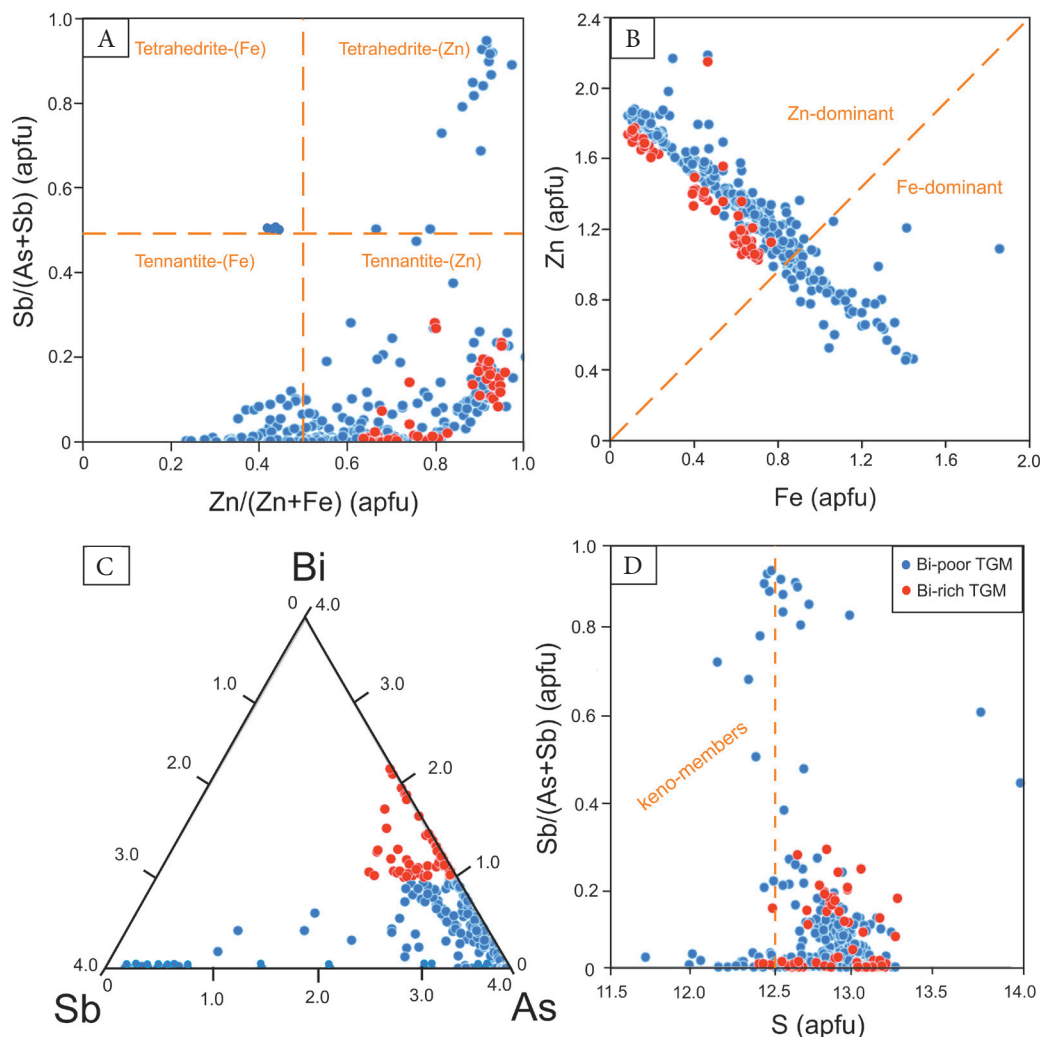


Fig. 6. Compositional relationships in tetrahedrite group minerals from Miedzianka-Ciechanowice (based on 321 analyses): A) diagram of $Sb/(As+Sb)$ vs. $Zn/(Zn+Fe)$; B) diagram of Zn vs. Fe substitution; C) compositional plot of TGM in terms of the As-Bi-Sb triangle (in apfu); D) diagram of $Sb/(As+Sb)$ vs. S

All Bi-rich tennantite grains and *annivite* also contain elevated contents of Ag, reaching up to 0.09 apfu. The average empirical formula based on 71 analyses and 16 cations for Bi-rich tennantite-(Zn) to *annivite*-(Zn) is $(Cu_{10.01}Ag_{0.03}Zn_{1.54}Fe_{0.42})_{\Sigma=12.00}(Sb_{0.17}As_{2.40}Bi_{1.43})_{\Sigma=4.00}S_{12.88}$.

Bornite

This mineral is widespread in the research area. Two generations of bornite have been discovered. Bornite I occurs in quartz and quartz-calcite veins. It forms small intergrowths with chalcopryrite I, sphalerite I and pyrite up to 150 μm or fine, subhedral grains up to 100 μm in chalcopryrite I aggregates. It is accompanied by members

of tetrahedrite group minerals and galena I. Bornite I is characterized by the presence of $Cu \leftrightarrow Fe$ substitution. This generation contains higher contents of Fe and slightly lower contents of Cu than bornite II. Bornite I also contains only a small amount of Zn (up to 0.02 apfu). The empirical formula of bornite I, based on 6 cations, could be written as $Cu_{4.80-4.89}Fe_{1.09-1.20}Zn_{0.00-0.02}S_{4.15-4.30}$.

Younger bornite II is more abundant and forms massive aggregates up to 1.5 mm. It also creates intergrowths, usually with chalcocite (Fig. 5F) in quartz-calcite, calcite, calcite-dolomite, and baryte veins. Bornite II is accompanied by chalcopryrite II, sphalerite II, members of tetrahedrite-tennantite series, betekhtinite, galena II, löllingite,

arsenopyrite, wittichenite, stromeyerite, mawsonite, and stannoidite (Fig. 5D). Tiny inclusions of mawsonite up to 50 µm (Fig. 7A), and stannoidite are very common in bornite II aggregates, while bigger irregular aggregates are rare. Moreover, subhedral grains of chalcopyrite II and löllingite form streaks within massive bornite II. Veinlets of stromeyerite, chalcopyrite II, and tin sulfides were also discovered. In bornite-chalcocite aggregates accompanied by stromeyerite, rare silver phases (native silver, naumannite, hessite, cervelleite, mckinstryite, selenojalpaite, and proustite) were found. Bornite II is sometimes replaced by chalcocite. It contains significant contents of Ag (up to 0.04 apfu) and Bi (up to 0.02 apfu). The empirical formula of bornite II, based on 6 cations, could be written as $\text{Cu}_{4.91-5.05}\text{Fe}_{0.95-1.03}\text{Ag}_{0.00-0.04}\text{Bi}_{0.00-0.02}\text{S}_{3.81-4.06}$.

Chalcocite

This mineral is common only in the Friederike-Juliane dump in the southeastern part of the deposit where bornite-chalcocite ore has been described. Chalcocite forms irregular aggregates up to 500 µm and intergrowths with bornite II up to 800 µm (Fig. 7B), and rarely sphalerite II or betekhtinite (Fig. 7C–D) in calcite-dolomite and baryte veins. It sometimes replaces bornite II aggregates. It is accompanied by members of tetrahedrite group minerals, löllingite, galena II, mawsonite II, stannoidite II, and wittichenite. The presence of silver minerals within bornite-chalcocite aggregate in baryte II has also been confirmed. The most common is stromeyerite, which forms tiny veinlets, although intergrowths of native silver with chalcocite up to 100 µm were also found. Chalcocite also contains tiny inclusions of acanthite, naumannite, and cervelleite up to 20 µm. The chalcocite aggregates are sometimes cut by younger mawsonite-stannoidite II and chalcopyrite II veinlets. This mineral is close to the theoretical chemical composition and contains only small contents of Fe (up to 0.02 apfu) and Ag (up to 0.01 apfu). The empirical formula of chalcocite, based on the sum of 2 cations, could be written as $(\text{Cu}_{1.99-2.00}\text{Fe}_{0.00-0.02}\text{Ag}_{0.00-0.01})_{\Sigma=2.00}\text{S}_{1.00-1.01}$.

Betekhtinite

This mineral occurs as intergrowths up to 600 µm with older bornite II and chalcocite (Fig. 7C,D) in calcite and calcite-dolomite veins.

It is accompanied by sphalerite II, galena II, and löllingite. Betekhtinite contains more Pb (up to 0.83 apfu) than Fe (up to 0.44 apfu) as well as admixtures of Ag (up to 0.04 apfu), As (up to 0.02 apfu), Se (up to 0.02 apfu), Bi (up to 0.01 apfu), and Sb (up to 0.01 apfu). The empirical formula of betekhtinite could be written as $(\text{Cu}_{9.6-9.76}\text{Pb}_{0.73-0.83}\text{Fe}_{0.41-0.44})_{\Sigma=10.90}\text{S}_{6.20-6.40}$.

Native bismuth

Native bismuth forms fine, irregular aggregates (up to 80 µm) in massive chalcopyrite I, and intergrowths with galena I and TGM in quartz and calcite veins. It also occurs as fine, subhedral inclusions (up to 40 µm) within galena I and members of tetrahedrite-tennantite series. Bismuth is chemically homogeneous.

Wittichenite

It is a rare mineral that was discovered in calcite and baryte veins in the dump of the Friederike-Juliane shaft in the southeast part of the deposit. Wittichenite creates thin veinlets (up to 80 µm thick) with younger stromeyerite up to 800 µm in length (Fig. 7E), rarely forms intergrowths with bornite II and chalcocite, or bigger, irregular aggregates up to 400 µm in massive bornite II. It is usually accompanied by sphalerite II and minor amounts of löllingite and members of tetrahedrite group minerals, especially Bi-enriched tennantite-(Zn). Wittichenite contains significant amounts of Pb (up to 0.06 apfu), Se (up to 0.04 apfu) and Ag (up to 0.03 apfu). The general formula of wittichenite, based on the sum of 4 cations, could be written as $(\text{Cu}_{2.98-3.04}\text{Bi}_{0.93-0.96}\text{Pb}_{0.00-0.06}\text{Ag}_{0.00-0.03})_{\Sigma=4.00}(\text{S}_{2.86-2.94}\text{Se}_{0.00-0.04})_{\Sigma=2.90-2.94}$.

Galena

Galena is a widespread mineral in the studied samples; however, it usually occurs in minor amounts in the Miedzianka-Ciechanowice deposit. Two generations of this mineral have been discovered.

Galena I occurs as tiny euhedral and subhedral, separate grains up to 100 µm, and bigger aggregates up to 300 µm in size in hydrothermal quartz and quartz-calcite veins. It also forms intergrowths with chalcopyrite I, sphalerite I, bornite I, TGM, pyrite, arsenopyrite and löllingite. Galena I contains tiny inclusions of bismuth and sometimes fills the cracks in pyrite.

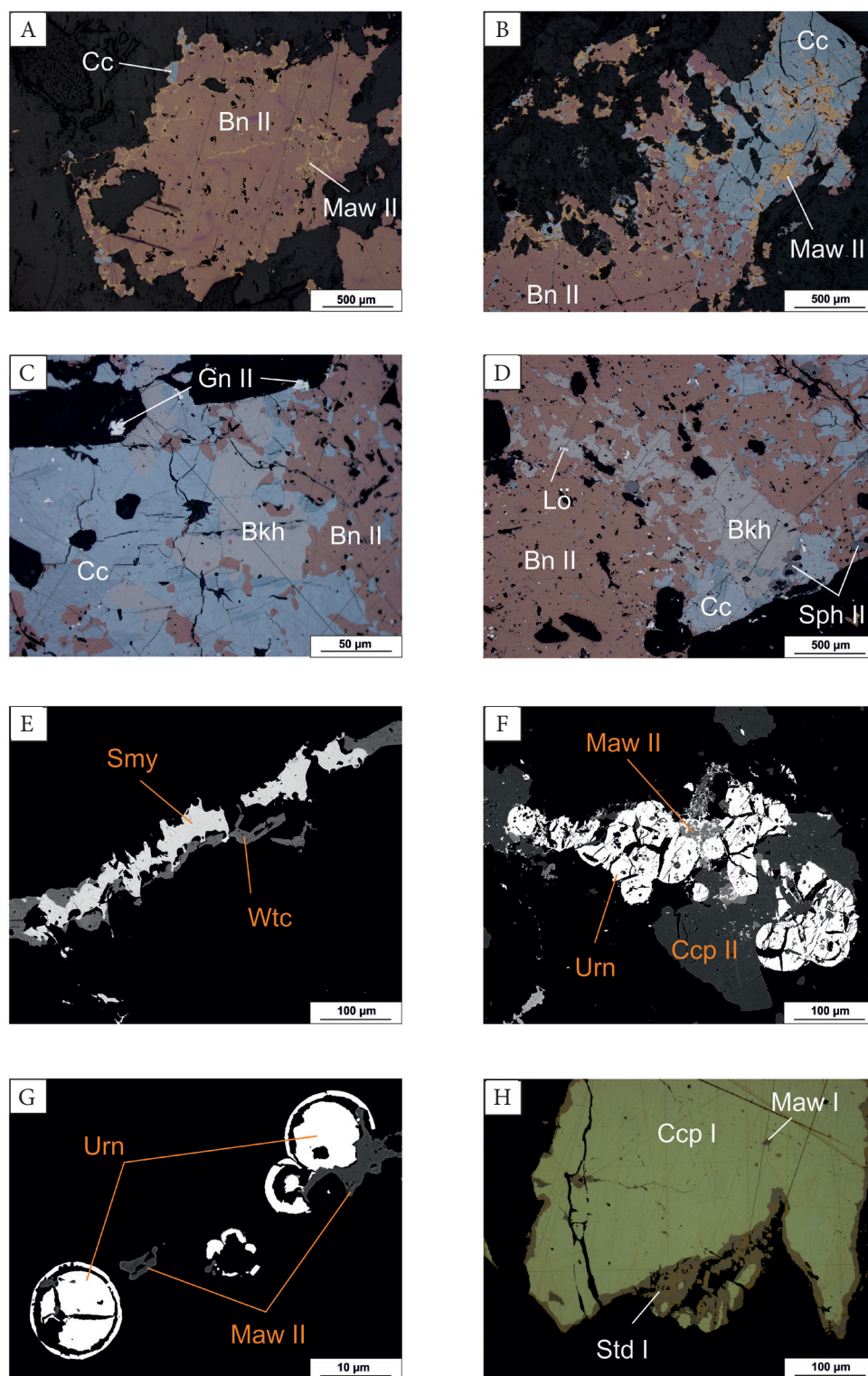


Fig. 7. Reflected-light (A–D, H) and back-scattered electron (E–G) images illustrating the main features of mineral assemblages: A) aggregate of bornite II with veinlets and inclusions of mawsonite II and chalcocite in calcite-dolomite vein; B) intergrowths of bornite II with chalcocite and accumulation of mawsonite II in baryte vein; C) intergrowths of chalcocite with bornite II and betekhtinite with tiny grains of galena II in calcite-dolomite vein; D) intergrowths of bornite II with chalcocite and betekhtinite with inclusions of löllingite and sphalerite II in calcite-dolomite vein; E) wittichenite-stromeyerite veinlets in baryte vein; F) intergrowths of uraninite with chalcocopyrite II and mawsonite II in calcite-dolomite veinlet; G) spheroidal uraninite with mawsonite II in calcite-dolomite veinlet; H) aggregate of chalcocopyrite I overgrown by younger stannoidite I and inclusions of mawsonite I in quartz-calcite vein

Fine subhedral grains of galena I have significant admixtures of Bi (up to 0.05 apfu), and Cu (up to 0.03 apfu), while bigger irregular aggregates and intergrowths of this mineral contain small contents of Fe, Cu and Bi (up to 0.02 apfu) and Zn (up to 0.01 apfu). The empirical formula of galena I, based on 1 cation, could be written as $(\text{Pb}_{0.90-0.99}\text{Bi}_{0.00-0.05}\text{Cu}_{0.00-0.03}\text{Fe}_{0.00-0.02}\text{Zn}_{0.00-0.01})_{\Sigma=1.00}\text{S}_{0.98-1.01}$.

Galena II occurs in calcite, calcite-dolomite, and baryte veins and rarely in quartz-calcite veins. It forms subhedral grains up to 150 µm or intergrowths with bornite II, chalcocite, TGM, Bi-rich TGM, and betekhtinite. Galena II is rarely accompanied by silver minerals, including stromeyerite, acanthite, and naumannite. It also encloses inclusions of acanthite and rare clausthalite. Galena II has significant contents of Ag (up to 0.04 apfu), but increased Se concentrations (up to 0.02 apfu) were also detected in smaller, subhedral grains with clausthalite. The empirical formula of galena II, based on 1 cation, could be written as $(\text{Pb}_{0.96-1.00}\text{Ag}_{0.00-0.04})_{\Sigma=1.00}(\text{S}_{0.96-1.00}\text{Se}_{0.00-0.02})_{\Sigma=0.98-1.00}$.

Uraninite

This mineral usually occurs in calcite-dolomite veinlets. Uraninite forms intergrowths with younger chalcopyrite II and mawsonite II (Fig. 7F) or creates characteristic spheroidal aggregates accompanied by mawsonite II (Fig. 7G). It contains significant contents of Ca (up to 0.20 apfu), Ti (up to 0.06 apfu) and low admixtures of Y (up to 0.02 apfu), Pb (up to 0.02 apfu), and Nd (up to 0.01 apfu).

Tin-bearing sulfides

The Sn-bearing sulfides, including mawsonite and stannoidite, are widespread in the studied samples and occur in all types of ore veins. They usually form irregular aggregates, intergrowths, veinlets, and fine inclusions in chalcopyrite I, bornite I and II, sphalerite I and II, TGM, galena I, and pyrite. The EMP analyses confirmed that mawsonite II is the most abundant tin-bearing sulfide in this paragenesis. Two generations of these minerals were discovered.

Mawsonite I is rare and creates predominantly small intergrowths up to 150 µm with chalcopyrite I and fine inclusions up to 40 µm (Fig. 7H) in quartz-calcite veins. It is associated with sphalerite I,

members of tetrahedrite group minerals, galena I, and pyrite. It contains small contents of Zn (up to 0.03 apfu). The empirical formula of mawsonite I, based on the sum of 9 cations, could be written as $(\text{Cu}_{5.90-6.04}\text{Fe}_{1.93-2.06}\text{Sn}_{1.00-1.03}\text{Zn}_{0.00-0.03})_{\Sigma=9.00-9.02}\text{S}_{7.74-8.07}$.

Mawsonite II, the most common tin sulfide, forms irregular aggregates up to 200 µm, veinlets exceeding 1 mm in length that cut through bornite II aggregates, and tiny inclusions in massive bornite II (Fig. 7A) in calcite-dolomite and baryte. It sometimes overgrows the bornite II aggregates (Fig. 9A) and creates bigger accumulations up to 600 µm in size (Fig. 9B). Mawsonite II veinlets also cut the older chalcocite aggregates (Fig. 7B). It sometimes occurs as intergrowths and veinlets with stannoidite II. It is accompanied by TGM, löllingite, chalcopyrite II, sphalerite II, rarely native silver, and uraninite. It contains small contents of Ag (up to 0.03 apfu). The empirical formula of mawsonite II, based on the sum of 9 cations, could be written as $(\text{Cu}_{5.80-6.09}\text{Fe}_{1.93-2.16}\text{Sn}_{0.95-1.04}\text{Ag}_{0.00-0.03})_{\Sigma=9.00}\text{S}_{7.49-8.12}$.

Stannoidite I forms irregular aggregates up to 200 µm, or tiny veinlets and inclusions up to 50 µm in chalcopyrite I in quartz-calcite veins. Rarely, stannoidite fills parts of voids in chalcopyrite I (Fig. 7H) and pyrite. Stannoidite I is accompanied by sphalerite I, minor amounts of galena I, and TGM. It is usually chemically pure, with only a few inclusions containing small contents of Ag (up to 0.01 apfu). The empirical formula of stannoidite I, based on the sum of 13 cations, could be written as $(\text{Cu}_{7.72-7.91}\text{Fe}_{2.50-2.70}\text{Sn}_{1.79-2.06}\text{Zn}_{0.53-0.79})_{\Sigma=13.00}\text{S}_{11.67-12.11}$.

Stannoidite II is rare and occurs in bornite II aggregates. It forms tiny inclusions up to 60 µm in bornite II, intergrowths with mawsonite or creates stannoidite-mawsonite veinlets cutting bornite II aggregates (Fig. 9A) in calcite-dolomite and baryte veins. Similarly to mawsonite II, stannoidite II is accompanied by TGM, chalcopyrite II, sphalerite II, and löllingite. It is usually chemically pure and does not contain any admixtures. The empirical formula of stannoidite II, based on the sum of 13 cations, could be written as $(\text{Cu}_{7.97-8.20}\text{Fe}_{2.16-2.22}\text{Sn}_{1.93-1.99}\text{Zn}_{0.71-0.82})_{\Sigma=13.00}\text{S}_{11.26-11.59}$. A comparison of mineralogical data for tin sulfides from this work and previous research from Miedzianka-Ciechanowice and Rędziny is presented in the diagrams below (Fig. 8).

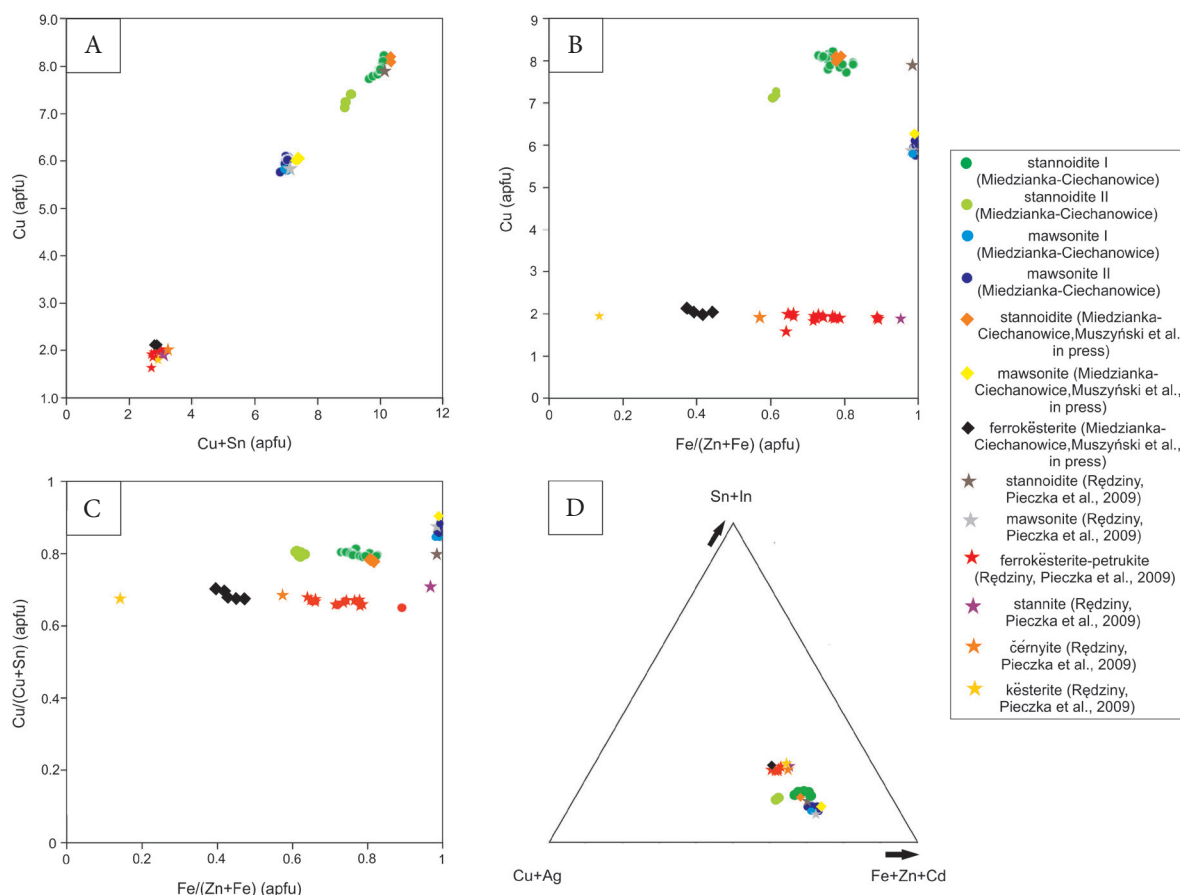


Fig. 8. Compositional relationships in the tin-bearing sulfides from the Miedzianka-Ciechanowice (based on 93 analyses) and Rędziny deposits: A) diagram of Cu vs. Cu+Sn; B) diagram of Cu vs. Fe/(Fe+Zn); C) diagram of Cu/(Cu+Sn) vs. Fe/(Fe+Zn); D) compositional plot of Sn sulfides in terms of the (Cu+Ag)–(Sn+In)–(Fe+Zn+Cd) triangle (in apfu) from Miedzianka-Ciechanowice and Rędziny

Silver minerals

Silver minerals are not very abundant in the samples studied. Generally, they occur in the dump of the Friederike-Juliane shaft, and rarely at Neu Adler in the southeastern part of the Miedzianka-Ciechanowice deposit. Silver minerals mostly occur in baryte II, rarely in baryte I, or calcite. They are associated with bornite-chalcocite aggregates and are sometimes accompanied by tennantite-(Zn) and löllingite. Silver minerals are represented by sulfides, tellurides, and selenides. Nine minerals were identified, including hessite, cervelleite, stromeyerite, native silver, acanthite, mckinstryite, proustite, selenojalpaite, and naumannite.

Hessite appears to represent the oldest silver phase in the Miedzianka-Ciechanowice deposit. It is a very rare mineral which occurs in

bornite-chalcocite ore and is accompanied by other silver minerals (mainly stromeyerite) in baryte veins; however, one subhedral grain was also found in a calcite vein. It forms tiny intergrowths with naumannite up to 15 μm in baryte II veins and is rarely overgrown by naumannite (Fig. 9C). This indicates that selenide minerals may be younger than other Ag-bearing phases. It contains low contents of Sb (up to 0.01 apfu) and Se (up to 0.01 apfu). The empirical formula of hessite, based on 2 cations, could be written as $(\text{Ag}_{1.99-2.00}\text{Sb}_{0.00-0.01})_{\Sigma=2.00}(\text{Te}_{0.99-1.00}\text{Se}_{0.00-0.01})_{\Sigma=1.00}$.

Cervelleite forms tiny intergrowths up to 15 μm with hessite and younger naumannite in baryte II veins (Fig. 9C). The EMP analyses confirmed that this mineral is chemically pure. The empirical formula of cervelleite, based on 4 cations, could be written as $\text{Ag}_{4.00}\text{Te}_{1.02}\text{S}_{0.95}$.

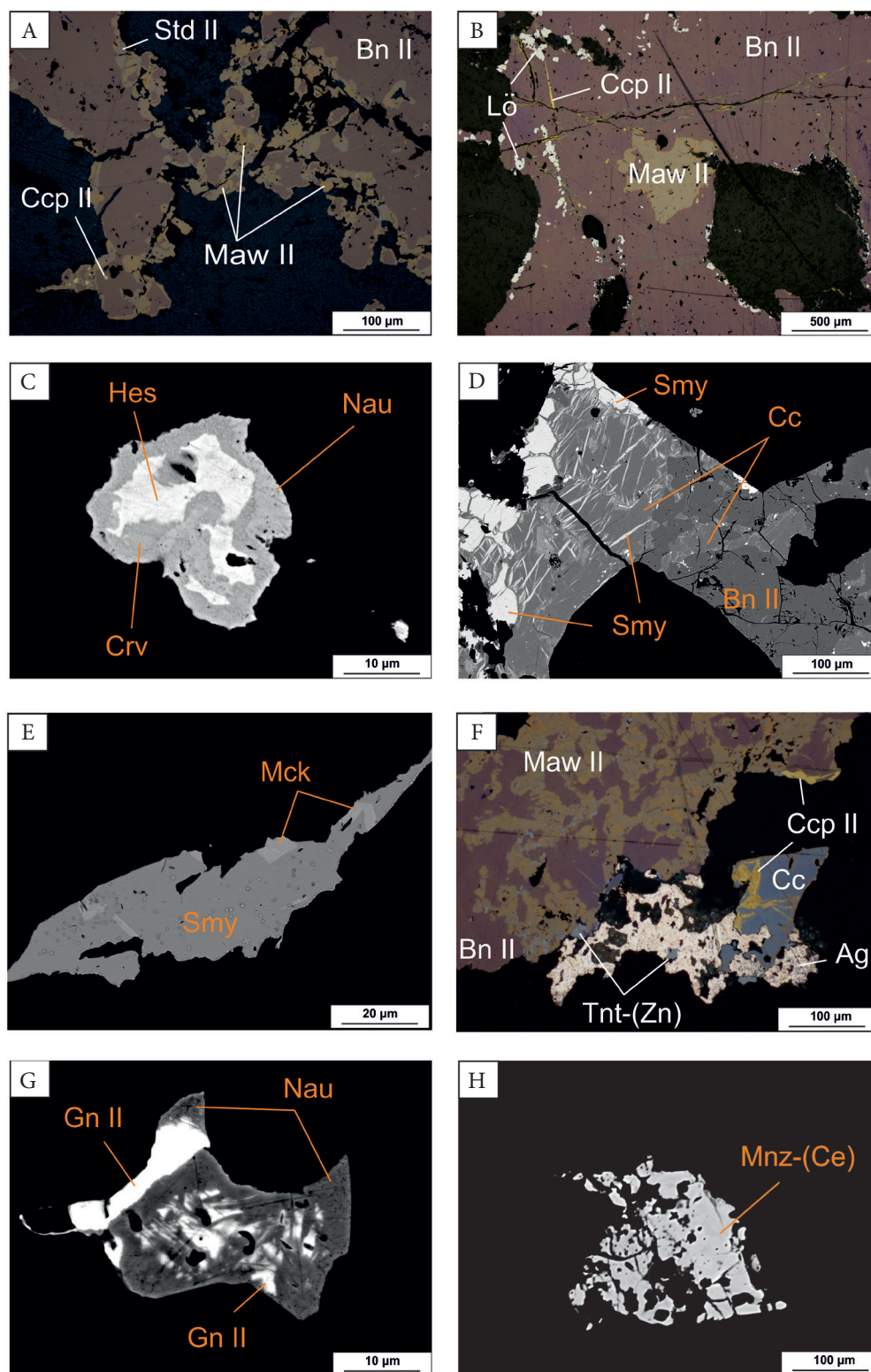


Fig. 9. Back-scattered electron (C–E, G, H) and reflected-light (A, B, F) images illustrating the main features of mineral assemblages: A) aggregates of bornite II overgrown by mawsonite II and inclusions of stannoidite II in calcite-dolomite vein; B) accumulation of mawsonite II in bornite II aggregate with inclusions of löllingite and chalcopyrite II veinlets in calcite-dolomite vein; C) tiny intergrowth of naumannite, hessite and cervelleite in baryte vein; D) intergrowths of chalcocite with bornite II and stromeyerite cut by stromeyerite veinlets in baryte vein; E) intergrowths of stromeyerite and mckinstryite in baryte vein; F) irregular aggregate of native silver with chalcocite and chalcopyrite II accompanied by bornite II, mawsonite II and tennantite-(Zn) in baryte vein; G) intergrowth of galena II with naumannite in baryte vein; H) monazite-(Ce) in quartz vein

Stromeyerite is the most common silver mineral in the samples studied. It mostly occurs in baryte II, and rarely in calcite-dolomite veins. Stromeyerite primarily forms thin veinlets (up to 80 µm thick) with older wittichenite (Fig. 7E) in bornite II aggregates and host rocks, such as baryte II or calcite-dolomite veins. The length of these veinlets varies from 200 to 800 µm. It also creates intergrowths with bornite II and chalcocite (Fig. 9D), mckinstryite (Fig. 9E), or proustite. Stromeyerite veinlets sometimes cut through the bornite-chalcocite aggregates and are accompanied by tennantite-(Zn). Fine grains of acanthite are found along the border of stromeyerite and bornite II. It is sometimes replaced by proustite. Stromeyerite is usually chemically pure and, except for Fe (up to 0.01 apfu), does not contain any admixtures. The empirical formula of stromeyerite, based on 2 cations, could be written as $(\text{Ag}_{0.96-0.97}\text{Cu}_{1.02-1.04}\text{Fe}_{0.00-0.01})_{\Sigma=2.00}\text{S}_{0.97-1.03}$.

Native silver usually forms irregular aggregates up to 250 µm in baryte II. It rarely creates separate subhedral grains up to 80 µm in host rocks. It is usually associated with bornite II, chalcocite, and mawsonite II (Fig. 9F). Native silver is rarely accompanied by members of tetrahedrite group minerals, mostly tennantite-(Zn), and chalcopyrite II. It contains small admixtures of S (up to 0.02 apfu), Hg (up to 0.01 apfu) and Cu (up to 0.01 apfu).

Acanthite is a very rare mineral. It forms tiny, drop-like inclusions up to 20 µm in galena II and chalcocite. This mineral also occurs along the border of bornite II and stromeyerite aggregates. Acanthite sometimes forms very thin aggregates on the surface of bornite II. It contains low contents of Cu (up to 0.02 apfu) and Fe (up to 0.01 apfu). The empirical formula of acanthite, based on 2 cations, could be written as $(\text{Ag}_{1.98-1.99}\text{Cu}_{0.00-0.02}\text{Fe}_{0.00-0.01})_{\Sigma=1.99-2.00}\text{S}_{1.04-1.32}$.

Mckinstryite forms intergrowths with stromeyerite up to 30 µm in baryte II (Fig. 9E). It also creates fine inclusions in bornite II, where it is accompanied by chalcocite, stromeyerite, and proustite. It contains low contents of Fe (up to 0.03 apfu). The empirical formula of mckinstryite, based on 2 cations, could be written as $(\text{Ag}_{1.19}\text{Cu}_{0.78}\text{Fe}_{0.03})_{\Sigma=2.00}\text{S}_{1.00}$.

Proustite forms fine, anhedral, and subhedral grains up to 30 µm within bornite-chalcocite aggregates in baryte II. It is accompanied by stromeyerite and mckinstryite. It rarely creates intergrowths with stromeyerite, wittichenite and is accompanied by löllingite. Proustite sometimes replaces the older stromeyerite. It contains significant content of Cu (up to 0.07 apfu) and small concentrations of Zn (up to 0.02 apfu), Fe (up to 0.02 apfu), and Cd (up to 0.01 apfu). The empirical formula of proustite, based on 3 cations, could be written as $(\text{Ag}_{2.93-2.95}\text{Cu}_{0.00-0.07}\text{Zn}_{0.00-0.02}\text{Fe}_{0.00-0.02}\text{Cd}_{0.00-0.01})_{\Sigma=3.00}\text{As}_{0.90-0.95}\text{S}_{2.73-2.94}$.

Selenojalpaite is very rare, and only two anhedral grains up to 20 µm were discovered. This mineral occurs in bornite-chalcocite aggregates, which are cut by stromeyerite-wittichenite veinlets. It shows increased contents of S (up to 0.45 apfu) and Fe (up to 0.16 apfu). Low admixtures of Bi and Pb up to 0.02 apfu were also detected. The empirical formula of selenojalpaite, based on 4 cations, could be written as $(\text{Ag}_{2.72-3.02}\text{Cu}_{0.87-1.12}\text{Fe}_{0.07-0.16}\text{Bi}_{0.00-0.02}\text{Pb}_{0.00-0.02})_{\Sigma=4.00}\text{Se}_{2.80-2.87}\text{S}_{0.37-0.45}$.

Naumannite occurs as tiny inclusions up to 20 µm in galena II or as anhedral grains in chalcocite. It is usually accompanied by other silver minerals. This mineral sometimes forms intergrowths with older galena II (Fig. 9G) and sometimes replaces it. Naumannite rarely overgrows hessite and creates tiny intergrowths with it up to 15 µm (Fig. 9C). It contains only low contents of Cu (up to 0.01 apfu). The empirical formula of naumannite, based on 2 cations, could be written as $(\text{Ag}_{1.99-2.00}\text{Cu}_{0.00-0.01})_{\Sigma=2.00}\text{Se}_{0.99-1.01}$.

Löllingite

This mineral occurs in quartz, quartz-calcite, calcite-dolomite, and rarely in baryte veins. It forms separate euhedral and subhedral grains up to 200 µm in chalcopyrite I aggregates or creates veinlets and streaks of tiny subhedral crystals within bornite II, with lengths not exceeding 500 µm (Fig. 9B). Löllingite usually overgrows older arsenopyrite grains (Fig. 5A). It is accompanied by members of tetrahedrite group minerals, mawsonite II, galena I and II, rarely chalcocite, and chalcopyrite II. Löllingite usually overgrows older arsenopyrite grains. It contains

significant contents of Cu (up to 0.06 apfu), Co (up to 0.02 apfu), Bi (up to 0.02 apfu), and Ni (up to 0.01 apfu). Löllingite is also chemically variable and contains high contents of S that reach up to 0.30 apfu. This influences the wide As/S ratio range from 5.51 (in S-rich löllingite) up to 95.25 (in S-poor löllingite). The general formula of löllingite, based on 1 cation, could be written as $(\text{Fe}_{0.90-0.99}\text{Cu}_{0.00-0.06}\text{Co}_{0.00-0.02}\text{Bi}_{0.00-0.02}\text{Ni}_{0.00-0.01})_{\Sigma=1.00}(\text{As}_{1.64-1.94}\text{S}_{0.02-0.30})_{\Sigma=1.94-1.96}$.

Cubanite

It is a very rare mineral, and only two tiny subhedral grains up to 35 µm were discovered. Cubanite occurs in arsenopyrite aggregates in quartz veins. It is accompanied by chalcopyrite I and pyrite. It does not contain any admixtures. The empirical formula of cubanite, based on 3 cations, could be written as $\text{Cu}_{0.98-1.04}\text{Fe}_{1.96-2.02}\text{S}_{2.91-2.96}$.

Clausthalite

It is a very rare mineral that forms tiny, drop-like inclusions up to 30 µm within galena II in calcite-dolomite veins. Galena II with clausthalite is usually accompanied by chalcopyrite I, sphalerite I, and members of tetrahedrite group minerals. Clausthalite is characterized by a varied chemical composition. The Se content ranges from 0.59 to up to 0.64 apfu, while the content of S ranges from 0.26 to 0.40 apfu. It confirms a wide range of $\text{Se} \leftrightarrow \text{S}$ substitution. Moreover, clausthalite contains significant amounts of Cu (up to 0.09 apfu), Fe (up to 0.05 apfu), Bi (up to 0.02 apfu), and Ag (up to 0.02 apfu). The empirical formula of clausthalite, based on 1 cation, could be written as $(\text{Pb}_{0.84-0.94}\text{Cu}_{0.04-0.09}\text{Fe}_{0.00-0.05}\text{Bi}_{0.00-0.02}\text{Ag}_{0.00-0.02})_{\Sigma=1.00}(\text{Se}_{0.59-0.80}\text{S}_{0.26-0.40})_{\Sigma=0.97-0.99}$.

Monazite

It is a very rare accessory mineral that occurs in quartz veins. Monazite forms fine, irregular aggregates up to 150 µm that are usually cut by tiny quartz veinlets (Fig. 9H). It is accompanied by chalcopyrite I, bornite I, sphalerite I, and pyrite. Monazite-(Ce) was discovered in the Miedzianka-Ciechanowice deposit. It does not contain ThO_2 , but it does contain Pr (up to 0.08 apfu), Sm (up to 0.02 apfu), Y (up to 0.02 apfu), and Gd

(up to 0.01 apfu). The $(\text{La}/\text{Sm})_{\text{CN}}$ ratios range from 4.84 to 5.97 (mean = 5.43) with positive Ce anomalies and no significant Eu anomalies.

DISCUSSION

Bi-rich TGM in Sudetes and Bohemian Massif

Tetrahedrite-group minerals are very common sulfosalts in various types of hydrothermal ore deposits; however, their enrichment in Bi, especially above 1.00 apfu, is very rare. The Miedzianka-Ciechanowice area is the second place in Poland where Bi-rich TGM has been confirmed.

The Rędziny deposit, located in the contact zone of Karkonosze Granite in close proximity to Miedzianka-Ciechanowice, contains polymetallic mineralization with very rare Bi-rich tetrahedrite and tennantite. In contrast to the studied area, rare Bi-rich TGM was found in polymetallic veins (Gołębiewska et al. 2012). The Bi-rich tetrahedrite (more than 1.00 apfu of Bi), which was not reported in Miedzianka-Ciechanowice, occurs within diverse assemblages containing Sn-oxides (cassiterite, malayaite, mushistonite), Sn-bearing sulfides (stannite, chatkalite, stannoidite and mawsonite), relics of chalcopyrite, Ag-bearing bornite, tiny inclusions of acanthite, matildite, pavonite, Ag-bearing galena, Ag-enriched wittichenite, and bismuthinite. It contains high contents of Ag (up to 3.41 apfu) and Bi (up to 2.65 apfu) (Gołębiewska et al. 2012) in contrast to the studied area, where tetrahedrite has only 0.42 apfu of Bi and only 0.03 apfu of Ag. Similarly to Rędziny, the Bi-enriched tetrahedrite from the Miedzianka-Ciechanowice deposit occurs as inclusions within mawsonite II. The Bi-rich tennantite from Rędziny occurs in quartz-chlorite-arsenopyrite veins and forms grains up to a few tenths of a millimeter in size. Similarly to Miedzianka-Ciechanowice, it is accompanied by chalcopyrite, Fe-rich sphalerite, Se-bearing galena, bismuth, and wittichenite. However, it was recognized also in association with minerals of the aikinite series, bismuthinite, and Se-enriched ikonolite (Gołębiewska et al. 2012), which do not occur in this paragenesis, but have been recognized in this area (Muszyński et al., in press). The predominance

of tennantite-(Zn) over tennantite-(Fe) is typical for both deposits, however the Bi-rich tennantite from Rędziny shows broader ranges of Zn and Fe contents (from 0.00 to 1.86 apfu and from 0.27 to 2.00 apfu, respectively). It also contains lower Bi concentrations of up to 1.51 apfu (Gołębiewska et al. 2012) compared to Miedzianka-Ciechanowice, where the Bi content reaches up to 2.20 apfu. This suggests higher activity of Bi in Miedzianka-Ciechanowice at this stage of crystallization.

A wide range of As $\leftrightarrow$ Bi substitution was observed in both deposits. Moreover, Bi-rich tennantite grains are not enriched in Ag and do not contain insignificant contents in these locations. According to Gołębiewska et al. (2012), this could be related to the very low contents of Fe in the most Bi-enriched tennantite and the precipitation of silver minerals, which competed with TGM for Ag. Furthermore, similarly to the studied area, the Bi-enriched TGM (Bi content of less than 1.00 apfu) is variable, while Zn-rich members predominate over Fe-rich ones. Ag- and Bi-rich tetrahedrite, which was not discovered in Miedzianka-Ciechanowice, shows the opposite trend and confirms the strong correlation between Fe and Ag. Such a correlation was not observed in the studied area, where Zn-rich hydrothermal environments dominate. This corroborates the predominance of Zn-rich members over Fe-rich ones and the very low silver contents of TGM. According to Gołębiewska et al. (2012), even the extremely Bi-enriched TGM can form in Zn-poor conditions, and such enrichment is not related to Bi $\leftrightarrow$ Sb or As substitution. While the compositions of the Bi-rich TGM from Miedzianka-Ciechanowice do not confirm this trend, several other similarities between both locations have been confirmed. The substitution of Bi $\leftrightarrow$ As in tennantite is associated with an increase in the Zn content and depletion in Fe. In addition, Bi $\leftrightarrow$ Sb substitution is observed in tetrahedrites; however, this trend is more prominent in Rędziny. The gradual increase in Bi led to the predominance of Bi over Sb in Rędziny and over As in Miedzianka-Ciechanowice, which corroborates the presence of very rare *annivite*.

The chemical composition of the TGM in the studied area is related to precipitation, temperature, and the composition of the fluids. This has

been confirmed by previous studies (Pieczka et al. 2009, Gołębiewska et al. 2012), which estimated the formation temperature of the TGM from the Rędziny deposit. Based on similar associations, correlations, and mutual relations of TGM in the studied samples, it is clear that *annivite* and Bi-rich tennantite are the earliest-forming minerals of the TGM series. According to Gołębiewska et al. (2012), Bi-rich TGM crystallized at temperatures of 230–300°C, while the Bi-enriched tetrahedrite found within mawsonite was formed at about 290°C. *Annivite* probably crystallized at lower temperatures of around 260°C, although laboratory research does not confirm this suggestion. The Bi-rich tennantite was formed at a similar temperature range of 250–260°C. As the temperature decreased, the Bi-rich tennantite gradually lost Bi over the temperature range of 230–210°C. The Bi-enriched tetrahedrite is probably a remnant of this gradual decrease in temperature and loss of Bi from Bi-rich tetrahedrite, which was not observed in the studied samples. This mineral was formed in the temperature range of 210–230°C. As a result of further loss of Bi, Bi-free TGM crystallized at approximately 150–170°C (Gołębiewska et al. 2012).

Bi-rich TGM has also been reported in the Jáchymov mining district in the Czech Republic, where, similarly to the Bi-rich tennantite-(Zn) in Miedzianka-Ciechanowice, *annivite*-(Zn) but also Bi-rich tetrahedrite-(Zn) have been described (Velebil and Sejkora 2018, Sejkora et al. 2024). They occur within similar associations to the studied area, which also includes tennantite-(Fe), tetrahedrite-(Zn), bismuth, and wittichenite; however, in contrast to Miedzianka-Ciechanowice, it also contains other bismuth minerals, including bismite, walpurgite, and emplectite (Sejkora et al. 2024). The most abundant mineral phase is Bi-rich tennantite, while the other Bi-rich phases occur very rarely. The Bi-rich tennantite usually forms intergrowths with grains of bismite, relics of bismuth, and aggregates of emplectite up to 0.7 mm in size (Velebil & Sejkora 2018). The Bi content is lower than in the studied deposit, reaching up to 1.89 apfu. In the Jáchymov area, similarly to Miedzianka-Ciechanowice, the Zn-dominant members predominate over the Fe-dominant members.

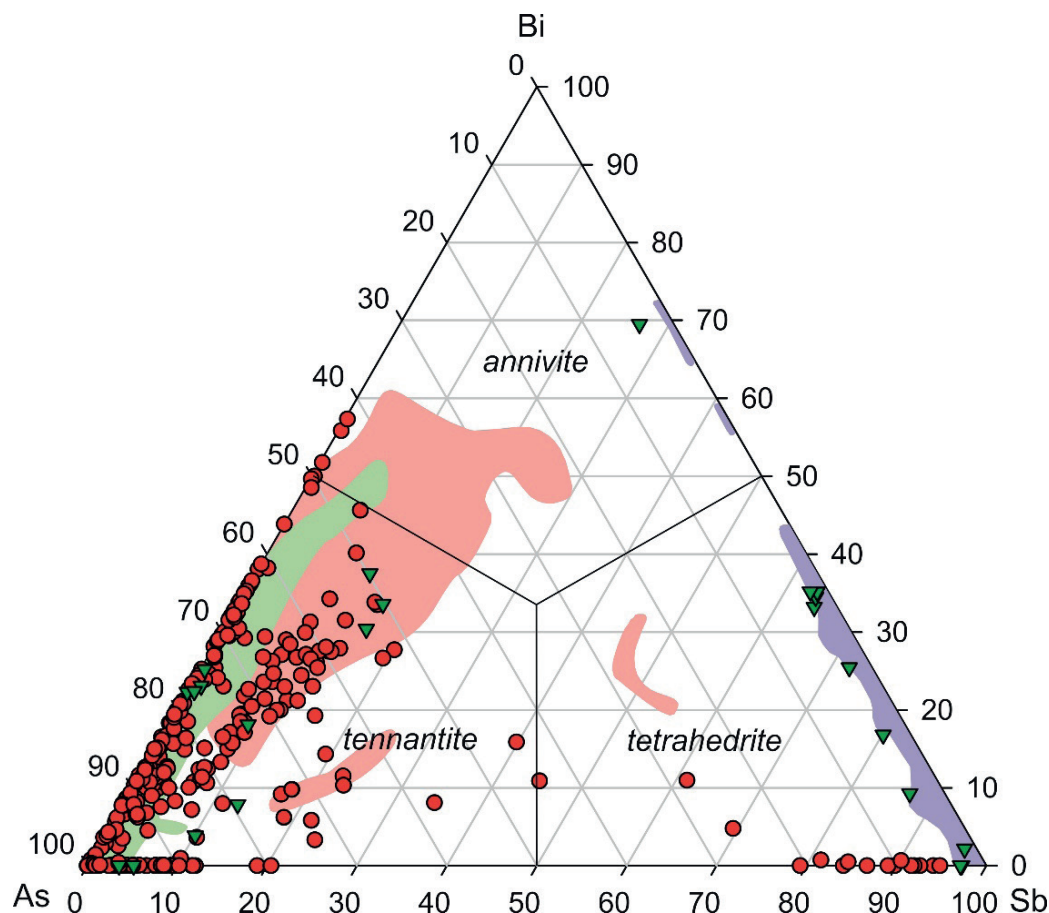


Fig. 10. As-Bi-Sb ratio (apfu) in Bi-rich TGM; red circles – Miedzianka-Ciechanowice (this study), green triangles – Rędziny (Gołębiewska et al. 2012); color fields correspond to Bi-rich TGM from Jáchymov (pink), Hřebečná (green) (Sejkora et al. 2024) and Příbram (blue) (Dolníček et al. 2024)

The Bi-rich tennantite in Jáchymov contains a low content of Ag, not exceeding 0.07 apfu (Sejkora et al. 2024), compared to 0.09 apfu in Miedzianka-Ciechanowice. Elongated, isometric, or irregular zones up to 50 μm in size were discovered within Bi-rich tennantite and tetrahedrite aggregates (Velebil & Sejkora 2018). The most Bi-rich zones, where Bi predominates over As (with Bi contents reaching up to 2.37 apfu), correspond to *annivite*. This mineral rarely forms anhedral grains up to 50 μm in size (Sejkora et al. 2024). A mineral with a chemical composition corresponding to the not-yet-approved *annivite*-(Fe), with a Bi content up to 1.98 apfu, was also discovered. The Bi-rich tetrahedrite is very rare and contains up to 1.20 apfu of Bi. It forms an irregular zone approximately 40 $\mu\text{m} \times 70 \mu\text{m}$ in size within Bi-rich tennantite, containing tiny grains

of *annivite*. The TGM from Jáchymov, similarly to Miedzianka-Ciechanowice, shows oscillatory zonation, which is related to the Bi content. The presence of Bi-rich TGM, especially *annivite*, indicates the high activity of Bi during the crystallization process in both deposits. A comparison of the Bi-rich TGM from Miedzianka-Ciechanowice, Rędziny, and Jáchymov is presented in a triangular diagram (Fig. 10).

Silver minerals in polymetallic veins

Silver-bearing phases are widespread in various hydrothermal ore deposits in the Sudetes, where they usually represent an accessory mineralization of Ag-minerals (Paulo & Salamon 1972, 1974, Mikulski 2005, 2010, Pršek et al. 2019, Mederski et al. 2020) or Ag-rich TGM (Piestrzyński & Mochnacka 2003, Gołębiewska et al. 2012, Pršek

et al. 2019, Mederski et al. 2020, Muszyński et al. 2023). This mineralization is mainly associated with base-metal mineralization hosted in polymetallic, quartz, quartz-carbonate, or baryte veins. Silver mineralization in baryte veins in Poland is very rare and has been identified only in Miedzianka-Ciechanowice, Bystrzyca Górna, and Boguszów deposits.

In the Czarnów polymetallic vein deposit, the silver mineralization is represented by argentite, matildite, treasurite, hessite, and Ag-Bi sulfotellurides (Mikulski 2010). In contrast to Miedzianka-Ciechanowice, the Ag-bearing minerals are usually associated with arsenopyrite and Bi phases. Argentite forms tiny inclusions up to 20 μm in size within arsenopyrite. Matildite creates grains up to 0.2 mm in amphibolite, which are cut by calcite veinlets containing arsenopyrite-chalcopryrite mineralization. Aggregates of treasurite up to 100 μm occur in calcite veinlets and are accompanied by quartz and chalcopryrite. Treasurite also coexists with bismuth as inclusions enclosed within arsenopyrite. Hessite, similarly to treasurite, creates inclusions up to 10 μm in arsenopyrite, and is accompanied by bismuth minerals and pyrrhotite. In contrast to hessite from Miedzianka-Ciechanowice, it contains contents of Se up to 1.37 wt.%. The Ag-Bi sulfotellurides occur with bismuth and bismuthinite and form xenomorphic grains in pyrrhotite-arsenopyrite ore (Mikulski 2010). Silver minerals precipitated at temperatures of less than 130–200°C (Mikulski 2010). In both deposits, the Ag mineralization had a low-temperature origin; however, the silver phases in Czarnów are associated with high-temperature arsenopyrite, while there is no relation between these minerals in Miedzianka-Ciechanowice.

In the Rędziny area, silver minerals are mainly represented by Ag-bearing sulfosalts such as matildite, berryite, gustavite, pavonite, benjaminite, and makovickyite. These minerals usually form thin-tabular or lath-like crystals, reaching up to 300 μm in size. They are most commonly found within polymetallic mineralization hosted in arsenopyrite-chlorite-quartz veins. The sulfosalts are often associated with other silver-rich phases such as cosalite, which contains up to 5.0 wt.% Ag, as well as Ag-bearing galena. Fine-grained inclusions

of acanthite, Ag-rich minerals from the tetrahedrite series, and the previously mentioned sulfosalts are also dispersed in several parts of the quarry, especially within mineralized schist zones. These silver-bearing phases often occur together with chalcopryrite, cubanite, bismuthinite, and minerals from the stannite group, which may contain up to 2.0 wt.% Ag. Additional associated minerals include Ag-rich wittichenite, gold, and bismuth. The highest silver contents were recorded in tetrahedrite-group minerals, with argentotetrahedrite-(Fe) containing up to 32.0 wt.% Ag. These highly silver-enriched minerals commonly occur in association with stannite-group phases, indicating a close paragenetic relationship. The crystallization temperature of the silver-bearing mineralization is estimated to be below 320°C (e.g., Pieczka et al. 2009, Gołbiowska et al. 2012).

In Boguszów, baryte deposit silver mineralization occurs as Ag-rich TGM and Ag-Sb sulfosalts, which have not been reported in the Miedzianka-Ciechanowice area. Similarly to Bystrzyca Górna and in contrast to the studied deposit, the Ag-bearing phases are Sb-dominant and are represented by pyrrargyrite, polybasite, Ag-enriched tetrahedrite, and kenoargentotetrahedrite-(Fe) (Meder-ski et al. 2020). Pyrrargyrite occurs as inclusions up to 50 μm across in galena or forms intergrowths with chalcopryrite reaching up to 100 μm . Polybasite creates rounded inclusions in galena up to 20 μm in size (Mederski et al. 2020). In comparison to Boguszów, the Miedzianka-Ciechanowice hydrothermal system contains a more diverse silver assemblage, including Ag-selenides, tellurides, sulfides, and native silver. Despite these paragenetic differences, the textural features of ores from both deposits indicate an increased concentration of Ag-rich phases during the younger epithermal stages. This thesis confirms the presence of Hg in native silver from Miedzianka-Ciechanowice. According to Siuda (2012), the occurrence of silver with an increased Hg content is typical for silver precipitating from epithermal solutions at temperatures of approximately 200°C.

Silver mineralization is not exclusively related to baryte veins. Several types of ore veins with quartz, carbonate, baryte, and baryte-fluorite gangue are observed at the Grudno deposit in the

Western Sudetes (Paulo 1994). Similarly to Miedzianka-Ciechanowice, coarse-grained white and pink baryte have been described; however, white baryte is the main constituent of the veins. Barytes from Grudno, similarly to Miedzianka-Ciechanowice, differ in Sr contents from 0.2 to 2.0 wt.%, but they do not host silver minerals (Paulo 1994). In contrast to the Miedzianka-Ciechanowice deposit, pyrargyrite and freibergite in Grudno are related to quartz-calcite veins (Paulo & Salamon 1972, Paulo 1994).

In Radzimowice, the main ore mineralization is related to quartz-sulfide-carbonate veins, including hessite, volynskite, acanthite, treasurite, and gustavite (Paulo & Salamon 1974, Mikulski 2005). The hessite and volynskite, which represent the oldest silver phases, were precipitated in a Bi-Te-Au-Ag-Pb-S mineral stage while the remaining minerals crystallized during the sulfosalt stage (Mikulski 2005). Similarly to Miedzianka-Ciechanowice, hessite seems to be the oldest Ag-bearing phase, but in contrast to the studied deposit, it usually occurs as rounded inclusions in Co-enriched arsenopyrite. It also creates intergrowths with calcite and Ag-Pb-Bi sulfosalts (Mikulski 2005). Ag-Pb-Bi sulfotellurides also form fine-grained intergrowths with magnetite and ankerite, which replace earlier arsenopyrite and chalcopyrite aggregates. Similar to Miedzianka-Ciechanowice, the members of the younger sulfosalt stage form mainly inclusions within galena.

Silver mineralization has been reported in the Przecznica-Gierczyn ore district, which is hosted by the Stara Kamienica Schist Belt (Cook & Dudek 1994), where disseminated and vein-type cassiterite-polymetallic mineralization has been discovered (Piestrzyński & Mochnacka 2003). Although this area, similarly to Miedzianka-Ciechanowice, is located within the metamorphic cover of the Karkonosze Granite, both deposits differ significantly. Cassiterite is the main ore mineral in the Przecznica-Gierczyn area (Piestrzyński & Mochnacka 2003) while it occurs only in minor amounts in Miedzianka-Ciechanowice (Muszyński et al. 2025). Ag-bearing minerals represent accessory mineralization in both deposits, but their chemical compositions are different. In the Przecznica-Gierczyn area, silver minerals are

Sb-rich and include pyrargyrite and Ag-rich tetrahedrite (Piestrzyński & Mochnacka 2003). In contrast to Miedzianka-Ciechanowice, where Ag-bearing minerals are hosted in baryte, they are found in chlorite-sericite schists with quartz in Przecznica (Birecki 1959) or in chlorite schists with quartz in Gierczyn (Mochnacka et al. 1999). Pyrargyrite and Ag-rich tetrahedrite are also accompanied by chalcopyrite and tetrahedrite (Piestrzyński & Mochnacka 2003), while in Miedzianka-Ciechanowice, they are associated with bornite and chalcocite.

Silver has been reported in the Chełmiec carbonate-sulfide vein type deposit in the Kaczawa Mountains, however, in contrast to Miedzianka-Ciechanowice, it occurs primarily in members of the freibergite series, namely argentotetrahedrite-(Fe) and tetrahedrite-(Fe), and rarely in matildite (Muszyński et al. 2023). The highest silver contents were reported from rims of TGM grains. Argentotetrahedrite-(Fe), which is younger than the Ag-poor TGM, forms brighter zones and crystallized at temperatures of 170–200°C. It is accompanied by chalcopyrite and sphalerite (Muszyński et al. 2023). Chełmiec represents another locality in the Sudetes where silver mineralization is associated with Sb-rich mineral assemblages.

Silver is also the primary element associated with copper deposits of the Fore-Sudetic Monocline (Wodzicki & Piestrzyński 1994). It is the most abundant element in copper-bearing schist (Krucha & Mayer 2007, Kuzub-Budzyń & Piestrzyński 2017). Similarly to Miedzianka-Ciechanowice, native silver (Salamon 1979), naumannite (Pieczonka & Piestrzyński 2005), stromeyerite (Salamon 1979), mckinstryite (Salamon 1976, 1979), and acanthite (Harańczyk 1972) have been identified. A wide variety of Ag-bearing phases not reported from the studied area have also been discovered, including electrum (Salamon 1976, 1979), jalpaite (Kucha & Salamon 1972, Salamon 1979), küstelite (Salamon 1979), silver amalgams (Salamon 1979, Piestrzyński & Tylka 1992), eugenite (Kucha 1986), pavonite (Kucha 1998), and chlorargyrite (Kucha 1990). Native silver forms aggregates up to a few millimeters in size and creates intergrowths with chalcocite, bornite, Cu-Fe-Ag sulfides, tennantite,

and stromeyerite. In contrast to Miedzianka-Ciechanowice, silver contains not only Hg but also Cu, Au, Pt, Fe, and S (Kozub-Budzyń & Piestrzyński 2017). Stromeyerite is the most common silver sulfide in this area (Salamon 1979, Kucha 2007, Piestrzyński 2007, Pieczonka 2011) and occurs with native silver and silver amalgams (Kozub-Budzyń & Piestrzyński 2017). It usually creates intergrowths with chalcocite, bornite, native silver, and silver amalgams, and also forms inclusions in veinlets that contain bornite, chalcopyrite, and chalcocite. It has contents of Hg up to 3.60 wt.% (Kozub-Budzyń & Piestrzyński 2017). Mckinstryite occurs as intergrowths with native silver, silver amalgams, chalcocite, and bornite. It sometimes creates inclusions with stromeyerite in bornite-chalcocite veinlets (Kozub-Budzyń & Piestrzyński 2017). Naumannite forms tiny intergrowths up to 5 µm with native silver in bornite veinlets and chalcocite and bornite accompanied by tennantite. Despite the different genetic type, the Ag-bearing minerals in the Cu-Ag deposit of the Fore-Sudetic Monocline occur with chalcocite and bornite, similarly to Miedzianka-Ciechanowice, which are the main ore minerals (Piestrzyński 2007, Pieczonka 2011). Furthermore, they are usually enriched in Ag (Kozub-Budzyń & Piestrzyński 2017).

Veins with silver mineralization are also found in the stratiform base-metal deposit in Horní Město in the Czech Republic. These veins are mainly composed of, among others, K-feldspar, albite, quartz, calcite, and dolomite (Dolníček et al. 2019b). The Ag-bearing minerals include native silver that is enriched in Hg, members of freibergite series, pyrargyrite, proustite, stephanite, miargyrite, allargentum, Ag-rich tennantite (up to 14 wt.% Ag), and Ag-rich tetrahedrite (up to 17.5 wt.% Ag), similar to Miedzianka-Ciechanowice (Fojt et al. 1992, Dolníček et al. 2019b). The most widespread Ag-bearing minerals in this deposit are argentotetrahedrite-(Zn) and argentotetrahedrite-(Fe), as well as kenoargentotetrahedrite-(Zn) and kenoargentotetrahedrite-(Fe). It creates xenomorphic grains up to 1.5 mm in size, sometimes overgrowing older pyrite, arsenopyrite, and sphalerite, or forms thin veinlets. The grains contain small inclusions of pyrargyrite

and galena. Pyrargyrite creates xenomorphic and elongated grains up to up to 350 µm in size or thin veinlets. It usually intergrows with freibergite and encloses all other silver minerals except for freibergite series. Miargyrite is very rare and forms tiny inclusions up to 20 µm within pyrargyrite. Allargentum occurs in feldspar and is rimmed by a thin layer of pyrargyrite (Dolníček et al. 2019b). In contrast to Miedzianka-Ciechanowice, younger paragenesis with Ag-bearing minerals exhibits Sb enrichment and As depletion. It confirms the presence of pyrargyrite, allargentum and miargyrite, while only proustite was reported in the studied area. The Miedzianka-Ciechanowice deposit also typically contains both Sb- and As-bearing ore minerals; however, a predominance of As- over Sb-phases is clearly visible, especially in TGM, where tennantite is much more abundant than tetrahedrite. The chemical compositions of ore minerals and their mutual relations suggest that Cu-Zn-Pb-Sn±Bi±Ag paragenesis in Miedzianka-Ciechanowice may represent an early product of the crystallization process.

The results described by Dolníček et al. (2019a) indicate that As prevails in the early phase and Sb in the later phase in the Řepová deposit near Mohelnice in the Czech Republic. Ag-rich TGM, freibergite series, silver amalgams, and acanthite have been discovered in this area. Similarly to Miedzianka-Ciechanowice, several silver-rich phases, including argentotetrahedrite-(Fe) and silver amalgams, occur in baryte veins. The Ag-rich tetrahedrite forms inclusions in galena, while acanthite is very rare and replaces galena or chalcopyrite (Dolníček et al. 2019a). In contrast to the studied area, baryte is the oldest component of the vein and contains lower contents of SrO (up to 0.27 wt.%) (Dolníček et al. 2019a). According to Dolníček et al. (2019a), the silver in Řepová was concentrated during the later stages of hydrothermal activity and has a low-temperature origin. The mineral associations, chemical composition and textural development in the Miedzianka-Ciechanowice deposit point to a paragenetic sequence: base metal sulfides + Bi-rich TGM → Bi-phases: wittichenite, native bismuth → Sn-bearing sulfides: mawsonite, stannoidite → Ag-bearing minerals: hessite, cervelleite, stromeyerite, native silver, acanthite, mckinstryite,

proustite, selenojalpaite, naumannite. The mineral succession of the Miedzianka-Ciechanowice deposit suggests a progressive evolution of the hydrothermal system.

CONCLUSIONS

The mineralogical and geochemical investigations conducted in the Miedzianka-Ciechanowice deposit provide new insights into its mineralization, with the main findings of this study summarized as follows:

1. The Cu-Zn-Pb-As-Sn±Bi±Ag paragenesis is hosted by quartz, quartz-calcite, calcite, calcite-dolomite, and baryte veins in the Miedzianka-Ciechanowice deposit.
2. Two types of baryte – white (baryte I) and pink (baryte II) – were described in the studied area. Baryte I hosts mainly base metal mineralization, while baryte II contains a rich suite of silver minerals.
3. Very rare Bi-rich tennantite-(Zn) with Bi contents surpassing 1.00 apfu was discovered during the laboratory research. It usually occurs as zones enriched with Bi within tennantite-(Zn). A pronounced extent of Bi ↔ As or Sb substitution was also observed in TGM.
4. Highly Bi-enriched zones containing up to 26.44 wt.% (2.20 apfu) Bi were detected within Bi-rich tennantite-(Zn). The predominance of Bi over As indicates the presence of *annivite* in this area.
5. Silver minerals are quite widespread in the Sudetes; however, they are hosted mainly by baryte veins in Miedzianka-Ciechanowice, especially pink baryte. Various Ag-bearing sulfides, tellurides, selenides, and native silver were described. Their mutual relations and mineral associations suggest that tellurides represent the oldest Ag-bearing minerals, while selenides seem to be the youngest ones.
6. In contrast to other ore localities from the Sudetes (Bystrzyca Górna, Boguszów, Grudno and Chełmiec, among others), the ore assemblages occurring within the Miedzianka-Ciechanowice deposit are mainly As-dominant. The As seems to be prevailing in the early stage of ore precipitation.
7. The general paragenetic sequence can be defined as: base metal sulfides + Bi-rich TGM → other Bi-bearing phases → Sn-bearing sulfides → Ag-bearing minerals.

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