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Mineralogy and geochemistry of Cu-Sn-Bi ores from the Miedzianka-Ciechanowice deposit, Sudety Mts., Poland

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Miedzianka-Ciechanowice is a hydrothermal vein-type quartz and quartz-carbonate-sulphide deposit in the eastern metamorphic cover of the Karkonosze Granite in the Sudeten Mts. Within this diverse deposit, polymetallic Cu-Sn-Bi mineralization was identified. Two ore mineral stages of precipitation were recognised: I – a high-temperature mineralization stage in skarn; and II – a medium and low-temperature stage of vein mineralization. Stage I, associated with skarns, is represented by rutile, magnetite I and II, cassiterite and minor amounts of sulphides (sphalerite, pyrite, chalcopyrite and galena). Stage II, associated with quartz or quartz-carbonate veins, is represented by pyrrhotite, pyrite, arsenopyrite, cobaltite, gersdorffite, sphalerite, chalcopyrite, minerals of the tetrahedrite-group, roquesite, bornite and galena. In addition a wide range of tin sulphides: stannoidite, mawsonite, ferrokesterite and bismuth sulphosalts (bismuthinite, aikinite, ikunolite, gustavite, lillianite, heyrovskýite, vikingite, berryite and matildite) were identified. Minerals of the Cu-Sn-Bi associations were formed mainly in massive aggregates of chalcopyrite in quartz veins, less often in magnetite or sphalerite in skarns. In the Sudeten Mts., the presence of various tin and bismuth associations is rare and usually represents accessory mineralization.

Key words: Miedzianka-Ciechanowice, Cu-Bi-Sn association, bismuth sulphosalts, tin sulphides, hydrothermal mineralization.

INTRODUCTION

The Sudety Mts. area is characterised by the occurrence of many diverse polymetallic hydrothermal deposits (Piestrzyński et al., 1992; Madziarz, 2009a; Mochnacka et al., 2009, 2012). Many of these have been exploited for several hundred years (e.g., Dziekoński, 1972; Madziarz and Sztuk, 2006; Madziarz, 2009a, b). The Karkonosze-Izera Massif is the most famous mining area, where many polymetallic hydrothermal deposits occur in its Polish part, such as the Stara Kamienica stratiform tin deposits (Małek and Mikulski, 2021), Krobica-Gierczyn deposit (Pietrzela, 2019), the Rędziny quartz-vein-type deposit (Pieczka et al., 2007; 2009), the Czarnów quartz-sulfide-vein-type deposit (Mikulski, 2010) and the Miedzianka-Ciechanowice quartz-carbonate-baryte vein deposit (Mochnacka et al., 2012). Many of these deposits, where mining has ended, have not been sufficiently mineralogically studied by modern methods. The Miedzianka-Ciechanowice area is one such old mining area in the Rudawy Janowickie Mts., where tens of hydrothermal veins associated with post-Variscan granite magmatism have been documented (Mochnacka et al., 2012). The polymetallic mineralization in this deposit is associated with quartz-carbonate-baryte-veins which contain sulphides, sulphosalts, magnetite, bismuth, silver and uranium minerals (Zimnoch, 1978; Siuda and Gołębiowska, 2011; Mochnacka et al., 2012; Siuda, 2012).

Despite its diverse mineralogy, the Miedzianka-Ciechanowice hydrothermal polymetallic vein deposit was recognised in earlier studies (Zimnoch, 1978; Siuda and Gołębiowska, 2011; Siuda, 2012; Mochnacka et al., 2012), but no new precise data related to primary mineralization have been published from this deposit. This paper provides new data concerning the mineralogy, geochemistry and mineral association of this deposit, notably precise compositional data on the Sn-Bi paragenesis (tin sulphides, cassiterite, bismuth minerals) as the early mineral paragenesis in the deposit.

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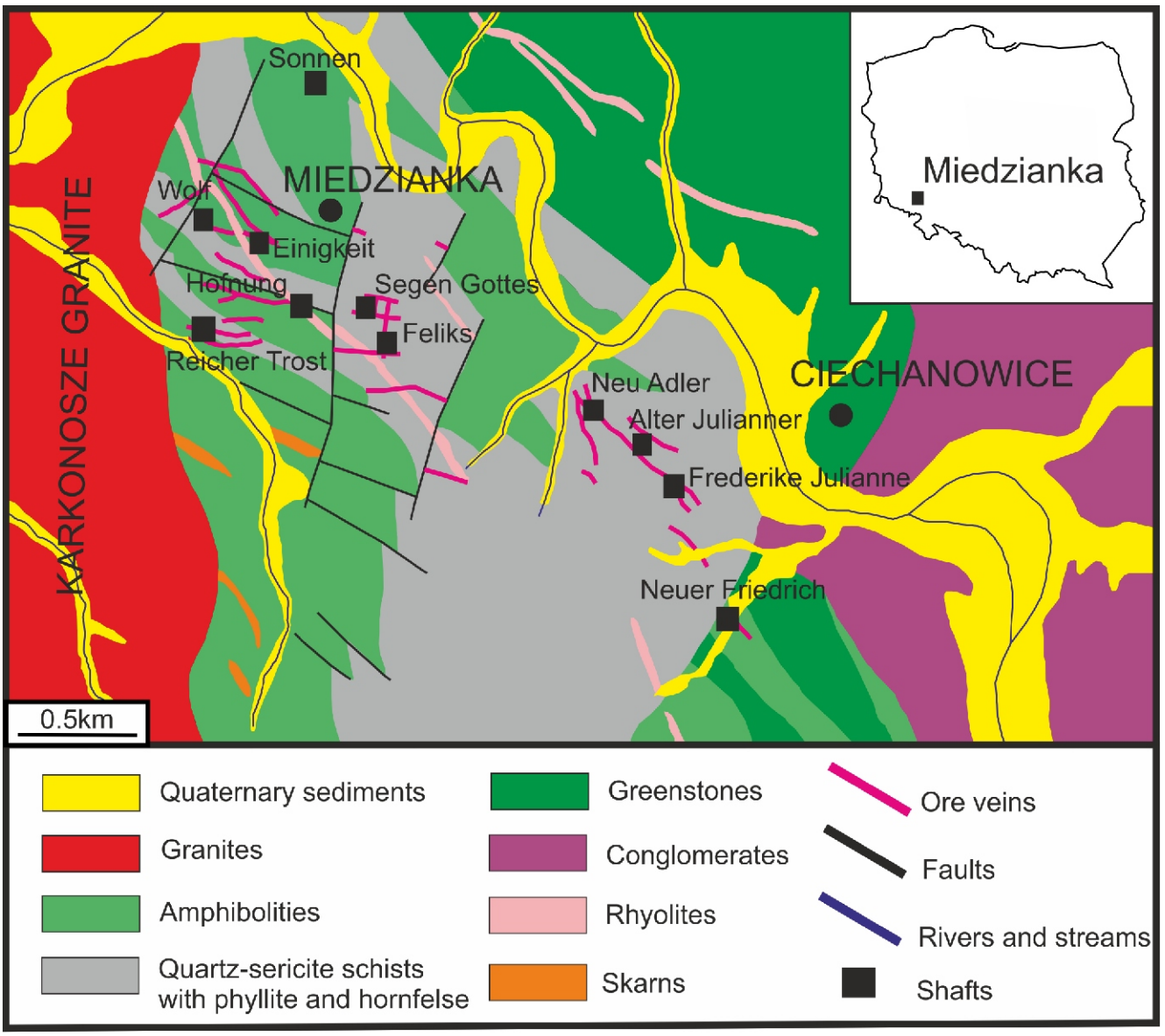

Fig. 1. Geological map of the Miedzianka-Ciechanowice area (modified from Berg, 1938; Siuda and Gołębiowska, 2011)

LOCALITY AND GEOLOGICAL SETTING

The research area is located in southwestern Poland, between the villages of Miedzianka and Ciechanowice. This area is located in the eastern part of the Karkonosze-Izera Massif (Mochnacka et al., 2012), in the northern part of the Rudawy Janowickie Mts., which form the eastern metamorphic cover of the Karkonosze Granite (Siuda and Gołębiowska, 2011). The Rudawy Janowickie mountain range is divided into three units: the metasedimentary-volcanic Kowary-Czarnów unit with the Kowary gneisses; the Leszczyniec volcanic unit; and the Przybkowice phyllite unit (Kozdrój, 2003). The Miedzianka-Ciechanowice area is included in the Kowary-Czarnów unit (Kozdrój, 2003) and is composed mainly of amphibolites and amphibolite schists, with small intercalations of mica-schist and quartz-sericite schist, greenstone and skarn (Siuda and Gołębiowska, 2011; Fig. 1). Younger rocks including rhyolites and pegmatites are related to the Karkonosze granite intrusion (Siuda and Gołębiowska, 2011). The rocks of the entire region were metamorphosed during Variscan orogenesis before the emplacement of the Karkonosze granite (Mazur et al., 2010) dated to ~312–315 Ma (Duthout et al., 1991; Kryza et al., 2014; Mikulski et al., 2020). The area of the Miedzianka-Ciechanowice deposit is associated with the Intra-Sudetic Fault, which is the boundary between the Karkonosze-Izera Massif and the Kaczawa Metamorphic Complex. This fault with its NW overall direction occurs in the north-eastern part of area (Teisseyre, 1968). Within the deposit there occurs a system of parallel faults of NW–SE direction, which are connected with Variscan movements (Teisseyre, 1968).

Two types of ore mineralization have been recognised in the Miedzianka-Ciechanowice deposit (Zimnoch, 1978, Mochnacka, 1982). The first is of skarn type: magnetite-sphalerite-pyrite mineralization occurring in the western and southwestern parts of Miedzianka village. Its formation is related to the metamorphism and metasomatism of lenses of carbonate rocks in contact with the Karkonosze granite intrusion. Typical minerals in this type of ore include magnetite, sphalerite, pyrite and pyrrhotite (Mochnacka, 1982). The second type is of a polymetallic vein type of mineralization. The hydrothermal

polymetallic veins (quartz, quartz-carbonate and baryte) in the Miedzianka-Ciechanowice area are very variable across the whole ore field. It is mainly the quartz veins that are mineralized and the ore veins have an E–W direction, and dip to the N or S (Zimnoch, 1961). In addition, the ore bodies are cut by shorter quartz and quartz-carbonate NW–SE-trending veins. 41 veins have been discovered in Miedzianka, whose thickness ranges from 0.01 to 3 m (Madziarz, 2010). The western field is known for its skarns and mainly Cu-bearing hydrothermal veins with uranium and tin minerals (Mochnacka et al., 2012). The eastern field, near Ciechanowice village, contains more diverse associations with copper, silver, bismuth, cobalt, and tin minerals (Mochnacka et al., 2012). The northern part of Miedzianka, on the other side of the Bóbr River, is characterized mainly by Pb-Zn mineralization (Mochnacka et al., 2012). Ore mineralization forms irregular, massive accumulations in quartz, carbonate or baryte veins, rarely veinlets or disseminations in the host rocks. The main ore minerals in the deposit are chalcopyrite and bornite (Mochnacka et al., 2012).

MATERIALS AND METHODS

Samples containing ore mineralization with Bi-Sn paragenesis were collected from old dumps of the Sonnen, Wolf, Einigkeit, Hofnung, Segen Gottes, Feliks and Neu Adler shafts in the Miedzianka ore field (Fig. 1). Skarns, amphibolites, quartz and carbonate vein material with macroscopic sulphide mineralization were collected on the dumps. Various textures of ores from the Miedzianka-Ciechanowice deposit are observed: massive, nested and veinlet. 45 samples were selected for microscopic observations in reflected light, 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 *JEOL Super Probe JXA-8230* and *Cameca SX-100* microanalyzers, respectively. The analyses were performed using the WDS method under the following conditions: accelerating voltage 20 kV and 25 kV (Banská Bystrica and Prague, respectively), beam current 20 nA and beam diameter 1 μm. Natural mineral standards (FeS_2, ZnS, PbS) and synthetic compounds (CdS, InAs, MnS, HgTe, PbTe, Sb_2S_3, Cu, Ag, Bi, Ni, Co, Se) were used for calibration. The wavelengths and detection limits are included in Appendix 1.

RESULTS

The ore mineralization which contains Cu-Sn-Bi paragenesis is dominated mainly by massive aggregates of chalcopyrite in quartz veins, amphibolites, or massive magnetite with sphalerite. Sphalerite I and II, pyrite I and II, cobaltite, gersdorffite, tin sulphides, galena, arsenopyrite, native bismuth and minor amounts of cassiterite, bornite, matildite, roquesite and canfieldite were identified in the massive chalcopyrite ore. In the massive magnetite-sphalerite ore, minor amounts of pyrrhotite, cassiterite, chalcopyrite, pyrite, galena and bismuth sulphosalts were found. Except for chalcopyrite and magnetite, minerals of the Cu-Sn±Bi ore paragenesis are not macroscopic and these were found during the microscopic study. The paragenetic sequence resulting from this study involves early findings by Mochnacka et al. (2012) as shown in Figure 2. The main ore mineral in the paragenesis is chalcopyrite, whereas magnetite, sphalerite, galena, cobaltite, pyrite, bornite and arsenopyrite are minor. Tin and bismuth minerals are mainly connected with chalcopyrite, less with galena, and they occur in form of inclusions, irregular aggregates and veinlets. A broad assemblage of Sn and Bi minerals was identified: stannoidite, mawsonite, ferrokesterite, native bismuth, bismuthinite, minerals from the lillianite homologous series (gustavite-lillianite series, heyrovskýite, vikingite), matildite, canfieldite and berryite. They are rarely accompanied by irregular aggregates of gersdorffite and chalcocite grains.

TiO_2 PHASE

This is the oldest mineral identified in the samples studied. The TiO_2 phase is very common and occurs in the skarns and amphibolites mainly as a product of hydrothermal alteration and the activity of hydrothermal solutions. It occurs as irregular or elongated crystals in the host rocks. The hydrothermal TiO_2 phase, in form of elongated crystals, is overgrown by chalcopyrite aggregates. Locally, it contains small crystals of cassiterite. The TiO_2 phase is generally free of any other chemical elements, and only locally increased contents of V_2O_3 (up to 0.05 wt.%) and Nb_2O_5 (up to 0.1 wt.%) were detected.

MAGNETITE

This mineral represents the oldest type of mineralization in the Miedzianka-Ciechanowice deposit. It was recognized in skarns and amphibolite in the north-western and western parts of this area, while in hydrothermal mineralization it is rare. The magnetite generally forms massive ore, rarely banded, only locally with sulphide nests or veins. Two generations of magnetite were recognized in the samples studied. The first generation (magnetite I) forms rounded and automorphic grains that build the cores of massive magnetite aggregates. A second generation (magnetite II) irregularly overgrows the early magnetite I as thin rims. Moreover, magnetite II creates intergrowths with sphalerite (Fig. 3A), creating massive magnetite-sphalerite aggregates up to a few mm in size. Aggregates of magnetite II locally contain inclusions of hematite, sphalerite, chalcopyrite, pyrrhotite, galena and cassiterite. Both magnetite generations are chemically pure and only small amounts of Si (up to 0.38 wt.%), Zn (up to 0.09 wt.%) and Co (up to 0.05 wt.%) were detected.

CASSITERITE

Except for TiO_2 phases and magnetite, cassiterite represents the earliest oxide mineral in the samples studied. Two generations of very rare cassiterite were recognised. Cassiterite I occurs in skarns where it forms small grains in magnetite II aggregates and intergrowths with rutile. It is accompanied by pyrrhotite and minor amounts of sphalerite, chalcopyrite and galena. Cassiterite II was found in quartz veins with chalcopyrite ore where it forms small grains up to 20 μm in size which are surrounded by stannoidite and mawsonite (Fig. 3B, C). It is locally accompanied by sphalerite II. These two generations differ in chemical composition. Cassiterite I contains significant contents of FeO (up to 1.59 wt.%), TiO_2 (up to 0.69 wt.%) and In_2O_3 (up to 0.53 wt.%), while Nb_2O_5 (0.12 wt.%), Ta_2O_5 (up to 0.09 wt.%) and SrO (up to 0.03 wt.%) were also detected. Cassiterite II has high contents of FeO (up to 2.99 wt.%) and small amounts of SiO_2 (up to 0.28 wt.%), Ta_2O_5 (up to 0.18 wt.%), SrO (up to 0.18 wt.%), WO_3 (up to 0.15 wt.%), V_2O_5 (up to 0.05 wt.%) and Nb_2O_5 (up to 0.03 wt.%).

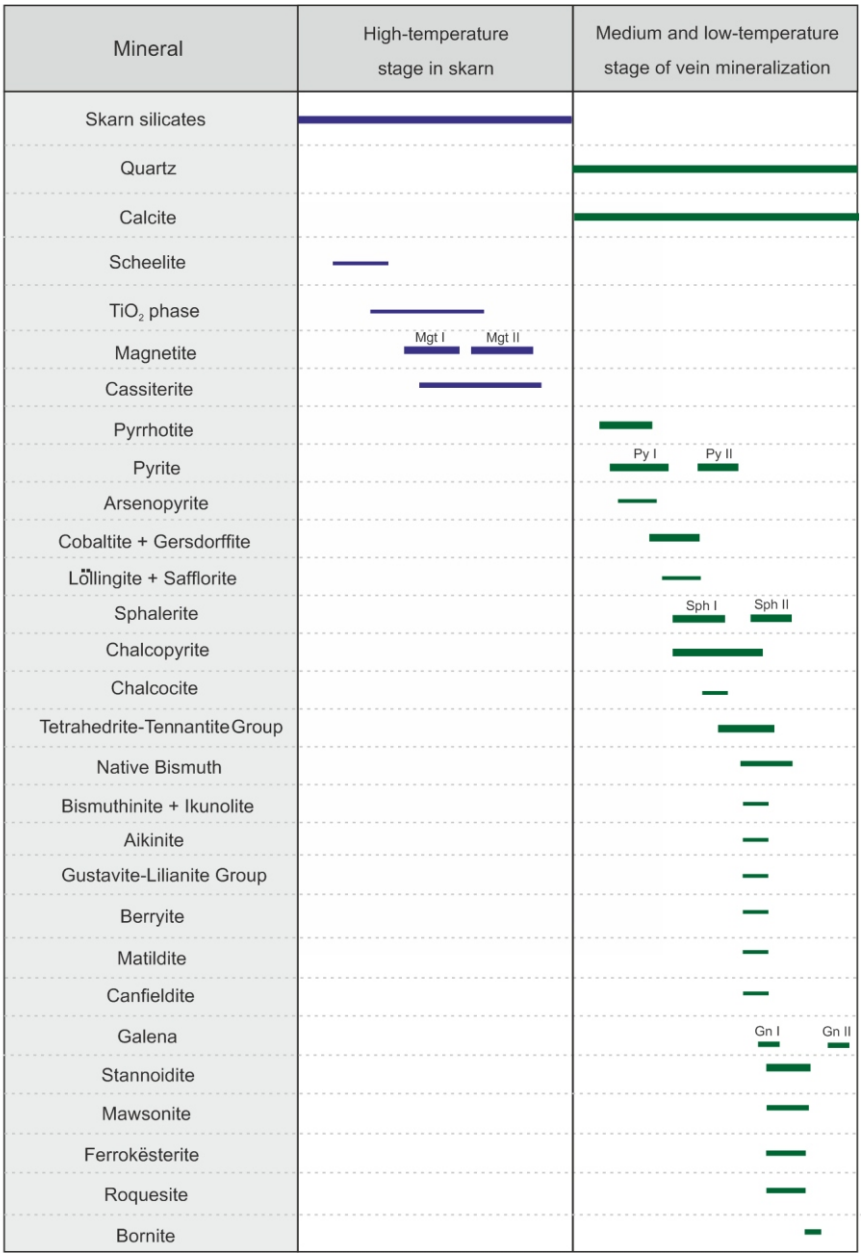

Fig. 2. Mineral succession of the Cu-Sn±Bi mineralization in the Miedzianka-Ciechanowice deposit based on results of this study and Mochnacka et al. (2012)

PYRRHOTITE

Pyrrhotite is a common mineral in the skarn ore or in hydrothermal Cu-bearing paragenesis in amphibolites. It forms mainly younger, tiny inclusions up to 10 μm across in magnetite or irregular intergrowths up to 70 μm in size with chalcopyrite, pyrite, sphalerite and galena. In places it forms massive structures in chalcopyrite ore up to 200 μm across. The pyrrhotite is commonly replaced by marcasite and Fe-hydroxides.

PYRITE

Pyrite is one of the main sulphide minerals in the deposit, it usually occurs with chalcopyrite; however, in a few samples it is a dominant ore mineral. Two generations of pyrite were discovered – the first one creates crystals up to 300 μm across with small inclusions of chalcopyrite and marcasite. Most of them are cracked, the cracks being filled by chalcopyrite. The second generation forms disseminated structures and occurs with chalcopyrite, sphalerite (Fig. 4A) and galena. Both generations of pyrite are chemically pure and only occasionally the second generation has higher contents of Ni (up to 0.11 *apfu*) and Cu (up to 0.05 *apfu*).

ARSENOPYRITE

Arsenopyrite is rare in the samples studied and usually forms separate idiomorphic crystals up to 50 μm in size or crystals up to 40 μm across in chalcopyrite, pyrite or sphalerite. Arsenopyrite crystals are usually cracked and replaced by chalcopyrite. In places arsenopyrite is overgrown by younger löllingite. It has small contents of Co (up to 0.04 *apfu*) and Ni (up to 0.03 *apfu*) without any zoning in BSE images. The empirical formula of arsenopyrite based on the sum of 1 cation could be written as: $(Fe_{0.94\text{-}1.00}Co_{0.00\text{-}0.04}Ni_{0.00\text{-}0.03})_{=0.98\text{-}1.03}As_{0.98\text{-}0.99}S_{1.00\text{-}1.02}$.

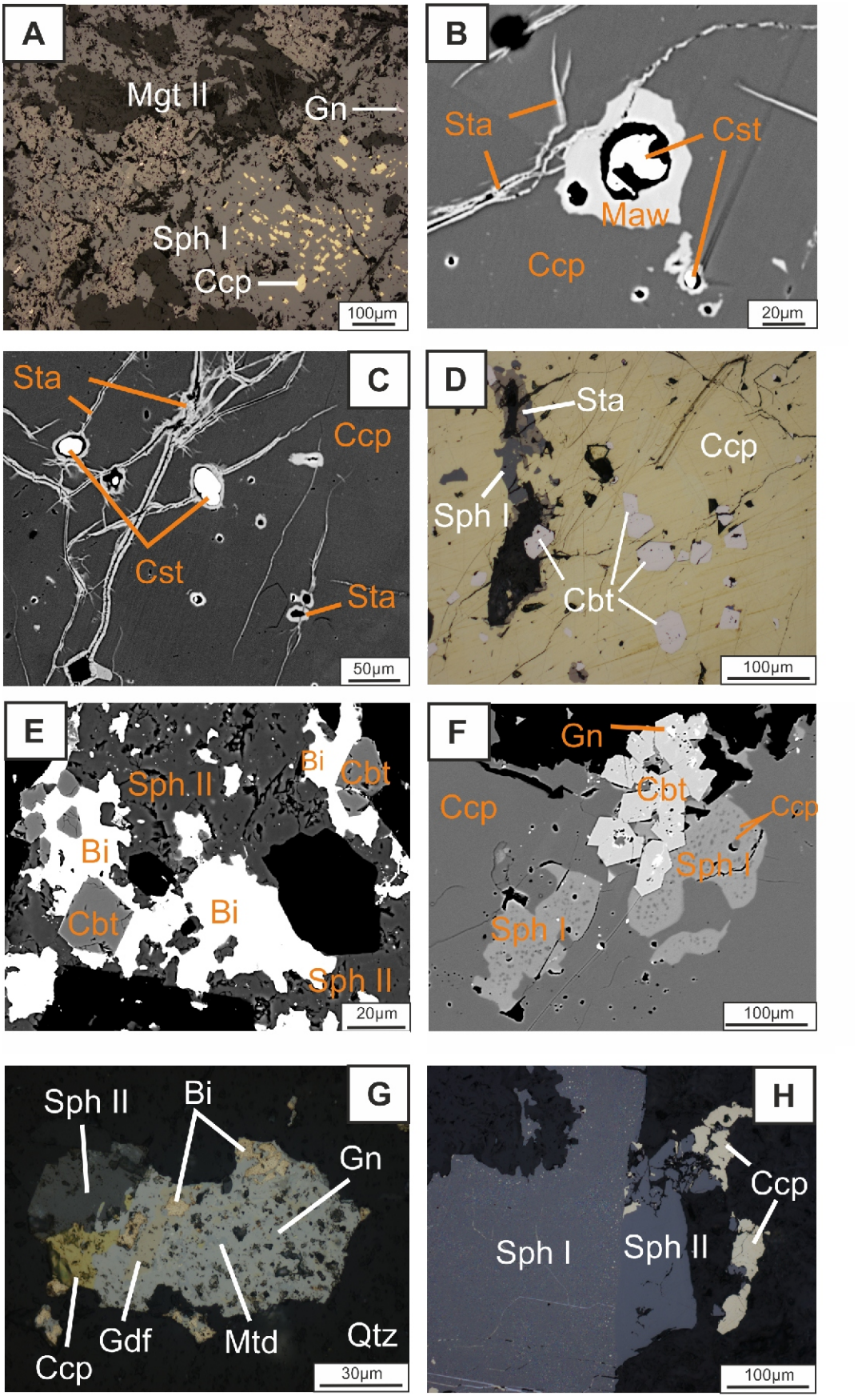

Fig. 3. Reflected-light (A, D, G, H) and BSE (B, C, E, F) images illustrating the main features of mineral assemblages

A – aggregates of magnetite II overgrown by sphalerite I with inclusions of chalcopyrite and galena; **B** – mawsonite surrounding a cassiterite grain in a chalcopyrite aggregate cut by stannoidite; **C** – grains of cassiterite surrounded by stannoidite in a chalcopyrite aggregate with stannoidite veinlets; **D** – cobaltite grains and an intergrowth of sphalerite I and stannoidite in chalcopyrite; **E** – intergrowth of sphalerite II with native bismuth and cobaltite grains; chalcopyrite is black; **F** – cobaltite grains with inclusions of galena with sphalerite I and chalcopyrite; **G** – galena with inclusions of gersdorffite, bismuth and matildite with chalcopyrite and sphalerite II; **H** – two generations of sphalerite with chalcopyrite in amphibolite; Mgt II – magnetite II; Sph I, II – sphalerite I and II; Ccp – chalcopyrite; Gn – galena; Bi – native bismuth; Cst – cassiterite, bismuthinite; Sta – stannoidite; Maw – mawsonite; Cbt – cobaltite; Gdf – gersdorffite; Mtd – matildite; Ttr – tetrahedrite

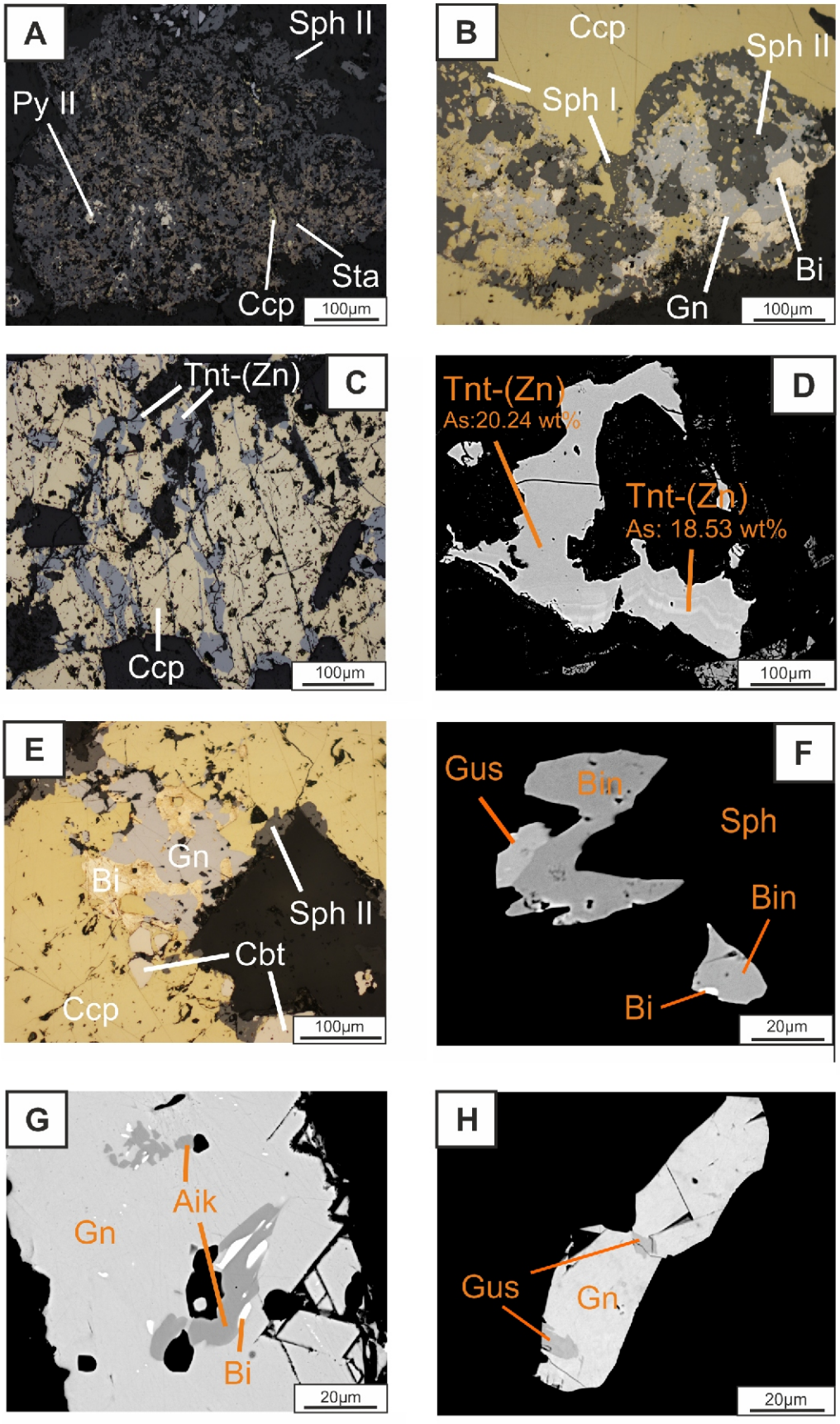

Fig. 4. Reflected-light (A–C and E) and BSE (D and F–H) images illustrating the main features of the mineral assemblages

A – sphalerite II with inclusions of stannoidite, chalcopyrite and pyrite; **B** – sphalerite I and II intergrown with galena and native bismuth in chalcopyrite; **C** – grains and veinlets of tennantite-(Zn) within chalcopyrite; **D** – zoned grain of tennantite; **E** – intergrowth of bismuth with galena in chalcopyrite with cobaltite grains and sphalerite II; **F** – bismuthinite with gustavite and bismuth in sphalerite; **G** – inclusions of aikinite and bismuth in galena; **H** – gustavite in crystal of galena in skarn; Py I, II – pyrite I and II; Tnt - tennantite; Bin – bismuthinite; Gus – gustavite; Aik – aikinite

COBALTITE

Cobaltite is a common accessory mineral in the paragenesis. It usually occurs as anhedral grains up to 150 μm in size. Fine crystals of this mineral occur in chalcopyrite (Fig. 3D) or in quartz and quartz-carbonate veins which cut the amphibolite schists. It was not observed in samples with magnetite. Cobaltite grains are crosscut by younger chalcopyrite and calcite veinlets and locally they are accompanied by native bismuth (Fig. 3E) or surrounded by stannoidite. They contain inclusions of galena (Fig. 3F), native bismuth and stannoidite. Cobaltite may be accompanied by safflorite-löllingite aggregates which locally overgrow cobaltite grains. The content of Co ranges from 24.88 wt.% (0.70 *apfu*) to 35.68 wt.% (0.96 *apfu*). Cobaltite contains significant admixtures of Ni – up to 5.88 wt.% (0.17 *apfu*) and Fe up to 4.69 wt.% (0.14 *apfu*). The As/S ratio is close to a stoichiometric value of 1 (0.97–1.00). The empirical formula of cobaltite based on the sum of 1 cation could be written as: $(Co_{0.70-0.95}Ni_{0.01-0.17}Fe_{0.03-0.14})_{=0.99-1.01}As_{0.92-1.03}S_{0.92-1.08}$.

GERSDORFFITE

Gersdorffite is a rare mineral, which occurs together with galena, bismuth and chalcopyrite (Fig. 3G) where irregular gersdorffite grains are embedded in sulphides. Generally, aggregates of gersdorffite are zonal with Ni-rich centres and Ni-Co rims. Contents of Co in the central part reach up to 0.07 *apfu* and in the rims up to 0.32 *apfu*. The Ni-rich centre has a small content of Fe and Bi (up to 0.08 and 0.01 apfu respectively); the Co-enriched part contains significant contents of Fe (up to 0.19 *apfu*) and Cu (up to 0.11 *apfu*). While the As/S ratio in Ni-rich centre ranges from 0.94 to 1.04, the As/S ratio in Ni-Co rims reaches up to 0.89. Moreover the (Ni+Co+Fe)/As ratio in the centre is 0.89 and in outer zone it is 1.01. The empirical formula of pure gersdorffite based on the sum of 1 cation could be written as:
$(Ni_{0.87-0.98}Fe_{0.01-0.08}Co_{0.00-0.07}Bi_{0.00-0.01})_{=1.00-1.02}As_{0.96-1.11}S_{0.98-1.06}$
and those of the Ni-Co rims is
$(Ni_{0.39-0.40}Co_{0.31-0.32}Fe_{0.18-0.19}Cu_{0.09-0.11})_{=0.99-1.00}As_{0.88-0.90}S_{1.01-1.02}$.

LÖLLINGITE-SAFFLORITE

Diarsenides of the löllingite-safflorite series are rare and occur in ore from amphibolite and quartz-carbonate veins. They usually overgrow cobaltite and arsenopyrite grains or form veinlet structures in chalcopyrite aggregates up to 300 μm across and consist of tiny, anhedral and subhedral crystals which do not exceed 20 μm. The löllingite contains small amounts of Cu (up to 0.04 *apfu*), Co (up to 0.02 *apfu*) and Ni (up to 0.01 *apfu*). Its general formula based on the sum of 1 cation could be written as:
$(Fe_{0.96-1.00}Cu_{0.01-0.04}Co_{0.00-0.02}Ni_{0.00-0.01})_{=1.02}(As_{1.92-1.99}S_{0.01-0.08})_{=2.00}$.
The safflorite occurs as intergrowths with löllingite, and does not form separate grains. It is chemically very variable and the content of Co ranges from 0.61 to 0.81 *apfu* and of As from 1.38 to 1.85 *apfu*. Safflorite contains significant contents of Fe (from 0.16 to 0.35 apfu) and small amounts of Cu (from 0.02 to 0.08 *apfu*). The empirical formula of safflorite based on the sum of 1 cation is:
$(Co_{0.61-0.81}Fe_{0.16-0.35})_{=0.96-0.97}(As_{1.38-1.85}S_{0.12-0.51})_{=1.89-1.97}$.

SPHALERITE

Sphalerite is a common mineral in the paragenesis. Two generations of sphalerite were identified (Fig. 3H). The earlier sphalerite I contains fine inclusions of chalcopyrite (Fig. 3A), rarely pyrrhotite and usually occurs as larger aggregates up to 200 μm across in massive chalcopyrite (Fig. 3E) or as intergrowths with chalcopyrite and magnetite. It usually shows the presence of voids and cracks. It contains significant contents of Cu (up to 0.07 *apfu*) and Fe (up to 0.05 *apfu*). Sphalerite II occurs as disseminated crystals in, or forms intergrowths with, chalcopyrite. Sphalerite II contains tiny inclusions of stannoidite (Fig. 4A) and sulphosalts of the gustavite-lillianite series but it is free of chalcopyrite inclusions. Locally it is accompanied by cobaltite, galena and native bismuth (Fig. 4B). It contains low amounts of Fe (up to 0.05 *apfu*) and Cd (up to 0.02 *apfu*). The empirical formula (based on the sum of one cation) of sphalerite I is: $(Zn_{0.87-0.95}Cu_{0.02-0.07}Fe_{0.01-0.05})_{=0.98-0.99}S_{0.98-1.02}$ and those of sphalerite II is: $(Zn_{0.94-1.00}Fe_{0.00-0.05}Cd_{0.00-0.02})_{=1.00-1.01}S_{0.97-1.00}$.

CHALCOPYRITE

Chalcopyrite is a main ore mineral in the Miedzianka-Ciechanowice deposit. It forms nest-like, massive and irregular aggregates up to 1 mm across or scattered grains in quartz veins and host rocks (amphibolite and sericite schists). The chalcopyrite usually forms intergrowths with sphalerite and contains inclusions of pyrite, bornite, galena, cobaltite-gersdorffite, tetrahedrite-tennantite series members and bismuth. This mineral is also present in sphalerite as fine inclusions as well as veinlets in pyrite, cobaltite or arsenopyrite, but it locally also replaces arsenopyrite grains. It has small contents of Bi and Zn (up to 0.01 *apfu*). The empirical formula (based on the sum of two cations) of chalcopyrite is $Cu_{0.98-1.00}Fe_{0.99-1.01}S_{1.88-1.94}$.

CHALCOCITE

This is a rare mineral which was found exclusively in the hydrothermal ore. It occurs as intergrowths with chalcopyrite and tennantite or creates tiny inclusions in chalcopyrite. It forms crystals up to 20 μm in size. This mineral is close to the theoretical chemical composition and does not contain any significant admixtures. The empirical formula of chalcocite based on the sum of 2 cations could be written as: $Cu_{1.99-2.00}S_{1.00-1.01}$.

TETRAHEDRITE-TENNANTITE SERIES

Members of tetrahedrite-tennantite series rarely occur with the Sn-Bi paragenesis. They usually occur as grains or veinlets which vary in thickness – from 50 μm to 500 μm (Fig. 4C) – in quartz and quartz-carbonate veins. The minerals of tetrahedrite-tennantite series also forms massive aggregates a few mm in size. Inclusions or intergrowths with chalcopyrite, sphalerite I and galena are common. Microprobe analyses showed a predominance of tennantite over tetrahedrite and Zn-members over Fe members. Four minerals represent this series: tetrahedrite-(Zn), tetrahedrite-(Fe), tennantite-(Zn), and tennantite-(Fe). Tetrahedrite-(Zn) and -(Fe) forms intergrowths with tennantite-(Zn) and chalcopyrite. The antimony content reaches up to 26.88 wt.% (3.62 *apfu*). Tetrahedrite-(Zn) and -(Fe) contain some small amounts of Cd (up to 0.07 *apfu*) and Ag (up to 0.02 *apfu*). Moreover tetrahedrite-(Zn) has a significant content of Bi (up to 0.09 *apfu*). Tennantite-(Fe) is rare and occurs as inner zones which are surrounded by tennantite-(Zn). Tennantite-(Zn) is the most common mineral in the tetrahedrite-tennantite series; it is commonly zonal (Fig. 4D) and passes into tetrahedrite-(Zn). The arsenic content reaches up 20.77 wt.% (4.03 *apfu)*. Some tennantite-(Zn) grains show zonation which is related to the contents of As and Sb (Fig. 4D). In addition, tennantite-(Zn) contains contents of Bi (up to 0.06

apfu), Cd (up to 0.04 *apfu*) and Ag (up to 0.03 *apfu*) while tennantite-(Fe) contains Cd up to (0.01 *apfu*). The empirical formula based on 16 cations for tetrahedrite-(Zn) is $(Cu_{10.02-10.08}Ag_{0.00-0.01}Zn_{1.61-1.62}Fe_{0.37-0.46}Cd_{0.00-0.02})_{=12.08-12.11}(Sb_{2.97-3.39}As_{0.46-0.75}Bi_{0.00-0.09})_{=3.81-3.85}S_{12.78-12.95}$, for tetrahedrite-(Fe) is $(Cu_{9.82-9.95}Ag_{0.00-0.02}Fe_{1.11-1.23}Zn_{0.57-0.88}Cd_{0.07})_{=11.71-11.94}(Sb_{1.95-2.53}As_{1.62-2.19})_{=4.14-4.15}S_{13.88-14.13}$, for tennantite-(Zn) $(Cu_{9.76-10.15}Ag_{0.00-0.03}Zn_{0.98-1.54}Fe_{0.45-1.13}Cd_{0.00-0.04})_{=11.82-12.26}(Sb_{0.00-0.47}As_{3.19-4.03}Bi_{0.00-0.06})_{=3.72-4.03}S_{12.71-13.26}$, for tennantite-(Fe) $(Cu_{10.05-10.23}Fe_{1.06-1.44}Zn_{0.46-0.85}Cd_{0.00-0.01})_{=11.97-12.13}(Sb_{0.00-0.41}As_{3.24-4.00})_{=3.65-4.00}S_{12.82-13.11}$

BISMUTH MINERALS

The Bi minerals are common phases in the hydrothermal paragenesis but they are rare in the skarns. Usually, they occur as inclusions or crystals in galena, rarely in chalcopyrite. Bismuth is the most common Bi mineral while the bismuthinite-aikinite series, ikunolite, members of gustavite-lillianite series, berryite and matildite are rare. Bismuth creates aggregates (up to 200 μm) which are overgrown by galena (Fig. 4E), cobaltite and pyrite. It occurs also as fine, subhedral inclusions (up to 50 μm in size) in galena and sphalerite or makes intergrowths with other bismuth minerals, and is chemically homogeneous.

Members of the bismuthinite-aikinite series are rare in the samples studied. Two members of this series, bismuthinite and aikinite, were identified on the basis of chemical composition. The bismuthinite is associated with bismuth, gustavite and galena and was found with sphalerite in skarn (Fig. 4F) and in chalcopyrite aggregate with galena in hydrothermal ore. The degree of aikinite type (n_{aik}) of substitution (Bi^{3+} + □ Pb^{2+} + Cu^{+}) was calculated using the formulae proposed by Topa et al. (2002). The bismuthinite contains small contents of Cu (up to 0.06 *apfu*) and Pb (up to 0.05 *apfu*) which give n_{aik} values from 2.25 to 5.26. The empirical formula of bismuthinite based on the sum of Ag + Bi + Sb + Fe + As + (Pb + Cu)/2 = 8 atoms could be written as $(Bi_{1.90-1.95}Cu_{0.00-0.06}Pb_{0.00-0.05})_{=1.95-2.01}S_{3.08-3.14}$.

Aikinite was identified in a single sample where it forms fine intergrowths with bismuth in galena up to 20 μm in size (Fig. 4G). It contains small amounts of Fe (up to 0.02 *apfu*) and Se (up to 0.01 *apfu*). The degree of aikinite type substitution (n_{aik}) ranges from 97.23 to 102.75%. The empirical formula of aikinite based on 3 cations could be written as $(Pb_{0.96-1.08}Cu_{0.95-1.01}Bi_{0.96-1.01}Fe_{0.00-0.02})_{=2.95-3.04}S_{2.91-2.95}Se_{0.00-0.01}$.

Ikunolite is very rare and forms tiny inclusions up to 20 μm across in sphalerite II. It contains significant content of Cu (up to 0.25 *apfu*) and contents of Se (up to 0.05 *apfu*), Pb (up to 0.04 *apfu*) and Ag (up to 0.03 *apfu*). The empirical formula of ikunolite based on 4 cations could be written as $(Bi_{3.73-3.76}Cu_{0.17-0.25}Pb_{0.00-0.04}Ag_{0.00-0.03})_{=3.97-4.01}S_{2.97-3.05}Se_{0.00-0.05}$.

Members of the lilianite homologous series were found in samples from skarns. Three members of this series were identified: gustavite-lillianite solid solution, vikingite and heyrovskýite. All members of the lillianite series are very rare and form fine inclusions up to 30 μm across in sphalerite II aggregates. Gustavite forms intergrowths with bismuthinite (Fig. 4F) or galena (Fig. 4H) and locally is accompanied by lillianite. This mineral contains significant contents of Cu (ranges from 0.10 *apfu* to 0.37 *apfu*) and Se (up to 0.11 *apfu*). Gustavite is characterized by high Ag+Bi - 2Pb substitution (from 83.25 to 104.71%). The N homologues value for gustavite ranges from 3.45 to 4.08 (Fig. 5). The empirical formula of gustavite based on 5 cations could be written as $(Pb_{1.01-1.14}Ag_{0.82-0.90}Bi_{2.68-2.98}Cu_{0.10-0.37})_{=4.96-5.04}S_{5.82-6.12}Se_{0.04-0.11}$.

Lillianite forms inclusions in sphalerite II, rarely in galena. It is locally accompanied by gustavite and bismuthinite. Lillianite contains high contents of Ag up to 4.63 wt.% (0.51 *apfu*) and contents of Cu and Cd (up to 0.01 *apfu*). In comparison with gustavite, it is characterized by significantly lower Ag+Bi - 2Pb substitution (from 24.72 to 51.39%). The N homologues value for lillianite ranges from 3.89 to 4.00. The empirical formula of lillianite based on 5 cations could be written as $(Pb_{1.96-2.39}Bi_{2.24-2.52}Ag_{0.27-0.51}Cu_{0.00-0.01}Cd_{0.00-0.01})_{=4.77-5.14}S_{5.94-6.10}$.

Vikingite occurs as intergrowths with members of the gustavite-lillianite series in sphalerite aggregates from skarns. It forms tiny crystals up to 20 μm across in galena and sphalerite. The vikingite is Ag-poor, the amounts of Ag ranging from 2.09 wt.% (1.19 apfu) to 3.07 wt.% (1.73 apfu). It contains admixtures of Se up to 0.21 wt.% (0.16 apfu), Cd up to 0.09 wt.% (0.05 apfu) and Te up to 0.05 wt.% (0.05 apfu). In vikingite a low Ag+Bi - 2Pb substitution (16.56–23.78 %) was reported. The N homologues value for vikingite ranges from 5.25 to 5.64 which is in a good agreement with a theoretical value of N=5.5. The empirical formula of vikingite based on 26 cations could be written: $(Ag_{1.19-1.73}Bi_{8.93-9.86}Pb_{14.52-15.84}Cd_{0.01-0.05}Te_{0.00-0.05})_{=25.67-26.51}S_{29.96-30.73}Se_{0.02-0.16}$.

Heyrovskýite forms fine inclusions in sphalerite II accompanied by tiny irregular lillianite aggregates. It contains small admixtures of Se (up to 0.07 *apfu*), Te (up to 0.02 *apfu*), Cd (up to 0.01 *apfu*) and Cu (up to 0.01 *apfu*). In this mineral very low Ag+Bi - 2Pb substitution (13.45–16.86%) was observed. The N value ranges from 6.42 to 6.60 which is a little away from the theoretical value N=7. The empirical formula of heyrovskýite based on 16 cations could be written as $(Pb_{10.13-10.44}Ag_{0.65-0.81}Bi_{4.87-5.05}Te_{0.00-0.02}Cd_{0.00-0.01}Cu_{0.00-0.01})_{=15.84-16.15}S_{18.15-18.53}Se_{0.01-0.07}$.

Berryite is a very rare mineral which occurs in intergrowths with native bismuth accompanied by galena and matildite in quartz veins (Fig. 6A). This mineral forms elongated crystals up to 40 μm in size. It contains admixtures of Fe (up to 0.13 *apfu*) and Sb (up to 0.01 *apfu*). The empirical formula of berryite based on 15 cations could be written as $(Cu_{2.79-2.93}Ag_{1.92-2.25}Pb_{2.68-2.93}Bi_{6.97-7.21}Fe_{0.05-0.35}Sb_{0.01-0.02})_{=15.00-15.11}S_{16.05}$.

Matildite was found in galena aggregates. It usually forms intergrowths up to 20 μm across with bismuth, canfieldite and berryite, rarely with bismuthinite (Fig. 6A–C). This mineral has a low content of Se, from 0.66 to 1.16 wt.% (from 0.03 up to 0.06 *apfu*), and of Pb from 0.51 to 1.08 wt.% (up to 0.02 *apfu*). The empirical formula of matildite based on 2 cations could be written as $(Ag_{0.94-0.97}Bi_{0.99-1.02}Pb_{0.00-0.02})_{=1.96-1.98}S_{1.93-2.07}Se_{0.03-0.06}$.

SILVER MINERALS

Silver minerals are not very common in the paragenesis studied. Generally, only a few such minerals could be found in quartz-carbonate veinlets. They are accompanied by galena and bismuth and form small intergrowths with these minerals. They locally form tiny inclusions in galena crystals. Three minerals (except for Bi-bearing silver-enriched phases) represent a group of silver minerals including canfieldite, acanthite and matildite.

Canfieldite is a very rare mineral, which was identified in two samples only. It forms tiny intergrowths up to 20 μm in size with galena, sphalerite, bismuth and matildite or fine veinlets in galena (Fig. 6B, C). Canfieldite has a very high content of Te: up to 19.11 wt.% (up to 2.07 *apfu*) and admixtures of Bi (up to 0.19 *apfu*), Pb (up to 0.14 *apfu*), Fe (up to 0.06 *apfu*), Sb (up to 0.02 *apfu*) and Se (up to 0.02 *apfu*). The high content of tellurium al-

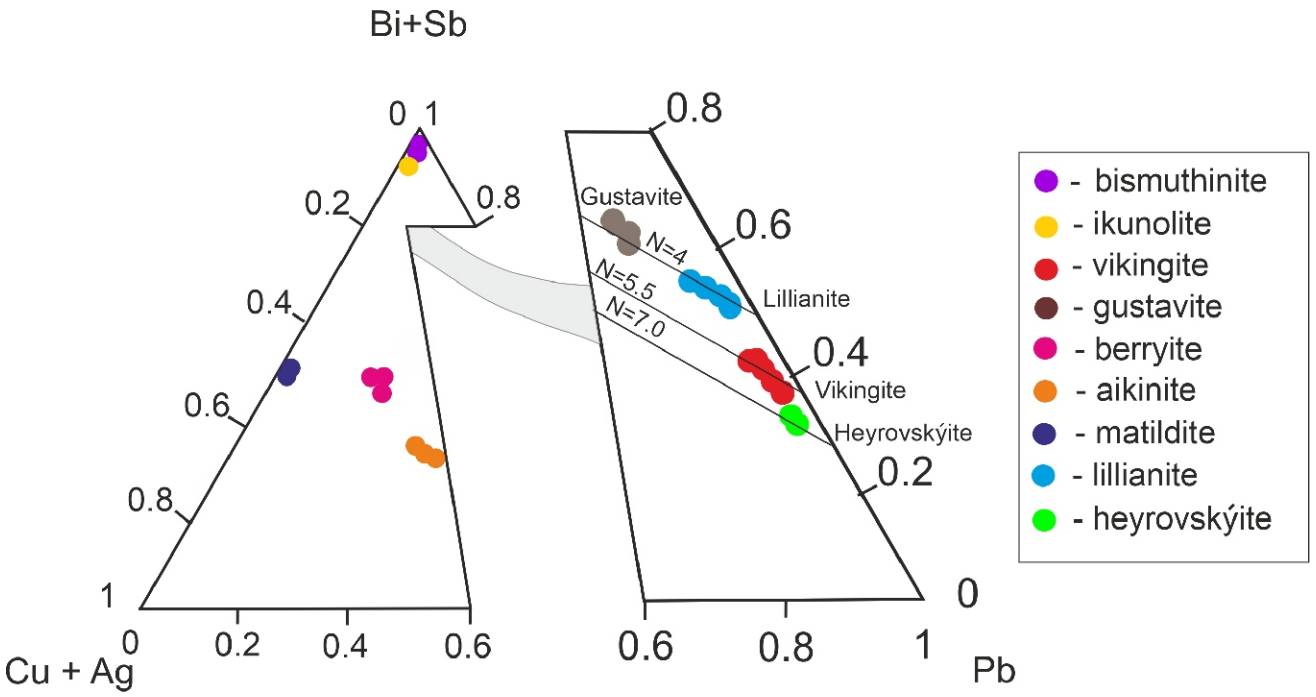

Fig. 5. Compositional plot of Bi sulphosalts in terms of the (Cu+Ag) – (Pb) – (Bi+Sb) triangle (in *apfu*)

lows to identify the studied phase as a Te-rich canfieldite. The empirical formula of Te-rich canfieldite based on 9 cations could be written as $(Ag_{7.71-7.87}Bi_{0.02-0.19}Pb_{0.00-0.14}Sn_{0.94-1.02}Fe_{0.04-0.06}Sb_{0.01-0.02})_{=8.99-9.03}S_{4.24-4.32}Te_{2.01-2.07}$.

Acanthite is a very rare mineral. It forms tiny inclusions in galena aggregates up to 30 μm across. It contains small admixtures of Cu (up to 0.02 *apfu*), Sb (up to 0.01 *apfu*) and Fe (up to 0.01 *apfu*). The empirical formula of acanthite based on 2 cations could be written as $(Ag_{1.97-1.98}Cu_{0.00-0.02}Sb_{0.00-0.01}Fe_{0.00-0.01})_{=1.99-2.00}S_{0.97-1.04}$.

GALENA

Galena is a common mineral in the samples studied; however, it usually occurs in minor amounts. Two generations of this mineral were discovered. Galena I occurs as tiny crystals up to 80 μm across in skarns where it is accompanied by sphalerite II, chalcopyrite and magnetite II or forms intergrowths up to 200 μm in size with chalcopyrite, sphalerite I and II, bismuth (Fig. 4E), cobaltite, gersdorffite, berryite (Fig. 6A), matildite and canfieldite (Fig. 6B, C) in hydrothermal veins. Moreover, it also contains inclusions of gustavite (Fig. 4H), lillianite, bismuth, aikinite (Fig. 4G) and matildite (Fig. 3G). Galena I has significant admixtures of Se (up to 0.06 *apfu*), Bi (up to 0.04 *apfu*) and Ag (up to 0.04 *apfu*) and also Fe (up to 0.02 *apfu*). Galena II occurs in hydrothermal quartz and quartz-carbonate veins and fills cracks in chalcopyrite, pyrite and sphalerite II. It rarely surrounds grains of cobaltite and sphalerite I grains or occurs as tiny inclusions in them. It usually does not contain any admixtures though some galena crystals have small contents of Fe and Cu (up to 0.01 *apfu*). The empirical formula of galena I based on 1 cation could be written as $(Pb_{0.92-0.98}Bi_{0.01-0.04}Ag_{0.00-0.04}Fe_{0.00-0.02})_{=1.00-1.01}(S_{0.96-1.03}Se_{0.00-0.06})_{=1.02-1.03}$ and those of galena II is $(Pb_{0.98-1.00}Fe_{0.00-0.01}Cu_{0.00-0.01})_{=1.00}S_{1.00-1.04}$.

TIN SULPHIDES

The Sn sulphides are widespread in the samples studied and were found in quartz and quartz-carbonate veins. They occur as irregular aggregations, veinlets and inclusions in chalcopyrite, rarely in sphalerite. Grains of cassiterite and roquesite are overgrown by tin sulphides, mainly stannoidite and mawsonite, and less by a ferrokësterite-like phase.

Stannoidite is the most common tin sulphide in the Miedzianka-Ciechanowice deposit. Mostly it forms irregular aggregates up to 300 μm in size in chalcopyrite and veinlets up to 1 mm across cutting chalcopyrite aggregates (Fig. 6D). Stannoidite locally forms tiny inclusions in chalcopyrite and sphalerite II (Fig. 4A). Moreover, this mineral fills parts of voids in chalcopyrite and cobaltite grains (Fig. 6E). The content of Sn varies from 15.81 wt.% (1.71 *apfu*) to 18.90 wt.% (2.21 *apfu*) and the content of Fe reaches up 12.70 wt.% (2.97 *apfu*). In this mineral, a wide range of Cu contents from 35.32 wt.% (7.15 *apfu*) to 40.32 wt.% (8.22 *apfu*) was observed (Fig. 7A). In addition, stannoidite occurring in sphalerite II is enriched in Zn from 2.57 wt.% (0.51 *apfu*) to 5.04 wt.% (1.02 *apfu*). Stannoidite is characterised by high Zn-Fe substitution and only occasionally it contains small contents of trace elements (up to 0.05 *apfu* of As, up to 0.01 *apfu* of In, Ag and Pb). The empirical formula of stannoidite based on the sum of 13 cations could be written as $Cu_{7.15-8.22}Fe_{2.01-2.97}Sn_{1.71-2.21}Zn_{0.51-1.02}S_{11.31-12.28}$.

Mawsonite usually occurs at the edges of voids in chalcopyrite and surrounds grains of cassiterite in chalcopyrite aggregates (Fig. 3B). It was found also in bornite grains where it forms fine zones up to 20 μm across. The content of Sn reaches up to 14.04 wt.% (1.03 *apfu*). This mineral contains the highest amounts of Fe, up to 14.02 wt.% (2.13 *apfu*), and Cu from 44.08 wt.% (5.88 *apfu*) to 47.87 wt.% (6.34 *apfu*). Moreover, mawsonite is usually chemically pure and does not contain any admixtures, especially of Zn which is present in other tin phases in the Miedzianka-Ciechanowice deposit (Fig 7B). The empirical formula of mawsonite based on the sum of 9 cations could be written as $Cu_{5.88-6.34}Fe_{1.88-2.13}Sn_{0.98-1.03}S_{7.67-8.07}$.

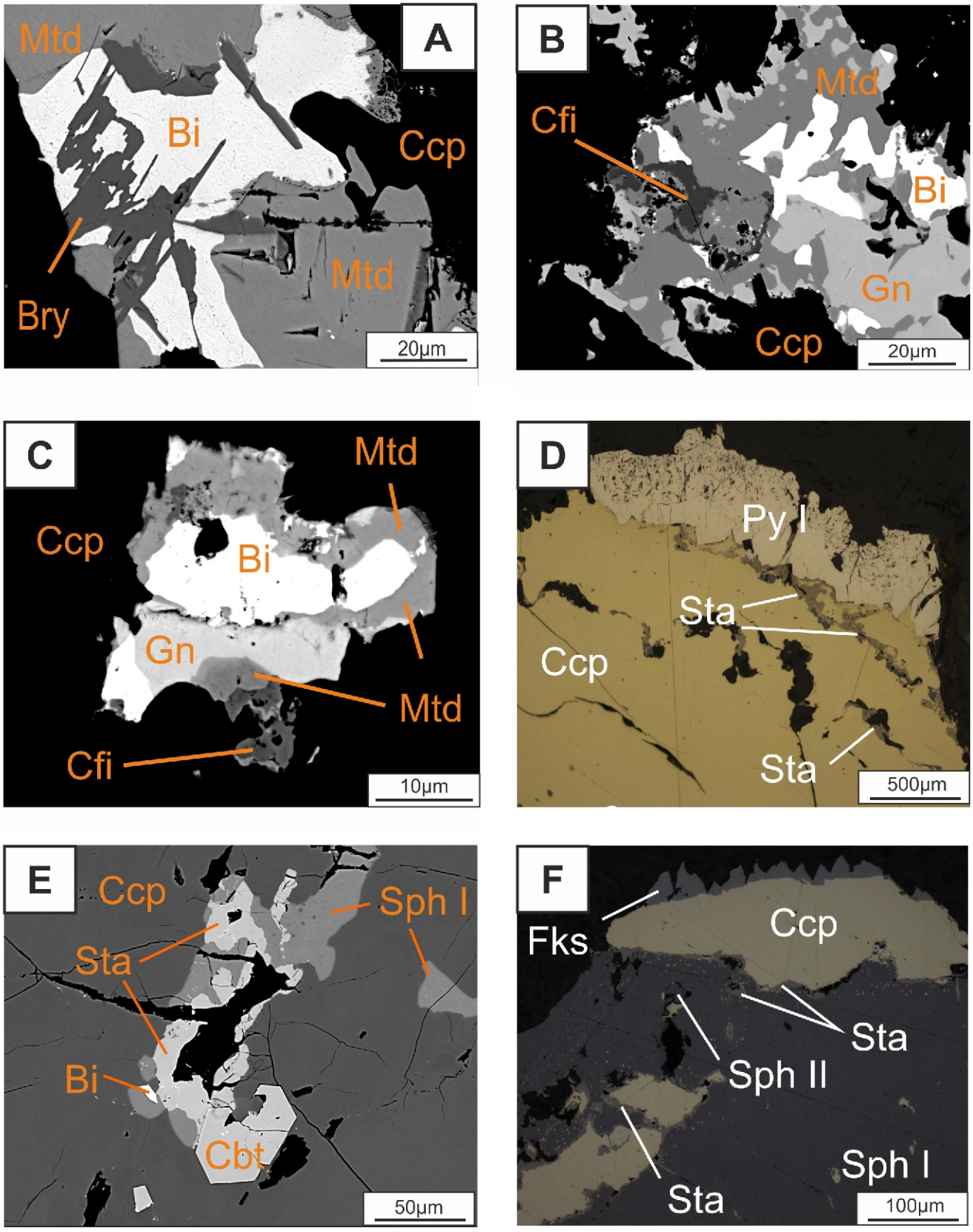

Fig. 6. BSE images (A–C, E) and reflected light (D, F) illustrating the main features of mineral assemblages

A – intergrowths of bismuth, berryite, matildite in chalcopyrite; **B** – intergrowths of matildite, galena, bismuth and canfieldite in chalcopyrite; **C** – intergrowths of native bismuth with galena, matildite and canfieldite in a chalcopyrite aggregate; **D** – veinlets of stannoidite in chalcopyrite and pyrite I; **E** – aggregates of stannoidite with sphalerite I, a cobaltite grain and bismuth in chalcopyrite; **F** – ferrokësterite at the edge of a chalcopyrite crystal and two generations of sphalerite with stannoidite; Fks – ferrokësterite; Cfi – canfieldite; Bry – berryite

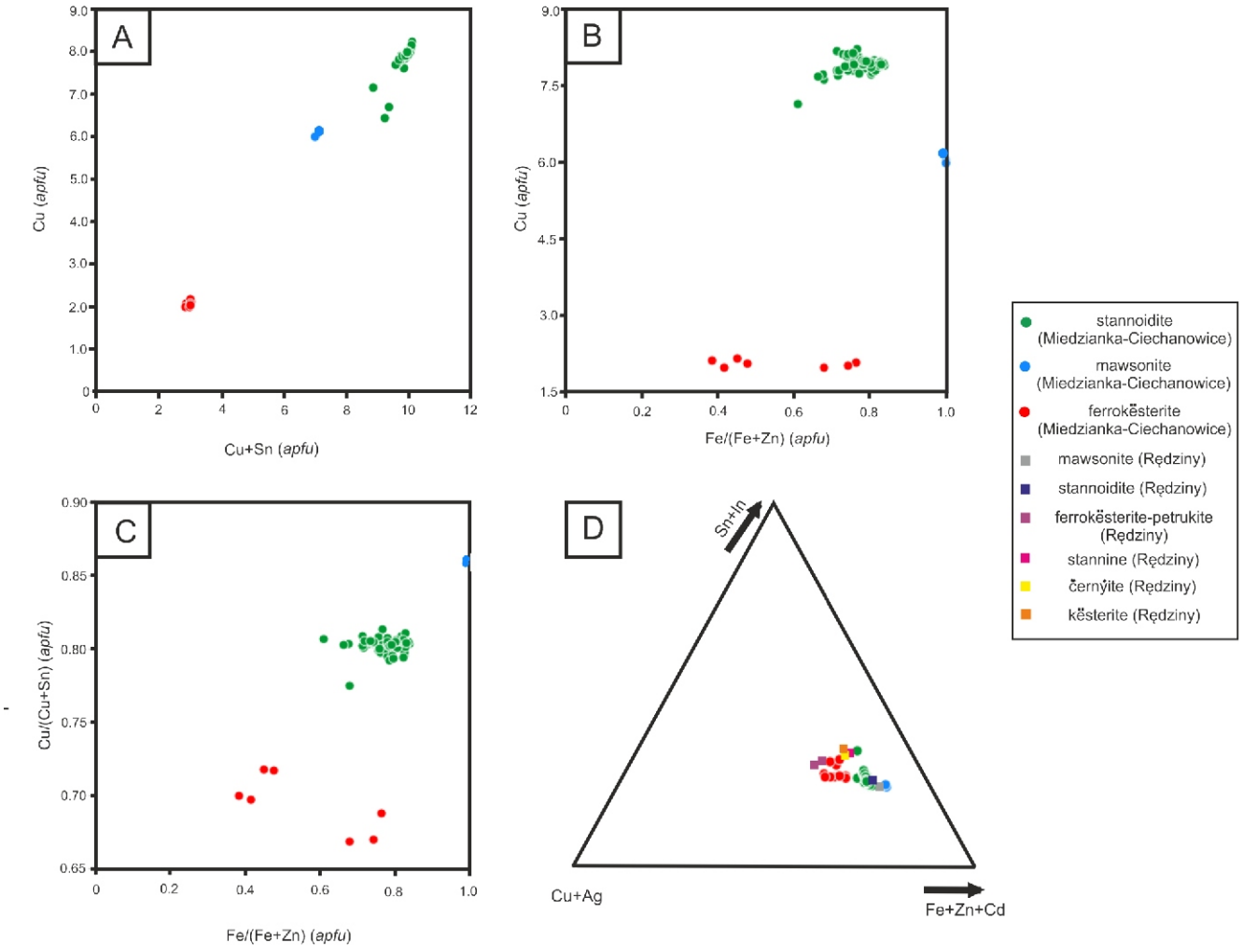

Fig. 7. Compositional relationships in the tin sulphides from the Miedzianka-Ciechanowice deposit

A – diagram of Cu vs. Cu+Sn; **B** – diagram of Fe/(Fe+Zn) vs. cations/S; **C** – diagram of Cu/(Cu+Sn) vs. Fe/(Fe+Zn); **D** – compositional plot of Sn sulphides in terms of the (Cu+Ag) – (Sn+In) – (Fe+Zn+Cd) triangle (in apfu) from Miedzianka-Ciechanowice and Rędziny (Pieczka et al., 2009)

The ferrokësterite-like phase is very rare. It is accompanied by chalcopyrite, pyrite and sphalerite I. It forms fine aggregates up to 20 μm in size in chalcopyrite or occurs at the edges of chalcopyrite aggregates (Fig. 6F). This phase is richest in tin among all the tin sulphides identified, the content of Sn ranging from 21.52 wt.% (0.76 *apfu*) to 27.31 wt.% (0.99 *apfu*). It is also characterised by the lowest content of Cu, ranging from 29.18 wt.% (1.98 *apfu*) to 33.92 wt.% (2.16 *apfu*; Fig. 7C). The ferrokësterite is characterised by Zn-Fe substitution. The content of Fe varies from 4.86 wt.% (0.38 *apfu*) to 10.43 wt.% (0.78 *apfu*) in ferrokësterite hosted by chalcopyrite aggregates and Zn ranges from 3.55 wt.% (0.23 *apfu*) to 9.17 wt.% (0.60 *apfu*) in grains accompanied by sphalerite I. This mineral contains only small contents of Cd (up to 0.01 *apfu*). The empirical formula of the ferrokësterite-like phase based on the sum of 4 cations could be written as $Cu_{1.98-2.22}Zn_{0.23-0.60}Fe_{0.38-0.78}Sn_{0.76-0.99}S_{3.79-3.90}$.

A comparison of compositional data for all tin sulphides identified from the Miedzianka-Ciechanowice deposit is shown in a triangular diagram (Fig. 7D).

ROQUESITE

This is a very rare mineral which was found in the chalcopyrite-stannoidite paragenesis in amphibolite. This mineral is accompanied by sphalerite I, bornite and cassiterite. Roquesite forms hypautomorphic grains up to 20 μm across. It is chemically pure with low contents of Fe – max. 0.05 *apfu* and Ga – max. 0.02 *apfu*. The empirical formula of roquesite based on 2 cations could be written as $(Cu_{1.01-1.04}In_{0.89-0.93}Fe_{0.04-0.05}Ga_{0.02})_{=2.00}S_{1.82-1.86}$.

BORNITE

This mineral usually forms intergrowths with chalcopyrite, sphalerite and pyrite. Some bornite crystals contain inclusions of mawsonite and are accompanied by members of the tetrahedrite-tennantite series. Bornite is close to the theoretical composition and only rarely it contains small amounts of Bi up to 0.36 wt.% (0.01 *apfu*). The empirical formula of bornite based on 6 cations could be written as $Cu_{4.96-4.97}Fe_{0.99-1.02}S_{3.93-4.05}$.

DISCUSSION

BISMUTH MINERALIZATIONS

Bismuth-bearing mineral associations are widespread in many different genetic types of hydrothermal mineralization in the Sudety Mts. (Mochnacka and Banaś, 2000; Pieczka et al., 2009; Mochnacka et al., 2009; Gołębiowska et al., 2012; Pietrzela, 2019; Foltyn et al., 2023; Muszyński et al., 2023). The most common mineral is bismuth while Bi sulphosalts are rare. In the Miedzianka-Ciechanowice deposit, bismuth minerals are accessory and are represented mainly by bismuth, less so by diverse Bi sulphosalts. A similar paragenesis of Bi minerals was described in hydrothermal mineralizations at Rędziny (Pieczka et al., 2009; Gołębiowska et al., 2012), Chełmiec (Muszyński et al., 2023), Czarnów (Mochnacka et al., 2009), Radzimowice (Mikulski, 2005), Stara Kamienica–Gierczyn- Przecznica area (Foltyn et al., 2023) and Szklarska Poręba- Huta (Kozłowski and Karwowski, 1975; Kozłowski et al., 1975; Olszyński et al., 1976; Pieczka and Gołębiowska, 2012).

The Rędziny deposit, located in marbles in the contact zone of the Karkonosze Granite, contains various Bi minerals, including: ikunolite, members of the giessenite-izoklakeite series, gustavite, berryite, cosalite, pavonite, benjaminite, minerals of the aikinite-bismuthinite series, wittichenite and matildite (Pieczka et al., 2009; Gołębiowska et al., 2012). In contrast to Miedzianka-Ciechanowice, they form larger crystals and aggregates up to 1 mm in size within arsenopyrite crystals, sphalerite, galena and co-occurring with chalcopyrite and other subordinate ore minerals (Pieczka et al., 2009). Moreover some bismuth minerals occur within minerals of the tetrahedrite group (both Ag- and Bi-free and enriched; Pieczka et al., 2009). In addition some Bi-sulphosalts are enriched in Ag (Ag-rich wittichenite and cosalite) or related to Ag-bearing phases and form assemblages of Ag(Cu)–Pb–Bi(Sb) sulphosalts (Pieczka et al., 2009; Pieczka and Gołębiowska, 2012). Moreover, bismuth sulphoselenides and sulphotellurides – ikunolite, joséite-A, joséite-B and tetradymite – were described from quartz-chlorite-arsenopyrite veins (Pieczka et al., 2009). Typical for both localities is Ag+Bi-2Pb substitution in various phases, and galena is reported. According to Pieczka et al. (2009) the precipitation of Ag(Cu)–Pb–Bi(Sb) sulphosalts started at ~350–330°C from crystallization of pavonite, benjaminite, gustavite, berryite, members of the giessenite-izoklakeite series, cosalite, matildite and wittichenite which are associated with Ag-rich galena. In the next stage, at temperatures of 300–250°C, members of the aikinite group formed (Pieczka et al., 2009). On the base of the similarities and close proximity of Miedzianka and Redziny, we suggest a similar range of crystallization temperatures for the Bi-bearing paragenesis.

In the Chełmiec deposit, the Bi mineralization is represented by common bismuthinite, rare bismuth and matildite which has no relationship to other Bi minerals and occurs as separate crystals (Muszyński et al., 2023). The Bi minerals occur in a Ni-Co paragenesis especially with massive sulpharsenides (gersdorffite and cobaltite) with no galena, which is in a huge contrast to the Miedzianka-Ciechanowice deposit.

Accessory Bi mineralization in the form of tiny inclusions or intergrowths of Bi-bearing minerals in polymetallic ores have been found in many hydrothermal deposits in the Sudeten Mts., for instance in the Czarnów polymetallic vein-type deposit (Mochnacka et al., 2009), the Au–As–Cu quartz-sulphide vein type deposit in Radzimowice (Mikulski, 2005; Mikulski and Williams, 2014), the Gierczyn-Przecznica area in the Stara Kamienica Schist Belt (Wiszniewska, 1983; Foltyn et al., 2023) and in the pegmatite, aplogranite and quartz vein with W-Sn-Mo mineralization in Szklarska Poręba-Huta (Olszyński et al. 1976; Pieczka and Gołębiowska, 2002). In Czarnów, four Bi minerals were described: bismuth, bismuthinite, ikunolite and bismite (Mochnacka et al. 2009), which, similarly to Miedzianka-Ciechanowice, are associated with galena. In Radzimowice the Bi sulphosalts are represented by treasurite, gustavite and aikinite and are accompanied by bismuth and bismuthinite (Mikulski, 2005). Moreover, the Bi tellurides rucklidgeite and volynskite were discovered (Mikulski and Williams, 2014). In contrast to Miedzianka-Ciechanowice, native bismuth occurs as inclusions in arsenopyrite though also as intergrowths with bismuthinite in carbonate gangue (Mikulski, 2007). In the Stara Kamienica Schist Belt, in the Gierczyn-Przecznica area, the Bi mineralization is represented mostly by bismuth and garavellite (Foltyn et al., 2023). Similarly, to Miedzianka-Ciechanowice, they occur in chalcopyrite and are accompanied by galena and stannite. In the Szklarska Poręba-Huta quarry, the wolframite-scheelite-cassiterite mineralization is associated with bismuthinite, native bismuth, Bi sulphides and sulphosalts including members of aikinite series, cosalite, ikunolite and joséite-A. The Bi mineralization is associated with molybdenite, chalcopyrite, pyrite, sphalerite, pyrrhotite and marcasite (Kozłowski and Karwowski, 1975; Kozłowski et al., 1975; Olszyński et al., 1976; Pieczka and Gołębiowska, 2012). According to Kozłowski et al. (2002) the bismuthinite was formed at 270–245°C, and the native bismuth at 265 and 135°C. However Bi mineralizations represented by native bismuth and bismuthinite have also been reported in the Kowary (Mochnacka nad Banaś, 2000) and Krobica-Gierczyn areas (Pietrzela, 2019).

Another deposit which contains various bismuth minerals is the Obří důl Fe–Cu–As polymetallic sulphide skarn deposit in the West Sudetes, Bohemian Massif, Czech Republic (Veselovský et al., 2018). This deposit has some paragenetic and geochemical similarities to the Miedzianka-Ciechanowice deposit. At both locations, base metal mineralization is related to the Variscan intrusion of the Karkonosze-Izera Pluton. In addition, the Obří důl deposit is hosted by a porphyritic biotite granite, located a few hundred metres away from the contact with the Variscan Karkonosze-Izera Plutonic Complex (Ackerman et al., 2017; Veselovský et al., 2018). The deposit consists of three skarn orebodies which are related to regional and contact metamorphism and hydrothermal stages (Ackerman et al., 2017; Veselovský et al., 2018). In contrast to the Miedzianka-Ciechanowice deposit, pyrrhotite and arsenopyrite predominate in Obří důl while Bi mineralization, represented by bismuth, bismuthinite and matildite, is very rare (Veselovský et al., 2018). The bismuth minerals usually form tiny inclusions in arsenopyrite, galena and silicates (diopside and garnet) but native bismuth also forms associations with molybdenite and pyrrhotite (Veselovský et al., 2018). In contrast to Miedzianka-Ciechanowice, the bismuthinite contains admixtures of Cd (0.3–0.6 wt.%) and Zn (0.1–0.2 wt.%; Veselovský et al., 2018).

CASSITERITE

Tin-bearing mineralization in the Sudety Mts. is represented mainly by cassiterite, less commonly by tin sulphides. The most widespread mineral, cassiterite, occurs at many localities, including the Stara Kamienica Schist Belt (Piestrzyński and Mochnacka, 2003; Żelaźniewicz et al., 2003; Pietrzela, 2019; Małek and Mikulski, 2021), Rędziny (Mochnacka et al., 2001; Pieczka et al., 2007), Szklarska Poręba-Huta (Kozłowski et al.,

1975; Kozłowski and Sachanbiński, 2007), Czarnów (Mikulski, 2007, 2010; Mochnacka et al., 2009) and Piława Górna (Pieczka et al., 2013).

Cassiterite is the main tin mineral in the stratiform deposit in the Krobica-Gierczyn area in the Stara Kamienica Schist Belt. Two generations of cassiterite, which form disseminations in chlorite-mica-quartz schists, were distinguished (Wiszniewska et al., 1998; Zygo et al., 2023). They form grains mainly up to 0.2 mm in size (Mochnacka, 1985; Pietrzela, 2019). Similarly to the Miedzianka-Ciechanowice deposit, cassiterite occurs in paragenesis with sulphides and sulphosalts (Pietrzela, 2019): sphalerite, pyrrhotite, chalcopyrite, galena, tetrahedrite, pyrite, marcasite, bismuth, bismuthinite and bismuth sulphosalts (Karwowski and Włodyka, 1981; Wiszniewska, 1984; Pietrzela, 2019). It usually creates irregular aggregates, intergrowths with sphalerite, chalcopyrite, pyrrhotite and galena, or anhedral grains (Pietrzela, 2019; Zygo et al., 2023). In places, sulphides surround cassiterite grains and fill voids among these grains (Wiszniewska, 1984). Moreover, cassiterite is accompanied by ilmenite, rutile, magnetite and garnet (Wiszniewska et al., 1998, Michniewicz et al., 2006, Pietrzela, 2019) and contains inclusions of chlorite (Wiszniewska, 1984). According to previous research the first generation of cassiterite crystallized at the beginning of the high-temperature stage, in a temperature range of 460–420°C, whereas the second one crystallized together with sulphides at 365–325°C (Wiszniewska et al., 1998; Małek and Mikulski, 2021). The origin of mineralization is not fully known, however, the presence of admixtures of In (up to 0.15 wt.%) and Ta (up to 0.4 wt.%) suggests the hydrothermal origin of cassiterite (Pietrzela, 2019). Cassiterites in the Miedzianka-Ciechanowice deposit also contain admixtures of In_2O_3 and Ta_2O_5 (up to 0.53 wt.% and 0.18 wt.%, respectively), which can suggest their hydrothermal origin. According to Wiszniewska (1984) and Mochnacka et al. (2015), the origin of cassiterite, sulphides and sulphosalts is related to hydrothermal solutions connected with the Variscan evolution of the Karkonosze Granite. However, the source of hydrothermal fluids may be in the Izera Granite (Michniewicz et al., 2006). Due to the similarity of cassiterite occurrence in the same paragenesis with sulphides and sulphosalts (Wiszniewska, 1984; Pietrzela, 2019), and the presence of admixtures of In and Ta, it can be inferred that cassiterite from the Krobica-Gierczyn area and Miedzianka-Ciechanowice deposit is related to hydrothermal fluids from the Karkonosze Granite.

Cassiterite is one of the main ore minerals in Rędziny (Pieczka et al., 2007). It creates disseminated grains and occurs with sulphides and sulpharsenides in schists which cut the dolomite lens and in quartz-chlorite-arsenopyrite veins (Pieczka et al., 2009). Significant accumulation of this mineral occurs also in quartz-cassiterite-hematite-sulphide veins and nests. Moreover, small inclusions of cassiterite were found in sphalerite-ferrokësterite-chalcopyrite assemblages (Pieczka et al., 2009). Cassiterite is usually accompanied by arsenopyrite, pyrrhotite, pyrite (Pieczka et al., 2007) and, similarly to cassiterite II from the Miedzianka-Ciechanowice deposit, some cassiterite grains are surrounded by younger tin-bearing sulfides: stannite, stannoidite and mawsonite. In addition, in mineral phases from both deposits, tin is replaced by Fe, up to 2.0 wt.% Fe_2O_3 in Rędziny and up to 2.99 wt.% FeO in Miedzianka-Ciechanowice. Cassiterite from Rędziny has slightly higher contents of Ti (up to 2.6 wt.% TiO_2) and WO_3 (up to 1.2 wt.%), (Pieczka et al., 2009) than in the research area where admixtures of TiO_2 and WO_3 reach up 0.69 wt.% and 0.15wt.% respectively. In contrast to the Miedzianka-Ciechanowice deposit where cassiterite has contents of Ta_2O_5 (up to 0.18 wt.%) and Nb_2O_5 (up to 0.03 wt.%), cassiterite from Rędziny does not contain admixtures of Ta and Nb (usually below detection limits). In contrast to Miedzianka-Ciechanowice, some cassiterite grains show oscillatory zonation which depends on Fe content: dark zones are Fe-rich, brighter bands are Fe-poor (Pieczka et al., 2009). According to Pieczka et al. (2009) cassiterite was formed during the final stage of arsenopyrite formation at temperatures from 412 to 285°C. Undoubtedly, the origin of cassiterite at Miedzianka-Ciechanowice is related to high-temperature hydrothermal fluids which were followed by the sulphide medium and low-temperature stage of vein mineralization.

In the quarry at Szklarska Poręba-Huta, cassiterite was found in aplogranite and quartz veins with wolframite-sulphide mineralization (Kozłowski et al., 1975, 2002). It forms dispersed, subhedral grains accompanied by scheelite, wolframite, molybdenite, chalcopyrite and pyrite (Kozłowski et al., 2002; Mikulski and Stein, 2007; Mil et al., 2024). Similarly to Miedzianka-Ciechanowice, the cassiterite contains small admixtures of Fe (3–1 wt.%), Nb (to 0.2 wt.%) and Ta (to 0.1 wt.%; Kozłowski et al., 2002). According to fluid inclusion research, the cassiterite crystalized at temperatures of 515–470°C (Kozłowski et al., 2002).

Accessory cassiterite in the form of small, disseminated grains was found in the Czarnów (Mikulski et al., 2007; Zygo et al., 2023) and Piława Górna deposits (Pieczka et al., 2013). In the Czarnów polymetallic deposit, cassiterite was recognized in a chalcopyrite-sphalerite-cassiterite ore and its presence characterizes an early stage of crystallization (Mikulski et al., 2007; Mikulski, 2010). It is accompanied mainly by arsenopyrite, and, to lesser extent, by chalcopyrite, pyrrhotite, and pyrite. Cassiterite occurs as aggregates of euhedral or subhedral crystals up to 1 mm in size which form intergrowths with arsenopyrite (Zygo et al., 2023). Two types of cassiterite were distinguished: coarse-grained and fine-grained. They crystallized at temperatures of 440–384°C and 340–300°C, respectively (Mikulski et al., 2007; Zygo et al., 2023). In contrary to cassiterite from the Miedzianka-Ciechanowice deposit, it contains higher admixtures of In (from 0.2 to 2.6 wt.%), Ta (from 0.15 to 0.70 wt.%), however, it also has low contents of Nb_2O_5 (from 0.1 to 0.42 wt.%; Mikulski, 2007), TiO_2 (up to 0.2 wt.%) and WO_3 (up to 0.13 wt.%; Mochnacka et al., 2009).

TIN SULPHIDES

The most widespread Sn sulphide in the Sudety Mts. is stannite, which was reported in Rędziny (Pieczka et al., 2009), Czarnów (Mochnacka et al., 2009), the Krobica-Gierczyn area (Karwowski and Włodyka, 1981), Przecznica (Foltyn et al., 2023) and Radzimowice in the Kaczawa Mts. (Zimnoch, 1965, Mikulski, 2005). However, it represents only accessory mineralization. The tin mineralizations described from the Miedzianka-Ciechanowice area involving stannoidite, mawsonite and ferrokësterite are not very common and occur in the Rędziny (Pieczka et al., 2009) and Czarnów deposits (Mochnacka et al., 2009; Mikulski, 2010).

The Rędziny deposit is characterised by the presence of various assemblages along with Sn-bearing sulphides. They are represented by tiny inclusions up to 10 μm across of këstеrite, černýite and stannite in Ag-rich galena and inclusions of ferrokësterite in sphalerite (Pieczka et al., 2009). In addition, mawsonite, stannoidite and stannite coexist with chalcopyrite and Ag-rich phases including Ag-rich bornite, Ag-rich galena, Ag- and Bi-bearing tetrahedrite, and Ag-bearing galena (Pieczka et al., 2009). Similarly to the Miedzianka-Ciechanowice deposit, these Sn-bearing sulphides surround the older cassiterite grains (Pieczka et al., 2009; Gołębiowska et al., 2012). Within stannoidite aggregates in the contact zone with

cassiterite, an irregular aggregate of chatkalite was found (Pieczka et al., 2009). Stannoidite, stannite and mawsonite usually do not contain any admixtures; however, in contrast to the Miedzianka-Ciechanowice area, some stannoidite has significant contents of Zn (up to 3.0 wt.%) and Ag (up to 2.0 wt.%). Stannite and mawsonite contain Ag concentrations up to 0.8 wt.% and 1.3 wt.%, respectively (Pieczka et al., 2009). The tin-bearing sulphides of Rędziny coexist with silver minerals (Pieczka et al., 2009), which is in contrast to the area studied, where there occurs an Ag-poor association. According to Pieczka et al. (2009) the precipitation of Sn sulphides began at lower temperatures than that of cassiterite under increasing activity of Bi and Ag. Ferrokësterite and Zn-rich stannite crystallized in a temperature range 340–270°C, whereas stannite and chatkalite had formed at ~270–260°C, stannoidite at <270°C and mawsonite at ~240°C (Pieczka et al., 2009). A similar paragenetic sequence is observed in the studied mineralization at Miedzianka-Ciechanowice, where cassiterite is older than Sn sulphides and base metal paragenesis.

In the Czarnów polymetallic vein deposit, the Sn sulphides are represented by stannite, which was not discovered in Miedzianka-Ciechanowice, and ferrokësterite. Stannite forms intergrowths up to 20 μm in size with galena or sphalerite and occurs in pyrrhotite or at the border of pyrrhotite and chalcopyrite grains in quartz veins (Mikulski, 2010). Stannite contains significant amounts of Zn, up to 4.12 wt.%. The presence of Zn in stannite can suggest an activity of high-temperature fluids (Pieczka et al., 2009). Ferrokësterite forms tiny inclusions in sphalerite and chalcopyrite and contains significant amounts of Zn (average up to 4.95 wt.%). However, in contrast to ferrokësterite from the Miedzianka-Ciechanowice area, it has admixtures of Ag (up to 0.69 wt.%), Cd (up to 0.24 wt.%), In (up to 0.22 wt.%) and Se (up to 0.1 wt.%; Mochnacka et al., 2009). The chemical composition of ferrokësterite indicates that the precipitation of Sn sulphides in the Czarnów deposit is related to hydrothermal fluids. The crystallization temperature of this mineral is estimated at 320 ±5°C (Mochnacka et al., 2009) and this is consistent with the data from the Rędziny deposit (Pieczka et al., 2009). The origin of Sn sulphides from Miedzianka-Ciechanowice can be related to hydrothermal fluids and we suggest their similarity to the Rędziny and Czarnów range of crystallization temperature.

The source of Sn was connected with the pneumatolytic-hydrothermal stage within the Karkonosze Granite intrusion. Among Sn-bearing minerals, cassiterite represents the oldest Sn phase which additionally indicates the activity of hydrothermal solutions. Based on crystallization temperature and admixtures, two generations of this mineral were distinguished. Previous fluid inclusion research (Wiszniewska et al., 1998; Kozłowski et al., 2002; Małek and Mikulski, 2021) showed that cassiterite I crystallized at the beginning of the high-temperature stage at temperatures of 515–420°C, and cassiterite II was formed at 360–325°C in a high-temperature sulphide stage. The Sn sulphides precipitated at lower temperatures than cassiterite (340–240°C) in the following sequence: ferrokësterite stanine stannoidite mawsonite (Pieczka et al., 2009). In addition, the presence of admixtures such as In, Nb, Ta, Fe, Ti and W corroborates the high-temperature pneumatolytic–hydrothermal nature of the cassiterites within the metamorphic cover of the Karkonosze Granite in Miedzianka-Ciechanowice, Rędziny, Czarnów, the Stara Kamienica Schist Belt and Szklarska Poręba. Hydrothermal solutions had favourable conditions for penetration into the surrounding rocks due to the occurrence of numerous faults and fractures. In many above-mentioned locations, the Sn minerals are accompanied by Bi-bearing and base metal minerals. Such mineral assemblages indicate mineralization varying from high to low temperatures. Moreover, other similarities (i.e. similar chemical compositions and structural relations) indicate a common origin of the Cu-Sn-Bi mineralization and its regional nature which is likely related to the intrusion of the Karkonosze Granite. The Cu-Sn-Bi(Ag) paragenesis is common, especially in the northern and eastern parts of metamorphic cover of the Karkonosze-Izera Granite.

CONCLUSIONS

1. Two stages of Cu-Sn-Bi paragenesis were discovered in the Miedzianka-Ciechanowice deposit: a high-temperature mineralization stage in skarn and medium and a low-temperature stage of vein mineralization.

2. In the Miedzianka-Ciechanowice area, two generations of cassiterite were found: in skarn and in quartz veins. The presence of admixtures of In, Nb and Ta demonstrate a genetic relation between both cassiterite generations from the Karkonosze Granite.

3. Various Bi sulphosalts are rare in the Miedzianka-Ciechanowice deposit and occur in galena and sphalerite. The EPM analyses show a wide range of Ag+Bi - 2Pb substitution.

4. Phases of the lillianite homologous series are characterized by a low degree (<25%) of Ag+Bi - 2Pb substitution, except for gustavite (>90%).

5. The tin sulphides are represented by common stannoidite, rare mawsonite and a ferrokësterite-like phase which contains up to 27.31 wt.% of Sn.

6. This study confirms that the Cu-Sn-Bi paragenesis is common and similar to that of other locations within the cover of the Karkonosze Granite, which indicates the regional nature of this mineralization. Despite this, in certain locations it is developed differently. The reason for this may be the different geochemical nature of the rocks forming the substrate of the hydrothermal mineralization.

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APPENDIX 1

Minerals	Banská Bystrica		Prague	
	Wavelengths	Detection Limit	Wavelengths	Detection Limit
sulpharsenides, arsenides and pyrite	SbL_α, BiM_α, CuK_α, NiK_α, FeK_α, SK_α, CoK_α, AsL_α	Sb – 0.03 wt.%, Bi – 0.05 wt.%, Cu – 0.03 wt.%, Ni – 0.02 wt.%, Fe – 0.02 wt.%, S – 0.01 wt.%, Co– 0.02 wt.%, As – 0.07 wt.%,	SnL_α, PbM_α, CuK_α, NiK_α, FeK_α, SK_α, CoK_α, AsL_β	Sn – 0.04 wt.%, Pb – 0.1 wt%, Cu – 0.04 wt.%, Ni – 0.03 wt.%, Fe – 0.02 wt.%, S – 0.02 wt.%, Co– 0.03 wt.%, As – 0.09 wt.%,
tetrahedrite, tennantite and bornite	HgM_α, AgL_α, MnK_α, BiM_α, PbM_α, ZnK_α, FeK_α, CuK_α, SK_α, SbL_α, AsL_α, SeL_α	Hg – 0.1 wt.%, Ag – 0.09 wt.%, Mn – 0.02 wt.%, Bi – 0.05 wt.%, Pb – 0.05 wt.%, Zn – 0.03 wt.%, Fe – 0.02 wt.%, Cu – 0.02 wt.%, S – 0.01 wt.%, Sb – 0.02 wt.%, As – 0.06 wt.%,	AgL_α, MnK_α, BiM_β, PbM_α, ZnK_α, FeK_α, CuK_α, SK_α, SbL_α, AsL_β, SeL_β	Ag – 0.08 wt.%, Mn – 0.03 wt.%, Bi – 0.18 wt.%, Pb – 0.1 wt.%, Zn – 0.06 wt.%, Fe – 0.03 wt.%, Cu – 0.04 wt.%, S – 0.02 wt.%, Sb – 0.04 wt.%, As – 0.1 wt.%,
for Bi minerals and galena	AgL_α, BiM_α, CuK$_\alpha$, FeK_α, SK_α, PbM_α, SbL_α, AsL_α	Ag – 0.1 wt.%, Bi – 0.3 wt.%, Cu – 0.03 wt.%, Fe – 0.02 wt.%, S – 0.01 wt.%, Pb – 0.05 wt.%, Sb – 0.02 wt.%, As – 0.08 wt.%,	AgL_α, BiM_β, CuK$_\alpha$, FeK_α, SK_α, PbM_α, SbL_α, SeL_β	Ag – 0.09 wt.%, Bi – 0.1 wt.%, Cu – 0.05 wt.%, Fe – 0.03 wt.%, S – 0.02 wt.%, Pb – 0.1 wt.%, Sb – 0.05 wt.%, Se – 0.1 wt.%,
sphalerite	AgL_α, CuK_α, SnL_α, MnK_α, FeK_α, ZnK_α, SK_α, CdL_α, HgM$_\alpha$, GaL_α, AsL_α	Ag – 0.09 wt.%, Cu – 0.03 wt.%, Sn – 0.03 wt.%, Mn – 0.01 wt.%, Fe – 0.01 wt.%, Zn – 0.03 wt.%, S – 0.01 wt.%, Cd – 0.01 wt.%, Ga – 0.03 wt.%, As – 0.06 wt.%, Hg – 0.1 wt.%,	PbM_α, AgL_α, CuK_α, SnL_α, MnK_α, FeK_α, ZnK_α, SK_α, CdL_α, InL_α, SeL_β	Pb – 0.1 wt.%, Ag – 0.06 wt.%, Cu – 0.04 wt.%, Sn – 0.04 wt.%, Mn – 0.03 wt.%, Fe – 0.03 wt.%, Zn – 0.04 wt.%, S – 0.02 wt.%, Cd – 0.05 wt.%, In – 0.03 wt.%, Se – 0.1 wt.%,
Sn sulphides	AgL_α, CuK_α, SnL_α, MnK_α, FeK_α, ZnK_α, SK_α, CdL_α, InL_α, GaL_α, AsL_α	Ag – 0.1 wt.%, Cu – 0.03 wt.%, Sn – 0.03 wt.% Mn – 0.01wt.%, Fe – 0.01 wt%, Zn – 0.03 wt.%, S – 0.01 wt.%, Cd – 0.01 wt.% In – 0.01 wt.%, Ga – 0.03 wt.% As – 0.07 wt.%,	AgL_α, CuK_α, SnL_α, MnK_α, FeK_α, ZnK_α, SK_α, CdL_α, InL_α, PbM_α, CoK_α,	Ag – 0.06 wt.%, Cu – 0.05 wt.%, Sn – 0.04 wt.%, Mn – 0.03wt.% , Fe – 0.03 wt%, Zn – 0.06 wt.%, S – 0.02 wt.%, Cd – 0.01 wt.%, In – 0.03 wt.%, Pb – 0.09 wt.%, Co– 0.03 wt.%
cassiterite	Not measured	Not measured	PbM_α, AgL_α, CuK_α, FeK_α, BiM_β, SeL_β, TeL_α,	Pb – 0.1 wt.%, Ag – 0.08 wt.% Cu – 0.05 wt.% Fe – 0.04 wt.% Bi – 0.17 wt.% Se – 0.09 wt.% Te – 0.05 wt.%