Mineralogy and geochemistry of Cu-Ni±Co±Ag±Bi polymetallic ores from the Hintermühlergang vein in the Chełmiec deposit, Sudetes Mountains, Poland

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Chełmiec is a hydrothermal vein-type carbonate-sulphide deposit in the Kaczawa Mountains, where polymetallic Cu-Ni±Co±Ag±Bi mineralization occurs. Samples, collected from an old dump of the Hintermühlergang vein, were studied by reflected light microscopy and electron microprobe. Two mineral parageneses, Ni-Co±Bi and Cu-Zn-Pb±Sb±Ag, associated with two stages of precipitation, were discovered in samples from the Chełmiec deposit. The first stage is associated with quartz, and is represented by pyrite, arsenopyrite, gersdorffite, cobaltite, bismuth minerals (native Bi, bismuthinite, and matildite), pyrrhotite, marcasite and chalcopyrite. The second stage associated with siderite and quartz is represented by sulphides (sphalerite, chalcopyrite, galena, pyrite), tetrahedrite group minerals [tetrahedrite-(Fe), tetrahedrite-(Zn), tennantite-(Zn), and argentotetrahedrite-(Fe)], gersdorffite and bournonite. Two generations of sulpharsenides were discovered in the samples studied. The first is represented by massive gersdorffite-cobaltite aggregates, the second generation occurs as tiny zoned gersdorffite crystals. Sulpharsenides are characterized locally by presence of high amounts of As (up to 1.55 *apfu*). Silver in the Chełmiec ores is hosted mainly in tetrahedrite group minerals [from 0.07 to 2.07 *apfu* in tetrahedrite – (Zn) and -(Fe), and from 4.37 to 4.90 *apfu* in argentotetrahedrite-(Fe)], less in matildite. In the Sudetes, the presence of massive sulpharsenides is rare, whereas freibergite is much more common.

Key words: Chełmiec, Sudety, gersdorffite-cobaltite, sulpharsenides, tetrahedrite group minerals, hydrothermal mineralization.

INTRODUCTION

The Sudetes Mountains region is characterized by the presence of many different polymetallic hydrothermal deposits (Piestrzyński et al., 1992; Mikulski, 2005; Mochnacka et al., 2009, 2012). Hundreds of years of mining activity for various metals such as gold, silver, copper, iron, uranium, cobalt and tin has been documented (e.g., Dziekoński, 1972; Madziarz and Sztuk, 2006; Madziarz, 2009a, b). One of the mining areas is located in the Kaczawa Mountains, where many polymetallic hydrothermal deposits occur (Mikulski, 2005, 2007), e.g. the Radzimowice vein-type deposit (Mikulski, 2007), the Pławna-Lubomierz quartz-vein-type deposit (Mikulski, 2007), the Grudno quartz-sulphide-vein-type deposit (Paulo and Salamon, 1974a) and the Chełmiec quartz-baryte-sulphide-vein deposit (Paulo, 1970a, 1973). Many of these deposits, due to the abandonment of mining, have not been comprehensively explored, especially mineralogically. Many abandoned deposits in the area have not been studied by modern mineralogical methods. Chełmiec is one of the old mining areas in the Kaczawa Foothills, where dozens of hydrothermal veins associated with post--Variscan granite magmatism have been documented (Mikulski, 2007; Mochnacka et al., 2012). The polymetallic mineralization in the Kaczawa Foothills is associated with quartz-baryte-sulphide veins (Paulo, 1973, 1994), which contain sulphides, sulpharsenides, and sulphosalts e.g., tetrahedrite group minerals (TGM).

Despite the diverse mineralogy in the Chełmiec hydrothermal polymetallic deposit, recognized by early studies of Paulo (1970a, 1973), no new precise data on mineralogy and geochemistry have been published from this deposit. This paper contains new data on the mineralogy and mineral succession of the Chełmiec polymetallic deposit, providing precise chemical data on the sulphides, sulpharsenides, tetrahedrite group minerals and bismuth sulphosalts.

LOCALITY AND GEOLOGICAL SETTING

The research area is located in southwestern Poland, close to Chełmiec village. This area is located at the border of two large geological units: the Sudetes and the Fore-Sudetic Block (Kryza et al., 2004). It is associated with the Sudetic Marginal Fault which runs along the Świebodzice-Chełmiec-Złotoryja line and determines the geological structure of this area (Jerzmański, 1965). The Chełmiec area is situated in the Kaczawa Foothills and geologically belongs to the Paleozoic complex of the Kaczawa Mountains: the Chełmiec Unit (Fig. 1). This unit is limited by faults: the Myślinów Fault in the south, the Jerzmanicki Fault in the north, the Sudetic Marginal Fault in the north-east, and to the west by the edge of the Leszczyńska Basin (Baranowski, 1998; Baranowski et al., 1998). The Chełmiec Unit is composed of Ordovician quartz-sericite and sericite schists, Silurian quartz schists and quartzite, and volcanogenic rocks of Upper Silurian–Middle Devonian age (Wajsprych, 1974). The rocks of the entire region were metamorphozed during major folding in the Silurian, before the Late Devonian (Paulo, 1973). However, the Kaczawa Complex underwent the main phase of metamorphism, ranging from low grade to greenschist-facies metamorphism, during the Late Devonian and Early Carboniferous (Visean) (Mikulski, 2007). During the Carboniferous, the formation of a tectonic mélange took place and numerous hydrothermal veins developed. The younger rocks (Carboniferous to Lower Permian) are represented by platform intramontane fluvial and marine clastic deposits (Mikulski, 2007).

The hydrothermal polymetallic veins (siderite-sulphide and baryte) crosscutting the Chełmiec area, parallel to the fault direction, are filled mainly by siderite, quartz with minor sulphides (Paulo, 1973). The main host rocks are graphite schists. Ore mineralization is represented by pyrite and arsenopyrite with mi-
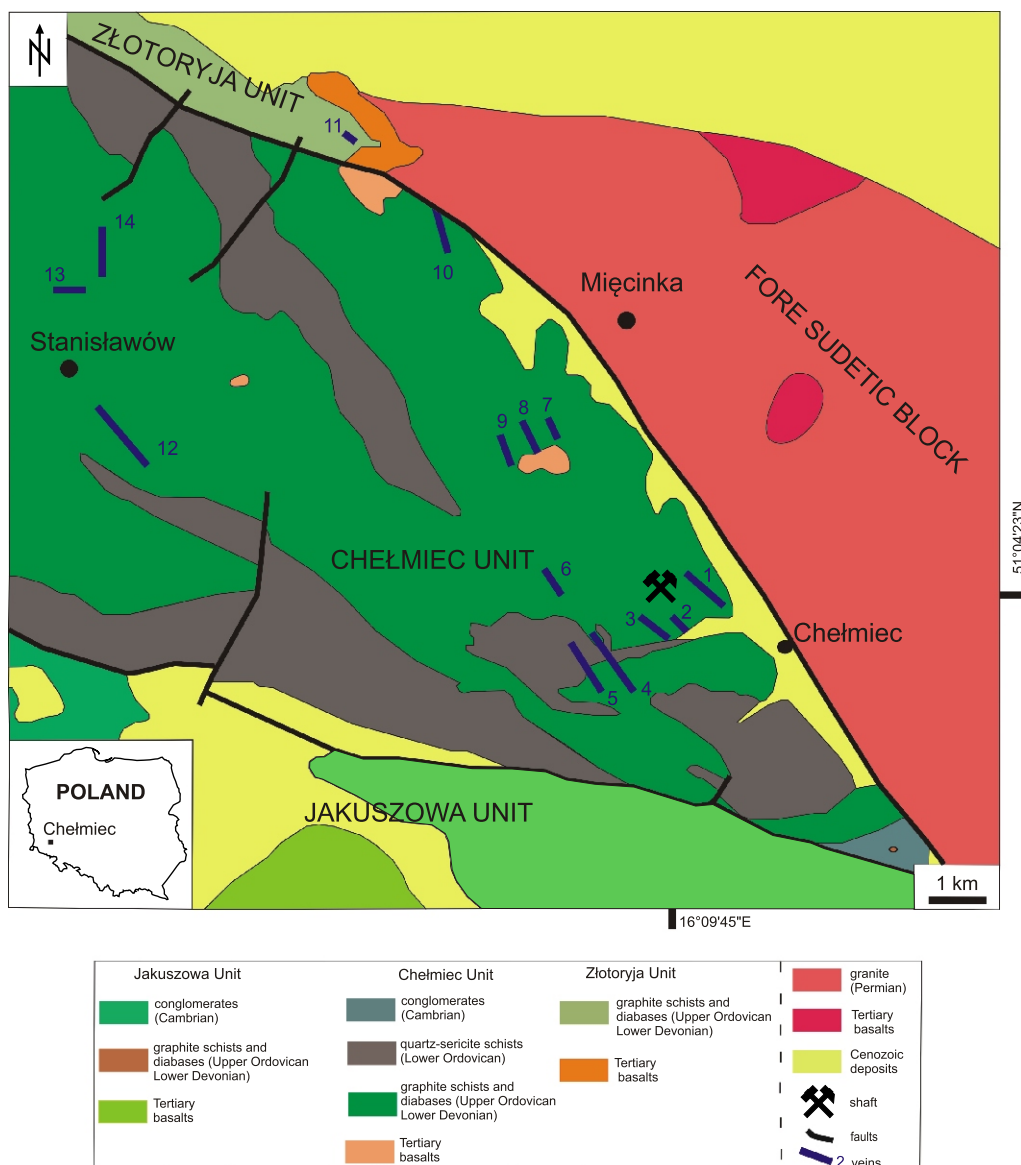

Fig. 1. Geological map of the Chełmiec area (modified from Paulo, 1973; Mikulski, 2007)

1 – Hauptgang vein; 2 – Hintermühlergang vein; 3 – Castle Mountain vein; 4 – Olejna vein; 5 – Kuźnica vein;
6, 7 – unnamed veins; 8 – Treues Freunderschaft vein; 9 – Dębowa vein; 10 – Jodłowa vein;
11, 12 – unnamed veins; 13 – Hauptgang, South vein; 14 – Krallager, North vein

nor Cu, Pb, Sb, Ni, Co, Bi, Ag sulphides, sulpharsenides and sulphosalts (Paulo, 1970a, 1973). The first stage of mineralization is commonly cataclased and that phenomenon is visible mainly in pyrite, Fe-Ni-Co sulpharsenides, sphalerite and chalcopyrite (Paulo, 1973). Four metallogenic events are distinguished in the area of Chełmiec; the first two were related to sedimentation processes and metamorphism, and the third and fourth events were most significant for the Cu-Ni-Co-Ag ore mineralization: Carboniferous to Permian (Variscan) and Triassic-Paleogene (post-Variscan) events. In the third metallogenic event carbonate sulphide veins, and in fourth quartz-gold-arsenopyrite and baryte-fluorite veins, were formed (Mikulski, 2007).

Fourteen hydrothermal veins are known in the Chełmiec unit (Mikulski, 2007; Fig. 1). The veins are from several hundred to ~1000 metres long and they are up to 4 m thick. The richest ore mineralization is connected with vein number 2 (Hintermühlergang) consisting of quartz, small amounts of siderite and ~30% of ore minerals including gersdorffite, sphalerite, galena, chalcopyrite, tetrahedrite, pyrite, bournonite, native bismuth, bismuthinite, arsenopyrite and marcasite (Paulo, 1970a, 1973).

MATERIALS AND METHODS

Samples containing ore mineralization were collected from an old dump of the vein number 2 – Hintermühlergang – located near Chełmiec village ~200 m from the forester's lodge, at GPS co-ordinates 51°04'23''N, 16°09'45''E (Fig. 1; Paulo, 1970a). Quartz and carbonate vein material with macroscopic sulphide mineralization may be found on the dumps. Various ore textures are observed at Chełmiec: massive, nested, breccia, and veinlets. Twenty-three samples were selected for microscopic observations in the reflected light, while ten representative samples were selected for microprobe studies.

Microprobe analyses were performed at the Laboratory of Critical Elements AGH - KGHM, WGGiOŚ, AGH Kraków, using a *JEOL Super Probe JXA-8230* microanalyzer. The analyses were performed using the WDS method under the following conditions: accelerating voltage 20 kV, beam current 20 nA and beam diameter 1 μm. The following wave lengths were used: AuM_α, SbL_α, BiM_α, CuK_α, NiK_α, FeK_α, SK_α, CoK_α, AsL_α (for sulpharsenides and pyrite), HgM_α, AgL_α, MnK_α, BiM_α, PbM_α, ZnK_α, FeK_α, CuK_α, SK_α, SbL_α, NiK_α, AsL_α (for tetrahedrite), AgL_α, BiM_α, CuK_α, FeK_α, SK_α, PbM_α, SbL_α, AsL_α (for Bi minerals, bournonite and galena) and AgL_α, CuK_α, CoK_α, SnL_α, MnK_α, FeK_α, ZnK_α, SK_α, CdL_α, InL_α, GeL_α, GaL_α, AsL_α (for sphalerite). Natural mineral standards (FeS$_2$, ZnS, PbS) and synthetic compounds (CdS, InAs, MnS, HgTe, PbTe, Sb$_2$S$_3$, Cu, Ag, Bi, Ni, Co, Se) were used for calibration. The detection limits for analysed elements were: for sulpharsenides and pyrite: Au – 0.1 wt.%, 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.%, for tetrahedrite: 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.%, Ni – 0.02 wt.%, As – 0.06 wt.%, for Bi minerals, bournonite and galena: 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.%, for sphalerite: Ag – 0.09 wt.%, Cu – 0.03 wt.%, Co – 0.02 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.%, In – 0.01 wt.%, Ge – 0.03 wt.%, Ga – 0.03 wt.%, As – 0.06 wt.%.

RESULTS

The ore mineralization mainly comprises massive aggregates of sphalerite and galena, with less common sulpharsenide masses. Two types of ore paragenesis were distinguished: (1) older quartz with Ni-Co±Bi mineralization and (2) younger quartz-siderite with Cu-Zn-Pb±Sb±Ag mineralization (Fig. 2). No samples were found within the material studied where these two parageneses occurred together or intersected. Their relationships in the paragenetic sequence were combined with study done by Paulo (1970a; Fig. 2). The first type of ore paragenesis (Ni-Co±Bi) is represented mainly by massive gersdorffite-cobaltite aggregates and arsenopyrite idiomorphic crystals. However, gersdorffite-cobaltite aggregates are characterized by the presence of inclusions of native bismuth, bismuthinite, pyrrhotite and matildite. The second type of ore paragenesis is represented by base metal sulphides (Cu-Zn-Pb±Sb±Ag) which occur as anhedral grains, irregular aggregates, or veinlets. All chemical analyses (for gersdorffite, cobaltite, bismuth minerals, matildite, tetrahedrite and sphalerite) are included in the Appendices 1–4.

PYRITE

There are two generations of pyrite in the samples studied. The first generation of pyrite occurs in the early stage of mineralization as small idiomorphic grains (up to 50 μm) and it overgrows arsenopyrite; the second represents the youngest phase, filling cracks in galena and forming veinlets up to 300 μm across. Each generation has low concentrations of Co, Ni, Cu and As, close to detection limits and not exceeding 0.1 wt.% (Appendix 1).
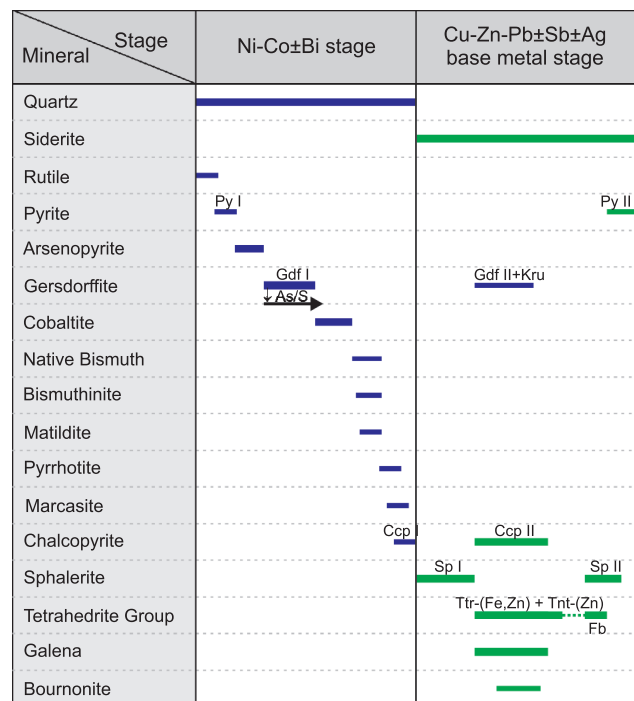

Fig. 2. Mineral succession of quartz-siderite and quartz ores from the Chełmiec Cu-Ni±Co±Ag±Bi mineralization based on the results of this study and Paulo (1970a)

ARSENOPYRITE

This mineral is not common and was found only in quartz-dominated samples. Excepting rutile and pyrite, arsenopyrite represents the oldest ore phase of the Ni-Co±Bi stage in the samples studied. It forms separate idiomorphic crystals a few mm in size (Fig. 3A) and usually occurs together with, and overgrows, pyrite. In places this mineral is overgrown by gersdorffite I. Arsenopyrite occasionally contains small amounts of Ni up to 0.57 wt.% (0.02 *apfu*) and Co up to 1.83 wt.% (0.03 *apfu*) without any zoning in BSE images (Appendix 1).

GERSDORFFITE-COBALTITE I

Sulpharsenides of the gersdorffite-cobaltite series are widespread in the samples studied from Chełmiec and occur in the first stage of ore mineralization. Usually, they form massive aggregates (>1 cm across) disseminated in quartz. In these massive sulpharsenide aggregates, cobaltite is rare and commonly occurs on the edges of these bodies, not forming single crystals (Fig. 3B–D). Although gersdorffite is more common, a compositional trend towards cobaltite As-rich gersdorffite was also observed (Fig. 3E, F) and this is associated with arsenopyrite, occurring on its edges (Fig. 3G, H). The textural relationships supported by the chemical composition as shown in the As *vs*. Fe/(Ni+Co+Fe) diagram (Fig. 4B) confirm that arsenopyrite was overgrown by gersdorffite or by As-rich gersdorffite. Inclusions and veinlets of younger native bismuth, bismuthinite (Figs. 3C, D and 5A, B) and pyrrhotite (Fig. 5A) are commonly in aggregates of minerals of the gersdorffite-cobaltite series. These massive aggregates are crosscut by younger chalcopyrite-marcasite veinlets. The content of Ni ranges from 0.22 to 0.97 *apfu* (Fig. 4C), of Co from 0.01 to 0.63 *apfu* and of Fe from 0.01 to 0.24 *apfu* (Appendix 1). In BSE images oscillatory zonation is clearly visible, brighter zones containing higher amounts of As than darker zones (Fig. 3E, F). Moreover, As↔S substitution was observed in the gersdorffite-cobaltite aggregates, the concentration of As in the first generation varies from 0.89 to 1.46 *apfu* and of S from 0.57 to 1.08 *apfu* (Fig. 5D). High As/S ratio is observed in the initial stage and is associated with high contents of Ni, then with increasing Co and Fe these ratios decrease to the stoichiometric value of 1. The general formula of gersdorffite I based on the sum of 1 cation may be written as: $(Ni_{0.43-0.97}Co_{0.01-0.42}Fe_{0.01-0.21})As_{0.98-1.46}S_{0.57-0.94}$. The general formula of cobaltite based on the sum of 1 cation is: $(Co_{0.42-0.63}Ni_{0.22-0.43}Fe_{0.09-0.24})As_{0.89-1.06}S_{0.90-1.08}$.

GERSDORFFITE II AND KRUTOVITE

The second generation of gersdorffite which occurs in the first stage of ore mineralization is represented by accumulations of individual crystals up to 250 μm across, embedded in galena and in bournonite-tetrahedrite veinlets. Gersdorffite II occurs as euhedral crystals showing oscillatory zonation and anhedral grains up to 100 μm in size (Fig. 5C, D). The content of Ni in gersdorffite II varies from 0.82 to 0.93 *apfu*, Co from 0.04 to 0.13 *apfu* and Fe from 0.01 to 0.11 *apfu* (Appendix 1). The gersdorffite II does not have as wide ranges of Ni as the sulpharsenides I; however, both generations contain similar range of As in the Ni-dominant member. In Ni-dominant sulpharsenides I and II similar trend of As is observed.

Two analyses belong to isotropic Ni-diarsenide – krutovite (As >1.50 *apfu*) (Figs. 4B and 5D) – and display the krutovite-gersdorffite solid solution. The krutovite from Chełmiec forms oscillatory zones in gersdorffite crystals (Fig. 4D). The formula of sulpharsenides II, based on the sum of 1 cation may be written as: $(Ni_{0.82-0.93}Fe_{0.01-0.11}Co_{0.04-0.13})As_{0.99-1.55}S_{0.44-0.89}$.

BISMUTH MINERALS

Bismuth minerals are associated with massive sulpharsenides I and occur in the first stage of ore mineralization. The most common Bi mineral is bismuthinite, while native bismuth and matildite are rare. They occur as fine, subhedral inclusions (up to 50 μm) in sulpharsenides I (Fig. 4A), in veinlets with marcasite and chalcopyrite crosscutting sulpharsenides I or as small crystals in quartz. Rarely they are replaced by pyrrhotite. Bismuthinite is chemically stoichiometric with a small degree of the aikinite type of substitution $Bi^{3+} + \square$ (vacancy) $\leftrightarrow Pb^{2+} + Cu^{+}$ (Topa et al., 2002); the value of n_{aik} is from 0.00 to 0.75. In bismuthinite the amount of Sb reaches up to 0.42 wt.% (0.07 *apfu)* and As to 0.39 wt.% (0.11 *apfu*), (Appendix 2). The empirical formula of bismuthinite based on 2 cations may be written: $Bi_{2.00}S_{2.97}$. The native bismuth is chemically homogeneous. Matildite is rare and only two separate crystals with no relationship with bismuthinite and native bismuth were found. The empirical formula of matildite based on 2 cations may be written: $Ag_{0.99}Bi_{1.00}S_{1.99}$ (Appendix 2).

SPHALERITE

Two generations of sphalerite were observed in the samples from Chełmiec; however, they occur in the second stage of ore mineralization. Older sphalerite I crystals and aggregates (up to cm size) show the presence of voids and cracks (Fig. 6A). It occurs as disseminated crystals or larger aggregates in quartz, less commonly in carbonate, in places being overgrown by chalcopyrite (Fig. 6B). Sphalerite II forms smaller crystals (up to 300 μm) and creates overgrowths with tetrahedrite and chalcopyrite, however, it is younger than these and does not contain any inclusions. Both generations of sphalerite differ mainly in their Fe content: sphalerite I contains from 0.04 to 0.22 wt.% (<0.01 *apfu*), and sphalerite II from 1.42 to 5.88 wt.% (0.02 to 0.06 *apfu*) of Fe. Both generations have significant contents of Cd – from 0.16 to 1.5 wt.% (up to 0.01 *apfu*), (Appendix 3). The general empirical formula (based on the sum of one cation) of sphalerite I is: $(Zn_{0.98-1.00}Cd_{0.00-0.01})_{\Sigma=0.99-1.00}S_{1.01-1.03}$ and sphalerite II: $(Zn_{0.87-0.95}Fe_{0.01-0.10}Cu_{0.01-0.05}Cd_{0.00-0.01})_{\Sigma=0.98-1.04}S_{1.01-1.05}$.

TETRAHEDRITE GROUP MINERALS

Tetrahedrite group minerals (TGM) occur in the second stage of ore mineralization in quartz-siderite veins and are common in the samples studied (Fig. 7A). Grains of these minerals vary in size, from 50 μm to 1 mm. They occur as grains or aggregates usually overgrown with chalcopyrite, older sphalerite I and younger sphalerite II or as veinlets with bournonite in galena (Fig. 6C–E). Two compositional sub-groups were distinguished: earlier Ag-poor TGM and later Ag-rich TGM. The Ag-poor TGM occurs less frequently with sphalerite II, which locally fills fractures in their crystals. Three minerals represent TGM (the tetrahedrite and tennantite series) in Chełmiec: tetrahedrite-(Zn), tetrahedrite-(Fe) (Fig. 6E–G) and rare tennantite-(Zn). Microprobe analyses show that tetrahedrite-(Zn) predominates over -(Fe), however,
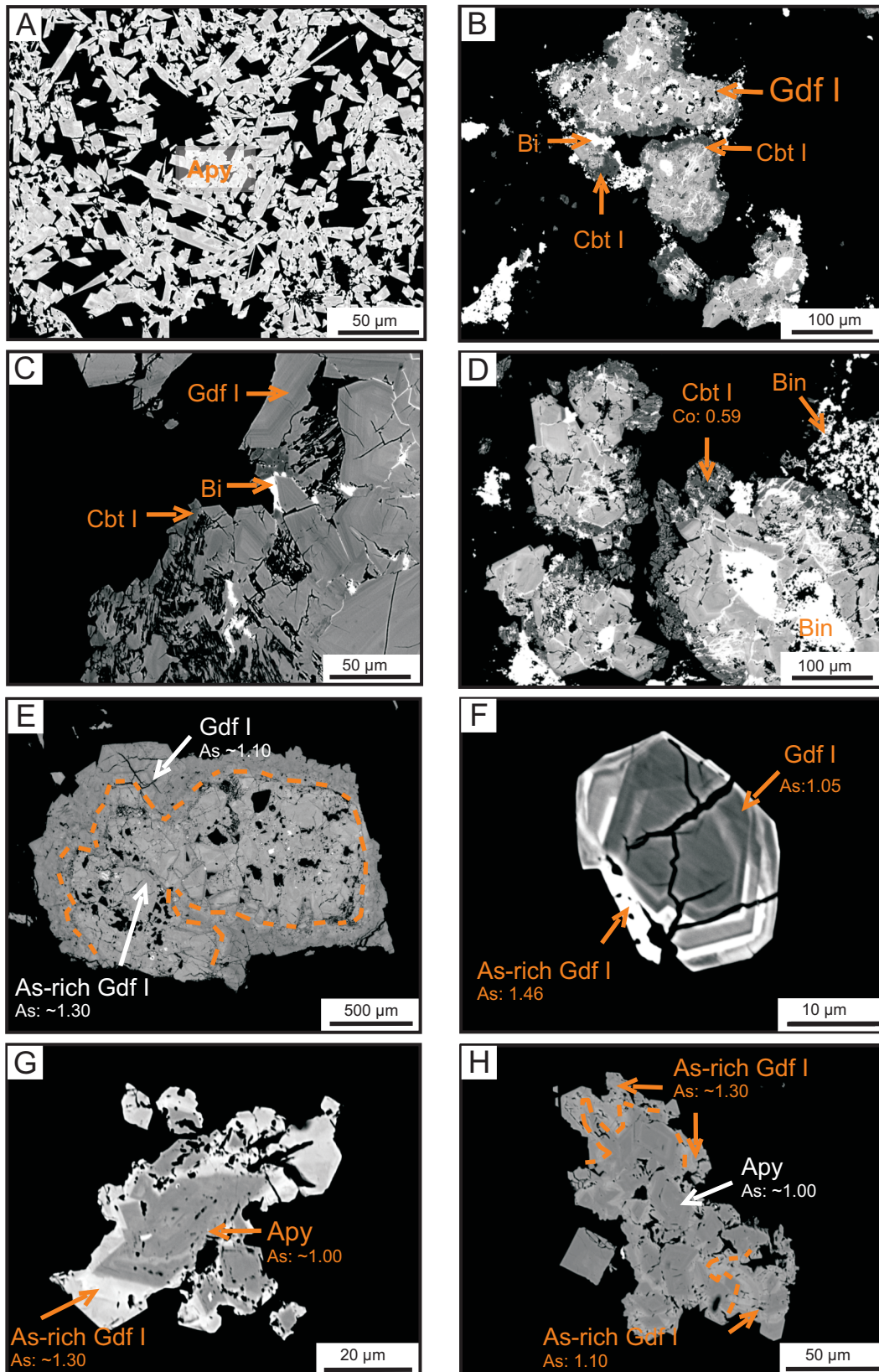
Fig. 3. Back-scattered electron images (A-H) illustrating the main features of the mineral assemblages

A – aggregates of idiomorphic arsenopyrite crystals; **B** – gersdorffite I overgrown by cobaltite I on edges with veinlets and droplets of native bismuth; **C** – gersdorffite I with cobaltite rims and native bismuth; **D** – aggregates of gersdorffite I with cobaltite rims and crystals of bismuthinite; **E** – gersdorffite I with As-rich gersdorffite I in core; **F** – gersdorffite I with As-rich gersdorffite I in outer growth zones; **G** – arsenopyrite overgrown by As-rich gersdorffite I; **H** – arsenopyrite overgrown by As-rich gersdorffite I. Apy – arsenopyrite; Bi – native bismuth; Bin – bismuthinite; Cbt I – cobaltite I; Gdf I – gersdorffite I; values of individual elements in *apfu*
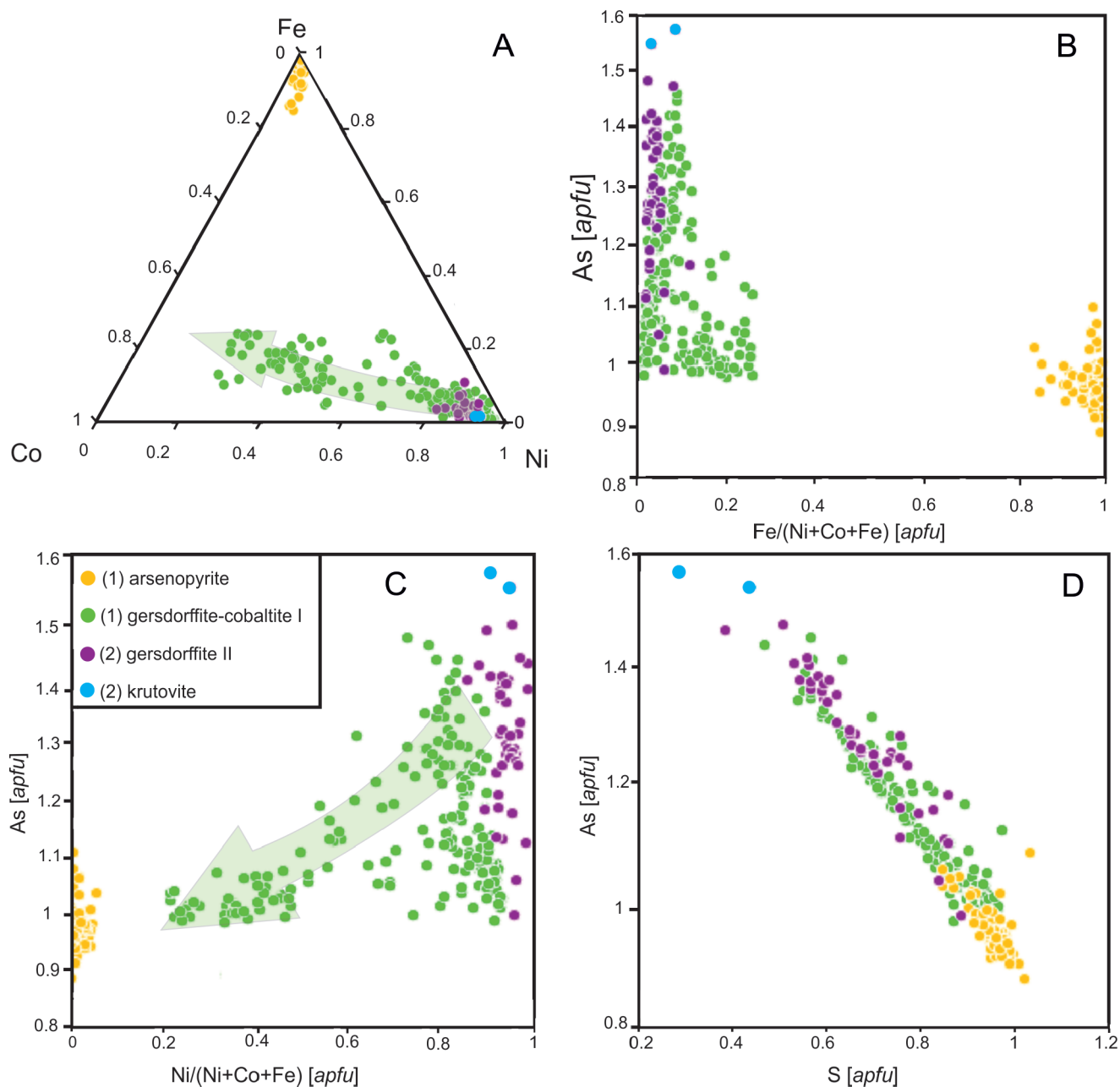
Fig. 4. Compositional relationships in the sulpharsenides from Chełmiec

A – diagram of Ni-Co-Fe substitution in the sulpharsenides (in *apfu*); **B** – diagram of As *vs.* Fe/(Ni+Co+Fe);
C – diagram of As *vs.* Ni/(Ni+Co+Fe); **D** – diagram of As *vs.* S in the sulpharsenides

EPM analyses indicate a wide range of Zn↔Fe substitution (Fig. 7B). This group is also characterized by the presence of Ag which reaches up to 13.13 wt.% (2.07 *apfu*). Arsenic content varies from 0.06 wt.% (0.01 *apfu*) to 9.79 wt.% (2.52 *apfu*) (Appendix 4). Tennantite-(Zn) is rare and occurs as zones in tetrahedrite-(Zn) crystals. The empirical formula of Ag-poor TGM based on 16 cations for tetrahedrite-(Zn) is $(Cu_{7.98-10.11}Ag_{0.07-2.07}Zn_{1.05-1.95}Fe_{0.11-0.99})_{\Sigma=12.09-12.26}(Sb_{1.89-4.14}As_{0.04-2.04})_{\Sigma=3.93-4.18}S_{12.68-13.39}$ and for tetrahedrite-(Fe) is $(Cu_{7.42-9.73}Ag_{0.23-2.03}Zn_{0.44-1.00}Fe_{1.01-2.18})_{\Sigma=11.97-12.08}(Sb_{3.56-4.01}As_{0.02-0.42})_{\Sigma=3.98-4.03}S_{12.35-13.20}$ (Appendix 4).

Younger than the previous Ag-poor TGM group are the Ag-rich TGM. These are represented by argentotetrahedrite-(Fe) and form rims on Ag-poor TGM aggregates. Argentotetrahedrite-(Fe) forms brighter zones than older Ag-poor TGM (Fig. 6H). According to the classification of the tetrahedrite group (Biagioni et al., 2020) the parts of the tetrahedrite group with amounts of Ag exceeding 3.00 *apfu* are classified as members of the freibergite series. Argentotetrahedrite-(Fe) is very rare in the samples studied and occurs as fine grains with sphalerite II and older chalcopyrite. Argentotetrahedrite-(Fe) is characterized by a predominance of Fe from 5.76 to 5.95 wt.% (from 1.84 to 1.94 *apfu*) over Zn from 0.57 to 1.33 wt.% (from 0.16 to 0.36
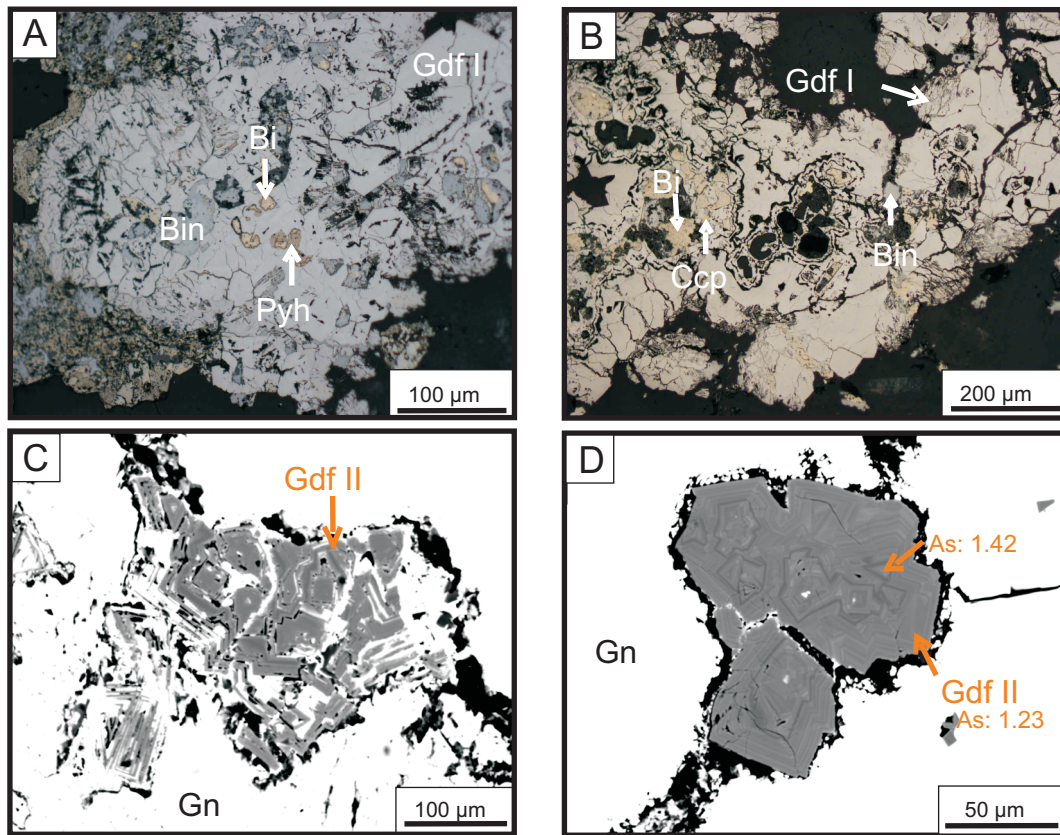
Fig. 5. Reflected-light (A, B) and BSE images (C, D) illustrating the main features of the mineral assemblages

A – massive gersdorffite I with inclusions of native bismuth, bismuthinite and pyrrhotite in a quartz vein; **B** – massive gersdorffite I with chalcopyrite, native bismuth, and bismuthinite aggregate in a quartz vein; **C** – zoned crystals of gersdorffite II in galena; **D** – zoned gersdorffite II in galena; Bi – native bismuth; Bin – bismuthinite; Ccp – chalcopyrite; Gdf – gersdorffite; Gn – galena; Pyh – pyrrhotite; values of individual elements in *apfu*

apfu) (Fig. 7D) and high contents of Ag ranging from 26.47 to 29.21 wt.% (from 4.37 to 4.90 *apfu*) (Fig. 7A, E). The amount of Sb reaches 26.46 wt.% (3.92 *apfu*) while the amount of As reaches only 0.18 wt.% (0.04 *apfu*) (Appendix 4). The empirical formula of freibergite series based on 16 cations is $(Cu_{5.05–5.50}Ag_{4.37–4.90}Zn_{0.16–0.36}Fe_{1.84–1.94})_{\Sigma=12.05–12.07}(Sb_{3.89–3.92}As_{0.02–0.04})_{\Sigma=3.93–3.94}S_{12.27–12.39}$.

GALENA

Galena is the main ore mineral in the samples studied from Chełmiec and occurs in the second stage of ore mineralization. Galena usually forms coarse-grained aggregates up to 3 mm across in siderite or quartz and fills cracks in quartz with signs of plastic deformation of the galena. Additionally, it forms small remnants or grains in the sphalerite-tetrahedrite-chalcopyrite aggregates, which are older than this TGM (galena is corroded by these phases). In places, TGM-bournonite veinlets associated with sphalerite I, tiny gersdorffite II crystals, bournonite (Fig. 6C) and pyrite are embedded in galena. It is commonly replaced by secondary minerals: covellite and cerussite. Galena is close to the theoretical chemical composition and has a very low content of trace elements (max. 0.01 wt.% of Ag, 0.05 wt.% of Cu and 0.18 wt.% of Sb) (Appendix 2).

BOURNONITE

Bournonite is rare and occurs in the second stage of ore mineralization in paragenesis with older Ag-poor TGM-(Zn) and -(Fe) and sphalerite I. It fills fissures and cracks inside galena (Fig. 6C) locally in association with Ag-poor TGM-(Zn). Bournonite veinlets with Ag-poor TGM reach up to a few mm thick. The EPM analyses confirm that bournonite is stoichiometric without any significant substitutions. The formula of bournonite based on 3 cations is close to: $Cu_{1.01–1.04}Pb_{0.97–0.99}Sb_{0.97–0.99}S_{2.97–2.99}$ (Appendix 2).

DISCUSSION

Ni-Co ASSOCIATION

Nickel-cobalt associations related to hydrothermal veins are not common in the Sudetes Mountains of Poland. At Chełmiec, Ni-Co minerals are represented mainly by sulpharsenides, namely by massive gersdorffite-cobaltite aggregates, less so by finely zoned gersdorffite crystals; however, this is only accessory mineralization. So far, apart from Chełmiec, the occurrence of massive Ni-Co mineralization is known only from the
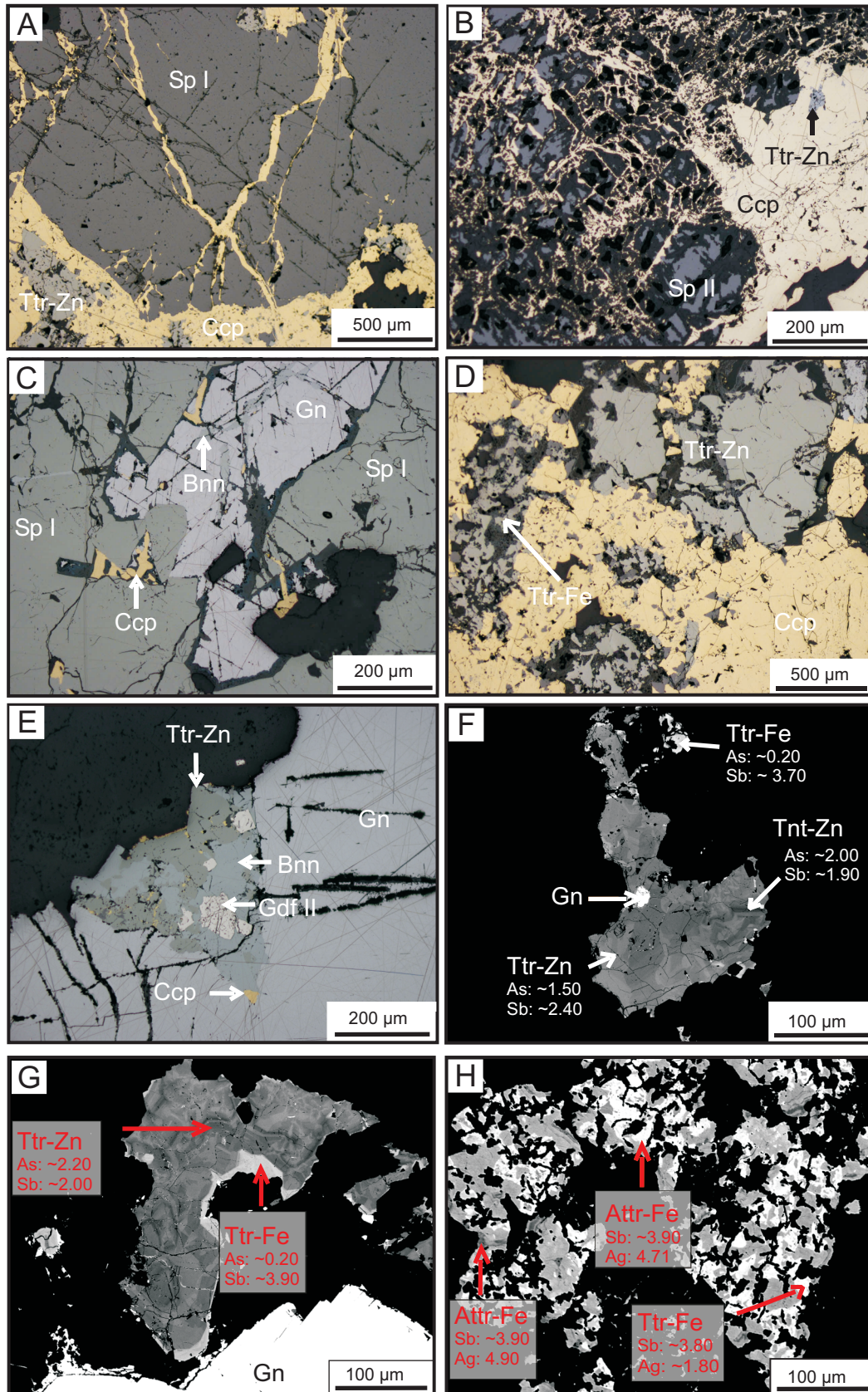
Fig. 6. Reflected-light (A–E) and BSE images (F–H) illustrating the main features of the mineral assemblages

A – sphalerite I crosscut by chalcopyrite – tetrahedrite-(Zn) veinlets; **B** – sphalerite II and older chalcopyrite with tetrahedrite-(Zn); **C** – aggregate of sphalerite I with chalcopyrite and galena crosscut by bournonite veinlet; **D** – crystals of tetrahedrite-(Zn) I with chalcopyrite and fine-grained tetrahedrite-(Fe); **E** – galena replaced by tetrahedrite-(Zn) -bournonite-chalcopyrite with crystals of gersdorffite II; **F** – tetrahedrite-(Zn) and - (Fe) with galena inclusion in quartz vein; **G** – grain of tetrahedrite-(Zn) I with thin rim of tetrahedrite-(Fe) with galena; **H** – aggregates of tetrahedrite-(Fe) replaced by argentotetrahedrite-(Fe). Attr-(Fe) – argentotetrahedrite-(Fe); Bnn – bournonite; Ccp – chalcopyrite; Gn galena; Gdf II – gersdorffite II; Sph I – sphalerite I; Tnt-(Zn) – tennantite-(Zn); Ttr-(Fe) – tetrahedrite-(Fe); Ttr-(Zn) – tetrahedrite-(Zn); values of individual elements in *apfu*
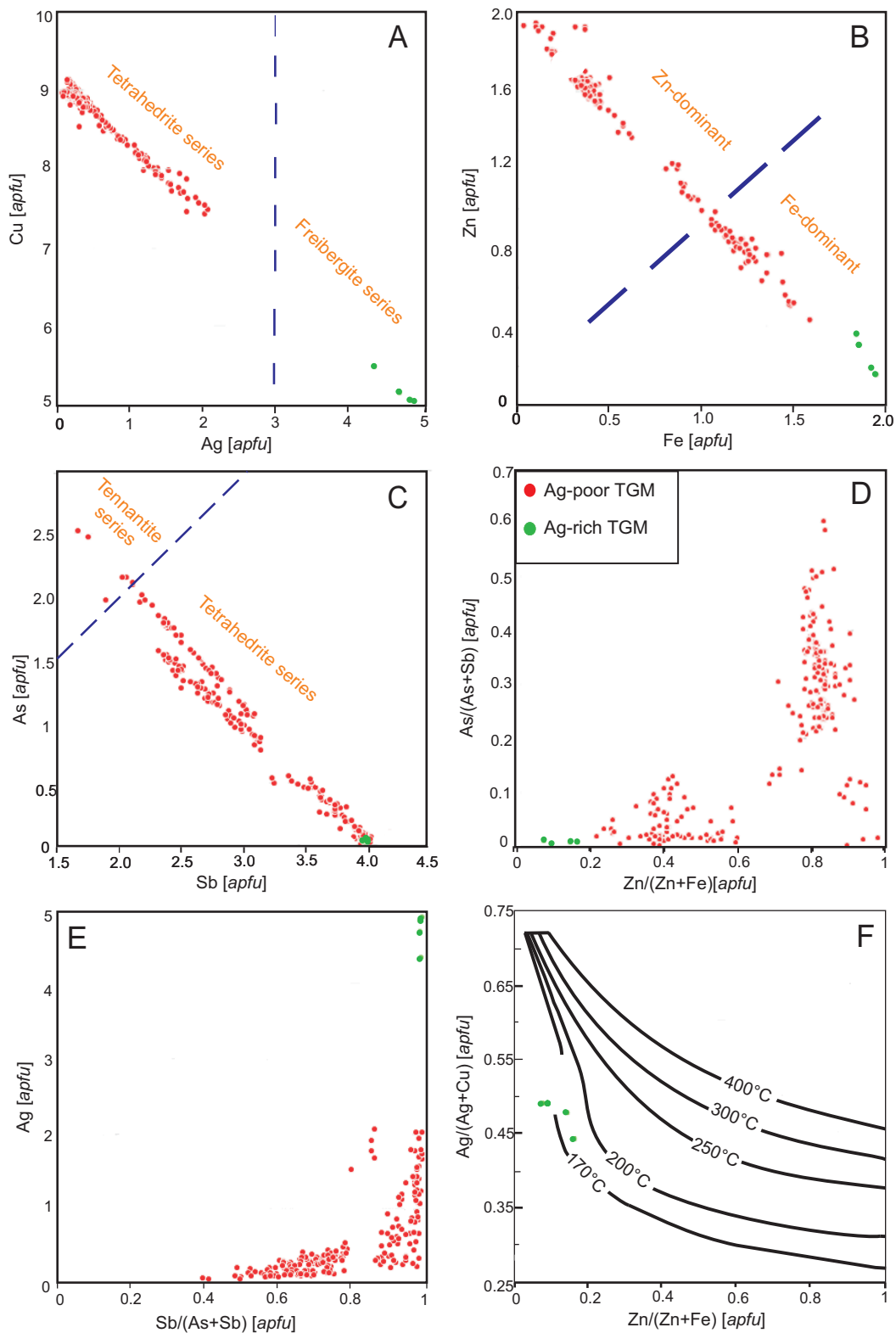
Fig. 7. Compositional relationships in the tetrahedrite group minerals from Chełmiec

A – diagram of Ag *vs.* Cu substitution; **B** – diagram of Zn *vs.* Fe substitution; **C** – diagram of Sb *vs.* As substitution; **D** – diagram of As/(As+Sb) *vs.* Zn/(Zn+Fe); **E** – diagram of Ag *vs.* Sb/(Sb+As); **F** – diagram of Ag/(Ag+Cu) *vs.* Zn/(Zn+Fe) (after Sack et al., 2005)

Dziećmorowice deposit in the Sowie Mountains, where it is represented by safflorite, rammelsbergite, löllingite, cobaltite, gersdorffite and Ni-skutterudite (Muszer et al., 2006; Kozioł, 2018; Pršek et al., 2021). In addition, in this deposit the presence of

base metal mineralization, Ag-rich minerals, and Bi assemblages is reported (Muszer et al., 2006). However, due to the higher activity of As, sulpharsenide (gersdorffite-cobaltite series) in the Dziećmorowice is less common than di- and tri-ar-

senides (Pršek et al., 2021). Similarly to Chełmiec, As-rich gersdorffite with up to 1.3 *apfu* of As also occurs in Dziećmoro-wice. The presence of sulpharsenides enriched in arsenic at the end of the paragenetic sequence in Dziećmorowice may indicate the replacement of di- and tri-arsenides by gersdorffite--cobaltite associations (Pršek et al., 2021). A similar trend was observed at Chełmiec, where As enrichment is observed at the beginning of participation of Ni-Co minerals.

Accessory Ni-Co mineralization in the form of small, disseminated sulpharsenide crystals in polymetallic ores has been found at many hydrothermal localities in the Sudetes Mountains: Przecznica polymetallic deposit (Piestrzyński et al., 1992), the Krobica-Gierczyn area (Pietrzela, 2019), the Ciechanowice polymetallic vein-type deposit (Mochnacka et al., 2012) and the Boguszów baryte-vein-type deposit (Mederski et al., 2020). In most cases, their presence in polymetallic ores is the result of leaching by hydrothermal fluids of mafic and ultramafic bedrock, or the surrounding rocks (e.g., Mederski et al., 2020). Sulpharsenides in the Przecznica polymetallic deposit are represented by cobaltite, gersdorffite, arsenopyrite and glaucodot (Piestrzyński et al., 1992; Pietrzela, 2019). Mineralization in the Przecznica area forms nests and irregular structures. Sulpharsenides occur together with pyrite, pyrrhotite, native Bi and löllingite. Similarly to Chełmiec, cobaltite, arsenopyrite, and pyrite were characterized as the oldest phases in the Przecznica deposit. In the Krobica-Gierczyn area, cobaltite, glaucodot and arsenopyrite occur. Cobaltite is enriched in Ni and Fe, glaucodot in Ni. Arsenopyrite from this deposit contains intergrowths with löllingite and admixtures of Co and Sb (Pietrzela, 2019). At Ciechanowice, polymetallic vein-type deposit cobaltite is the main Ni-Co phase; however, intermediate members of the gersdorffite-cobaltite series and arsenopyrite were also found (Mochnacka et al., 2012). In contrast to Chełmiec, cobaltite from Ciechanowice occurs as idiomorphic inclusions in chalcopyrite. It is also associated with pyrite, native bismuth, and chalcocite. Cobaltite locally forms spheroidal aggregates with gersdorffite. These are relics after replacing the previous associations and do not create significant accumulations (Mochnacka et al., 2012). In the Boguszów baryte vein-type deposit, Co-enriched gersdorffite and löllingite were described by Mederski et al. (2020). Gersdorffite forms rims around löllingite crystals in the sulphide aggregates. However, nickel-cobalt associations have also been reported in the Klecza-Radomice area, and are represented by gersdorffite, cobaltite and Co-rich arsenopyrite (Mikulski, 2007).

Sulpharsenides are also found at two other localities in the Czech Republic: the Jáchymov and Zálesí hydrothermal vein U-deposits (Ondruš et al., 2003; Fojt et al., 2005). In the Zálesí deposit, sulpharsenides are represented by cobaltite, Ni-cobaltite, arsenopyrite and glaucodote; however, these are rare. Nickel, cobalt, and iron arsenides including mono-, di- and tri-arsenides are more common (Fojt et al., 2005). In contrast to the Chełmiec deposit where cobaltite with a high content of Ni and Fe predominates, at Zálesí there occurs low Ni-Fe cobaltite. In the Jáchymov deposit, sulpharsenides are represented by gersdorffite, arsenopyrite and alloclasite and occur in quartz veins. Moreover, the Jáchymov deposit also contains arsenides, mainly di- and tri-arsenides: safflorite, rammelsbergite, löllingite, skutterudite and Ni-skutterudite (Ondruš et al., 2003). The arsenopyrites from the Chełmiec, Zálesí and Jáchymov deposits are usually chemically pure with small amounts of Ni-Co. Comparison of mineralogical data for sulpharsenides from Chełmiec, Zálesí, Jáchymov Boguszów, Ciechanowice, Przecznica and Krobica-Gierczyn is shown in a triangular diagram (Fig. 8).

Another deposit that, similarly to the first stage of Chełmiec Ni-Co mineralization, is hosted by siderite veins is Dobšiná in Slovakia (Kiefer et al., 2017) where the Ni-Co assemblages in siderite-sulphide veins are represented mainly by sulpharsenides, less arsenides and tri-arsenides. However, typical trends from arsenides to sulpharsenides and from Ni to Fe members are present (Chovan and Ozdín, 2003; Kiefer et al., 2017). Younger sulphide mineralization at Dobšiná is represented mainly by tetrahedrite and chalcopyrite, with fewer bismuth minerals. A similar sequence is observed in the first stage of Chełmiec mineralization, where Ni-Co sulpharsenides are older than the copper-bismuth paragenesis and base metal paragenesis. However, the second stage of Chełmiec base-metal mineralization practically does not occur in the Dobšiná deposit.

The characteristic feature of gersdorffite II from Chełmiec is its zonation, visible in BSE images. Oscillatory zonation in sulpharsenides is known from many hydrothermal deposits worldwide (Fanlo et al., 2004; 2006; Kiefer et al., 2017; Mauro et al., 2021; Mederski et al., 2021). The zonation is usually caused by As↔S substitution which may be combined with variable chemistry at the Ni-Co-Fe cationic position, which may be related to microenvironments and spatially restricted influx of the reducing agents responsible for the mineralization (Scharrer et al., 2019). Observations of the BSE images and comparison with the chemistry of the individual zones indicate that the oscillatory zonation present in sulpharsenides from Chełmiec is related not to substitutions at the cationic position, but to As↔S substitution. However, As↔S substitution correlates directly with Ni content, and more specifically, to the initial, stable stages of sulpharsenide crystallization, when Ni-dominant member – gersdorffite – was formed (Fig. 4B, D). This situation is observed within both generations of gersdorffite, so it is presumed that they are associated with the remobilization process, though from different parts of the veins (Fig. 2). Unfortunately, as mentioned earlier, no samples were found where the two parageneses intersected or occurred together. In addition, the presence of a wide range of As↔S substitution in the gersdorffite is due to the non-stoichiometric nature of the Ni-dominant sulpharsenide with higher arsenic content, as well as its wider stability field in the hydrothermal environment (Scharrer et al., 2019). Consequently, in addition to high As contents in many initial sulpharsenide-gersdorffites from Chełmiec, a few analyses fall within krutovite fields with high As contents (up to 1.55 *apfu*).

The origin and source of the hydrothermal vein mineralization at Chełmiec is not fully known. According to Paulo (1973) the quartz and quartz-siderite veins are post-orogenic, and the mineralization was formed after metamorphism of the surrounding rocks. This is indicated by the lack of major dynamic deformation of the veins, which are often found in the host rocks (Paulo, 1973). Metal provenance may be related to younger tectonic processes and leaching of Ni and Co from diabase occurring in this area (Wajsprych, 1974) and from mafic and ultramafic rocks lying deeper. The formation of Ni-Co mineralization is related to the reduction of Ni- and Co-bearing fluids by e.g., methane, graphite, organic matter or siderite (Markl et al., 2016; Burisch et al., 2017; Scharrer et al., 2019). In the Chełmiec deposit, graphite schists are the main host rocks, and graphite may act as a reducing agent. Undoubtedly, the origin of Ni-Co ores at Chełmiec is related to hydrothermal fluids with high sulphur activity, and thus they are not dominated by di- or tri-arsenide ores as in many other hydrothermal Ni-Co deposits (Scharrer et al., 2019).
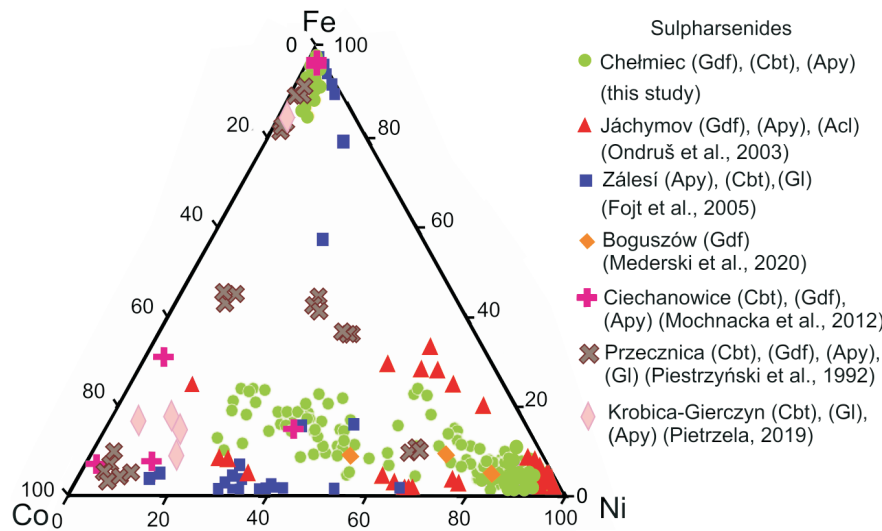
Fig. 8. The Ni-Co-Fe ratio (*apfu*) in sulpharsenides from Chełmiec, Jáchymov, Zálesí, Boguszów, Ciechanowice, Przecznica and the Krobica-Gierczyn deposit

Gdf – gersdorffite, Cbt – cobaltite, Apy – arsenopyrite, Gl – glaucodot, Acl – alloclasite

TETRAHEDRITE GROUP MINERALS

Tetrahedrite group minerals are widespread in many different genetic types of hydrothermal mineralization in the Sudetes Mountains (Paulo and Salamon, 1974a, b; Mochnacka et al., 2012; Siuda, 2012). Among them, silver-rich TGM including members of the tetrahedrite and freibergite series are typical of precious and base metal hydrothermal mineralization, are commonly associated with Ag-Sb sulphosalts, and occur in the Rędziny polymetallic deposit (Gołębiowska et al., 2012), Przecznica and Gierczyn polymetallic deposits (Piestrzyński and Mochnacka, 2003), Grudno quartz-sulphide-vein-type deposit (Paulo and Salamon, 1974a), Dziećmorowice-Stary Julianów hydrothermal polymetallic-baryte-quartz-calcite vein deposit (Petrascheck, 1933), Bystrzyca Górna baryte-quartz-vein deposit (Pršek et al., 2019), and Boguszów baryte-vein-type deposit (Mederski et al., 2020). These deposits have different mineralogies, this depending on the composition of th hydrothermal solution as well as on mineral paragenesis and temperature of crystallization. Using the graph drawn by Sack et al. (2005), the crystallization temperature of argentotetrahedrite-(Fe) was determined in the Chełmiec deposit (Fig. 7F) at 170–200°C. However, values of Ag/(Ag+Cu) ratio for all tetrahedrite group minerals are too low to show them on this graph (below 0.25 *apfu*). In contrast to Chełmiec, Ag-rich tetrahedrites from Rędziny occur mostly in galena in the form of small inclusions and crystallized at higher temperatures of ~250–~320°C (Gołębiowska et al., 2012). In addition, members of the freibergite series were also distinguished, occurring within pyrrhotite and Fe-rich sphalerite (Gołębiowska et al., 2012). Moreover, the Rędziny deposit contains more diverse silver and bismuth associations than does Chełmiec, including berryite, gustavite, cosalite and wittichenite (Gołębiowska et al., 2012). On the other hand, the TGM from Bystrzyca Górna show many similarities to the TGM from Chełmiec. In both deposits higher amounts of Ag were reported on rims of TGM grains (belonging to the freibergite series field) while cores have lower contents of Ag (Pršek et al., 2019). According to Pršek et al. (2019) the for-

mer Ag-bearing tetrahedrite was corroded by silver-rich fluids of younger paragenesis which led to the replacement of tetrahedrite by members of the freibergite series. However, members of the freibergite series which occur as elongated and fine inclusions in galena are characteristic of the Boguszów baryte deposit (Mederski et al., 2020). The Ag-richest argentotetrahedrite-(Fe) overgrows pyrargyrite and reaches up 5.78 *apfu* of Ag while zoned Ag-rich TGM form irregular aggregates up to 0.5 mm across. At both Boguszów and Chełmiec the textural features of ores indicate an increase in the share of Ag-phases during younger stages of crystallization. However, in contrast to Chełmiec, at Boguszów Hg-rich tetrahedrite was observed. Another difference between these deposits is the As-content of tetrahedrite group minerals, because at Chełmiec the amount of As reaches 2.52 *apfu* while at Boguszów it is 1.74 *apfu* only (Mederski et al., 2020). By contrast, members of the freibergite series from both localities are As-poor.

CONCLUSIONS

1. Two stages of mineralization are described in the Chełmiec hydrothermal carbonate-sulphide deposit: Ni-Co±Bi which occurs in quartz ores and Cu-Zn-Pb±Sb±Ag which is related to quartz-siderite ores.

2. At Chełmiec two generations of gersdorffite were distinguished: massive gersdorffite-cobaltite I aggregates and oscillatory zoned gersdorffites II. This chemical zoning is related to As↔S substitution.

3. The presence of krutovite indicates the higher activity of arsenic in the initial stages of sulpharsenide crystallization and a decrease in the activity of As in later stages, in which only gersdorffite precipitated.

4. Tetrahedrite group minerals are common in the Chełmiec deposit. The EPM analyses show a wide range of Zn↔Fe substitution.

5. Silver in the Chełmiec deposit occurs mainly in tetrahedrite group minerals, especially in members of the freibergite

series: [argentotetrahedrite-(Fe) and tetrahedrite-(Fe)], less in matildite. Higher amounts of silver occur in outer zones of tetrahedrite crystals.

6. According to the graph proposed by Sack et al. (2005), the crystallization temperature of argentotetrahedrite-(Fe) in Chełmiec was 170–200°C.

7. The Chełmiec deposit is the second location in the Sudetes, apart from Dziećmorowice, where the presence of massive Ni-Co sulpharsenides was confirmed. The other localities show only accessory and disseminated-type mineralization.

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