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Original paper

Ore mineralization in the Miedzianka area (Karkonosze-Izera Massif, the Sudetes, Poland): new information

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Abstract. The Miedzianka mining district has been known for ages as a site of polymetallic ore deposits with copper and, later, uranium as the main commodities. Although recently uneconomic and hardly accessible, the Miedzianka ores attract Earth scientists due to the interesting and still controversial details of their ore structure, mineralogy and origin. Our examination of the ore mineralization from the Miedzianka district was based exclusively on samples collected from old mining dumps located in the vicinity of Miedzianka and Ciechanowice, and on samples from the only available outcrop in Przybkowice. In samples from the Miedzianka field, chalcopyrite, pyrite, galena, bornite, chalcocite, digenite, arsenopyrite, magnetite, sphalerite, tetrahedrite-tennantite, bornite, hematite, martite, pyrrhotite, ilmenite, cassiterite and covellite are hosted in quartz-mica schists and in coarse-grained quartz with chlorite. In the Ciechanowice field, the ore mineralization occurs mainly in strongly chloritized amphibolites occasionally intergrown with quartz and, rarely, with carbonates. Other host-rocks are quartz-chlorite schist and quartzites. Microscopic examination revealed the presence of chalcopyrite, pyrite, sphalerite, galena, tetrahedrite-tennantite, bismuthinite, native Bi, arsenopyrite, löllingite, cassiterite, cobaltite, gersdorffite, chalcocite, cassiterite, bornite, covellite, marcasite and pyrrhotite. Moreover, mawsonite and wittichenite were identified for the first time in the district. In barite veins cross-cutting the greenstones and greenschists in Przybkowice, we found previously-known chalcopyrite, chalcocite and galena. The composition of the hydrothermal fluids is

suggested to evolved through a series of consecutive systems characterized, in turn, by Ti-Fe-Sn, Fe-As-S, Fe-Co-As-S, Cu-Zn-S and, finally, Cu-Pb-Sb-As-Bi compositions.

Key-words: Miedzianka, Ciechanowice, Przybkowice, Karkonosze-Izera Massif, ore deposits, mineral succession, geothermometry

1. Introduction

The hydrothermal, vein-type copper-uranium-polymetallic ore deposit of the Miedzianka district is located in the eastern part of the Karkonosze-Izera Massif (KIM), close to the Intra-Sudetic Fault (Fig.1; Mazur, Aleksandrowski 2001). The bulk of ore mineralization is located near the contact of the Czarnów Schist Formation (Teisseyre 1973) with the Karkonosze granite, but some underground workings in the easternmost part of the mining district were cut in rocks of the Leszczyniec Unit (Mazur, Aleksandrowski 2001).

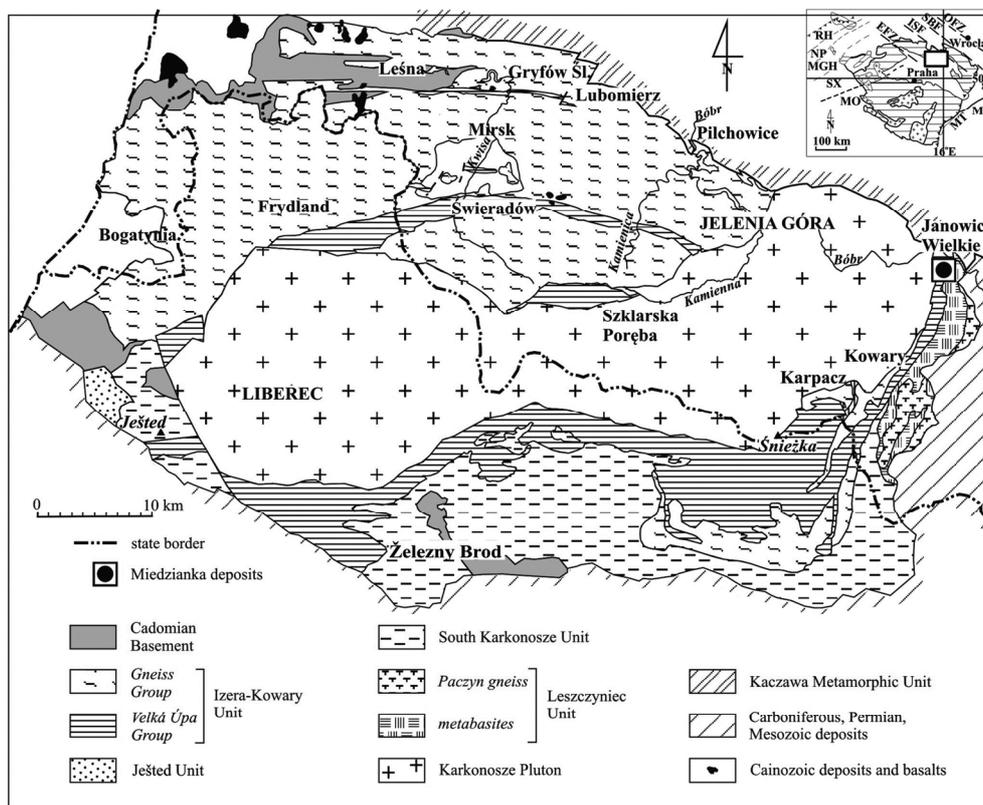


Fig. 1. Geological sketch map of the Karkonosze-Izera Massif (KIM; compiled from Chaloupsky 1989, Mazur 1995, Mazur, Aleksandrowski 2001, Oberc-Dziedzic 2003). Insert map: EFZ – Elbe Fault Zone, ISF – Intra-Sudetic Fault, MGH – Mid-German High, MO – Moldanubian Zone, MS – Moravo-Silesian Zone, NP – Northern Phyllite Zone, OFZ – Odra Fault Zone, RH – Rhenohercynian Zone, SBF – Sudetic Boundary Fault, SX – Saxothuringian Zone, TB – Teplá-Barrandian Zone. Insert shows the position of the KIM in the Bohemian Massif.

The mining operations, dating back to the beginning of the XIIth century (Dziekoński 1972), started in various parts of the district between Miedzianka and Ciechanowice. According to Berg (1938 and older references therein), there were four mining fields in operation, namely, the western field close to the Karkonosze granite and the central field (both named collectively as the Miedzianka field), the eastern field in Ciechanowice and the northern field located north of the Bóbr River. The latter field can be identified with the so-called “Lead Mountains” (Góry Ołowiane) which are a part of the Kaczawa Metamorphic Complex. Mineralization encountered in Przybkowice, close to the Ciechanowice mine, belongs spatially to the eastern field (Wojciechowski, Wolkowicz 1985), though the character of this mineralization resembles that of the northern field *sensu* Berg (1913). The copper, arsenic, lead, zinc, silver, gold and uranium ores were intermittently worked at several small mines (see Dziekoński 1972) with varying success until 1955 when all mines were finally closed and flooded (Zimnoch 1978). Numerous old mine dumps and several old adits still exist in the area. Some of the latter are preserved in excellent condition.

The geology of the Miedzianka district was described in detail by Websky (1853) and Krusch (1901), Berg (1913, 1938), Petrascheck (1933a, b), Schneiderhöhn (1941) and others. After World War II, new data on ore minerals from Miedzianka were published by Zimnoch (1967, 1978). The uranium mineralization was described in detail by Kaczmarek (1959), unfortunately, only in an unpublished industrial report.

According to Websky (1853), there were three “vein formations” in the Miedzianka district individually characterized by copper, lead and barite. In some cases, the barite veins, being the youngest, showed cross-cutting contacts with the older veins. In the copper vein formation, Websky (1853) identified four vein systems of different strikes, all younger than the Karkonosze granite.

Krusch (1901) found two types of ores: (i) contact-metasomatic, lensoidal oxide-sulphide body, including the bornite-dominated “blue deposit” and (ii) hydrothermal veins. The latter include the older, hornblende-chlorite-fluorite veins post-dating the metasomatic bodies, but pre-dating porphyry dykes and the younger, quartz-copper sulphide veins contemporaneous with the Intra-Sudetic Fault. The relationship of the hydrothermal ore veins to the Intra-Sudetic Fault was mentioned also by Berg (1913).

Petrascheck (1933a) described the magnetite deposit with associated pyrite and Cu, Zn, As, and Fe sulphides. He also observed zonal magnetite crystals which he regarded as proof of contact-metasomatic origin of the ore. Moreover, he related Cu and Ba veins to extrusive volcanism younger than the Karkonosze granite intrusion.

Schneiderhöhn (1941) described in detail the ores from the western and eastern fields. In the eastern field, he distinguished three generations of ore and gangue minerals, the first originating from metamorphic processes, and the later two related to hydrothermal ore formation. In the western field, he described, after Krusch (1901), the concordant, contact-metasomatic deposit and the high-temperature, hydrothermal vein-type deposit. He also compiled an instructive geological map of the deposit area.

In the Miedzianka district, the diversified ore-mineral assemblage was found and described, mostly in the XIXth century, by several German authors (e.g. Websky 1851, 1853, 1886, Fiedler 1863, Roth 1867, Traube 1888, Krusch 1901 and others, *vide* Zimnoch 1967, 1978, Lis and Sylwestrzak 1986 and Mikulski 2007). The assemblage includes, in

alphabetical order: acanthite, aikinite, antimonite, argentite, arsenopyrite, azurite, bismuthinite, bismutoferrite, bornite, brochantite, carrollite, cassiterite, chalcocite, chalcopyrite, chloanthite, chrysocolla, cobaltite, covellite, cuprite, digenite, electrum, erythrite, eugenite, Fe-hydroxides, galena, gersdorffite, gummite, hematite, ilmenite, linnaeite, löllingite, magnetite, malachite, marcasite, mimetite, native Ag, native As, native Bi, native Cu, nickeline, olivenite, polybasite, proustite, pyrite, pyromorphite, pyrrotite, rammelsbergite, safflorite, smaltite, rutile, sphalerite, stephanite, stolzite, stromeyerite, tenorite, tetrahedrite, uraninite, uranophane, volborthite, wulfenite and xanthoconite. Some new minerals were added after World War II by Zimnoch (1967, 1976, 1978), namely, galenobismutite, lievrite, luzonite, maghemite, martite, melnikovite, mushketovite and stibioenargite. Moreover, Kaczmarek (1959) mentioned autunite and torbernite. Some new publications, e.g. Pieczka et al. (1988), Holeczek and Janeczek (1991), Ciesielczuk and Bzowski (2003), Ciesielczuk et al. (2004), Siuda and Kruszewski (2006), Siuda et al. (2006, 2010), Siuda and Gołębiowska (2011) and Siuda (2012) provide data on secondary minerals.

The authors identified the minerals mawsonite and wittichenite, previously unknown from the Miedzianka district. They also present new data concerning the geochemistry of known ore minerals, ore structures and the ore-mineral succession.

2. Materials and methods

Over 100 polished sections were prepared and examined using a NIKON ore microscope.

The chemical compositions of selected minerals was analyzed with the CAMECA SX 100 microprobe at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances, University of Warsaw, under the following working conditions: acceleration voltage 15 kV, beam current 20 nA, counting time 20 s and background time 10 s. The raw results were processed using the PAP software (Pouchou, Pichoir 1985). Elemental analyses employed the following standards, analytical lines and crystals: S (sphalerite, K_{α} , PET); Ti (rutile, K_{α} , PET); Cr (Cr_2O_3 , K_{α} , PET); Mn (rhodonite, K_{α} , LIF); Fe (hematite, K_{α} , LIF); Co (Co metal, K_{α} , LIF); Ni (NiO, K_{α} , LIF); Cu (chalcopyrite, K_{α} , LIF); Zn (sphalerite, K_{α} , LIF); As (GaAs, L_{α} , TAP); Se (ZnSe, L_{α} , TAP); Nb ($LiNbO_3$, L_{α} , PET); Ag (Ag metal, L_{α} , PET); Cd (CdS, L_{α} , PET); In (InAs, L_{α} , PET); Sn (cassiterite, L_{α} , PET); Sb (InSb, L_{α} , PET); Te (PbTe, L_{α} , LIF); Ta (tantalite, M_{α} , TAP); W (scheelite, M_{α} , TAP); Pb (galena, M_{α} , PET); Bi (Bi_2Te_3 , M_{α} , PET).

3. Geological setting

The Karkonosze–Izera Massif (KIM, Fig. 1) (Mazur, Aleksandrowski 2001), the largest-scale geological unit in the West Sudetes, SW Poland, is situated at the NE peripheries of the Bohemian Massif. The central part of the KIM is occupied by the Variscan Karkonosze granite, which has been dated between 304 Ma and 328 Ma (Pin et al. 1987; Duthou et al. 1991; Kröner et al. 1994; Machowiak, Armstrong 2007). The boundary between the KIM and the Kaczawa Metamorphic Complex is the Intra-Sudetic Fault.

The eastern part of the KIM (Fig. 1) comprises two NNE-SSW-elongated metamorphic belts. The western metamorphic belt is composed of rocks belonging to the Czarnów Schist Formation (CSF; Teisseyre 1973) comprising chlorite-albite-muscovite-quartz schists and phyllites with intercalations of marbles, graphitic phyllites, quartzitic schists, quartzofeldspathic rocks and greenschists in its southern part, and albite-mica schists, quartzofeldspathic rocks, and striped amphibolites in its northern part. The eastern metamorphic belt includes metabasites and metagranites accompanied by metasediments represented by pyrite-bearing schists belonging to the meta-igneous Leszczyniec Unit (Kryza, Mazur 1995). The Przybkowice Unit is composed of greenschists and phyllites (Oberc 1961, Teisseyre 1973). All these rocks were metamorphosed and deformed during the Variscan orogeny (Mazur 1995), prior to the emplacement of the Karkonosze granite. At the contact with granite, the CSF rocks were transformed into hornfelses. The metamorphic formations are cut by Late Variscan porphyry dykes (Berg 1913), partly older and partly younger than the ore mineralization. Our study concerns ore mineralization in the Miedzianka district located at the northern termination of the two metamorphic belts, in the neighborhood of the Przybkowice Unit.

4. The Miedzianka field (Western field)

Three types of ore mineralization are known from the western mining field. These are (i) metasomatic magnetite ores, (ii) Cu-bearing hydrothermal veins and (iii) uranium-bearing hematite ores (Zimnoch 1978).

The metasomatic magnetite ores form a lensoidal body about 250-meters long that dips steeply to the northeast. It is concordant with the hosting carbonate- and calc-silicate rocks (Zimnoch 1978). The metasomatic nature of this ore has been earlier recognized by Krusch (1901) and Zimnoch (1967, 1978). The main economic-grade mineralization accumulated in hydrothermal veins dominated by copper and/or uranium minerals. The uranium mineralization - primary pitchblende accompanied by several secondary uranium minerals as well as galena, chalcopyrite and pyrite - was discovered in 1950. A detailed description can be found in Kaczmarek (1959).

In the samples collected from the dumps, we found chalcopyrite, pyrite, galena, bornite, chalcocite, digenite, arsenopyrite, magnetite, sphalerite, tetrahedrite-tennantite, bornite, hematite, martite, pyrrhotite, ilmenite, cassiterite and covellite. All are hosted in coarse-grained quartz veins with chlorite that cut the quartz-mica schists.

Ore minerals form irregular, massive accumulations and veinlets as well as disseminated structures. Occasionally, pseudo-layers concordant with the foliation of the host-rocks are evident. The two types of ore were analyzed, namely Cu-sulfide-dominated ore and magnetite-dominated ore.

4.1. Copper sulphide ore

In the copper sulphide ores, **chalcopyrite** is the main ore mineral. It forms intergrowths with bornite (Fig. 2) or pyrite. Chalcocite, digenite and covellite are also present. The observed intergrowths with pyrite form streaks underlining the foliation of the host-rocks. Usually, the sulphide ores also contain some amounts of members of the tetrahedrite-

tennantite series. Small inclusions of galena and accumulations of idiomorphic arsenopyrite crystals also occur.

Chalcopyrite exhibits a stable chemical composition (Tab. 2): Fe (28.9-30.1wt%), Cu (34.2-35.2wt%) and S (34.8-35.2wt%). In a few crystals, increased amounts (<0.03wt%) of Se were detected. **Pyrite** shows somewhat variable contents of Fe (44.5-47.6wt%) and S (52.2-54.0wt.%) and small amounts of Ni and Co. Two crystals of **native Bi** contained 98.4 and 99.1wt% Bi, and small quantities of Fe.

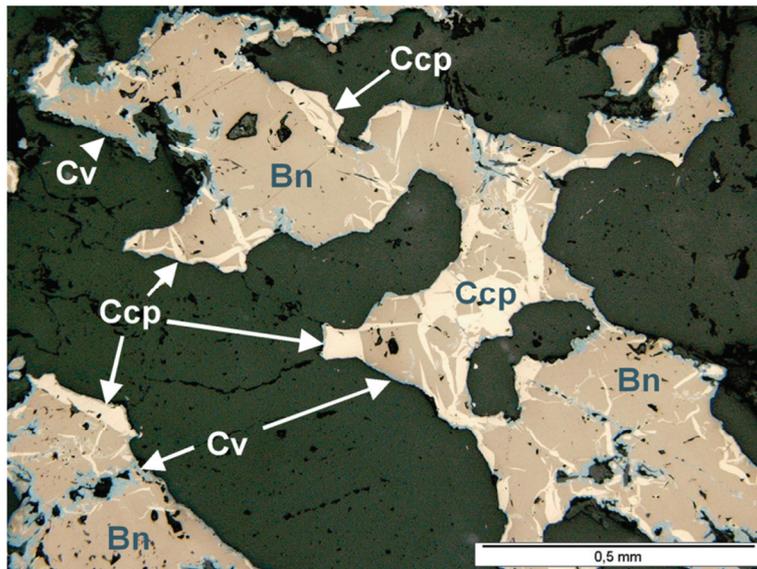


Fig. 2. Irregular accumulation of bornite (Bn) partly replaced by chalcopyrite (Ccp) and covellite (Cv). Miedzianka, sample M-6. Reflected light, 1 polar.

4.2. Magnetite ore

The magnetite ore is composed of massive accumulations of coarse (up to several millimeters across) magnetite grains intergrown with sphalerite. Microscopic examination reveals two generations of magnetite. The first generation builds the cores of mineral aggregates and exhibits granular- to rounded shapes. The second generation overgrows the first and can be easily identified under the microscope due to its poor polishing properties (Fig. 3). The outer (external) parts of the aggregates are characterized by idiomorphic, distinctly-zoned, rhomboidal magnetite crystals (Fig. 4).

The BSE images reveal the zonation of the magnetite crystals, earlier described by Zimnoch (1978). In the outer parts of magnetite grains, anisotropic **hematite** of higher reflectance may be the result of martitization. In some parts, radial hematite (specularite) grows onto magnetite aggregates (Fig. 3). Intergrowths of magnetite with chalcopyrite, pyrite and **arsenopyrite** were also observed. Small inclusions of **cassiterite** occur in some magnetite aggregates (Fig. 3). The chemical composition of cassiterite from sample M-11 is shown in Table 1.

Pyrrhotite forms irregular accumulations with pyrite, scarce pentlandite and with chalcopyrite. **Marcasite** occurs as a replacement of pyrrhotite in samples dominated by pyrrhotite. This replacement starts from cracks in or at the edges of pyrrhotite aggregates. In many samples, pyrrhotite is almost completely replaced by marcasite and by Fe-hydroxides. The iron sulphides typically show evidence of weathering.

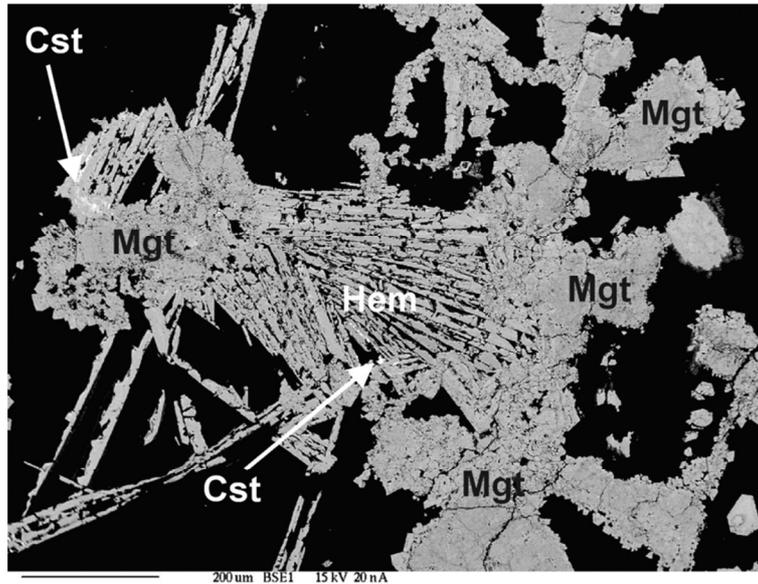


Fig. 3. Irregular accumulation of magnetite (Mgt) and radial specularite (Hem). Two generations of magnetite are visible; older magnetite in the core of aggregates and a younger, hipidiomorphic, magnetite overgrowth. Small inclusions of cassiterite (Cst) are evident. Miedzianka, sample M-11, BSE image.

TABLE 1

Chemical composition of cassiterite from the Miedzianka field analysed by microprobe (average of three measurements).

Compound	Concentration (wt%)	Cation	Atom p.f.u.
Fe ₂ O ₃	0.35	Fe	0.0065
MnO	0.02	Mn	0.0004
WO ₃	0.00	W	0.0000
Nb ₂ O ₅	0.12	Nb	0.0014
Ta ₂ O ₅	0.00	Ta	0.0000
TiO ₂	2.30	Ti	0.0427
SnO ₂	96.42	Sn	0.9490
<i>Total</i>	99.21		

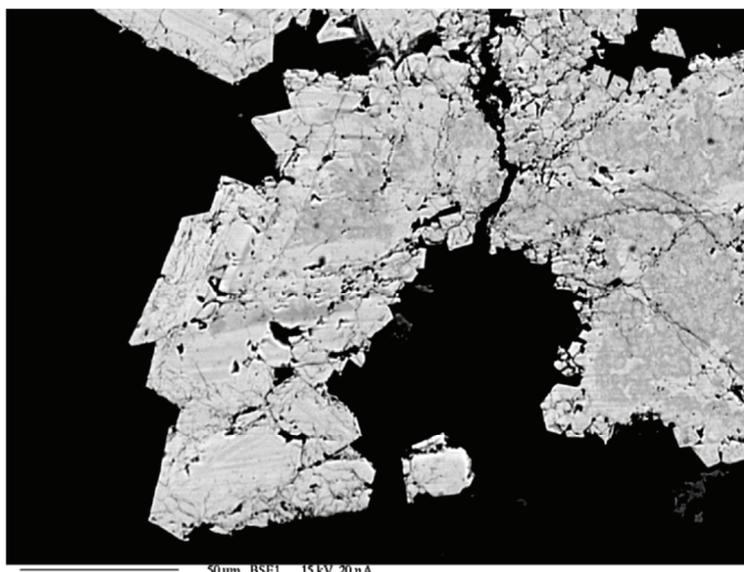


Fig. 4. Nest-like accumulation of hipidiomorphic magnetite crystals (younger generation) with clear growth zoning. Miedzianka, sample M-11. Reflected light, 1 polar.

5. The Ciechanowice field (Eastern field)

In the Ciechanowice area, many old mine dumps were re-exploited in recent years, exposing quite fresh, unweathered ore fragments. Microscopic examination enabled identification of a quite diversified assemblage of ore minerals including chalcopyrite, pyrite, sphalerite, galena, tetrahedrite-tennantite, bismuthinite, native Bi, arsenopyrite, löllingite, cassiterite, cobaltite, gersdorffite, chalcocite, cassiterite, bornite, covellite, marcasite, pyrrhotite and rutile. Moreover, microprobe analyses allowed us to identify mawsonite and wittichenite, which had not been found previously in the Ciechanowice ore.

The ore mineralization is hosted mainly in amphibolites in some cases intergrown with quartz and rare carbonates. Dark minerals composing amphibolites are usually strongly chloritized. Minor host rocks are quartz-chlorite schists and quartzites.

The ore minerals form irregular, nest-like accumulations or veinlets, several millimetres thick, together with quartz. Moreover, disseminations concordant with the foliation of the host-rocks also occur.

Chalcopyrite is the main ore mineral except for a few samples in which pyrite predominates. Locally, arsenopyrite or bornite are also present in appreciable quantities. Chalcopyrite forms irregular, nest-like aggregates, over 1 cm in diameter, scattered in the host-rocks or in quartz veinlets. It is commonly intergrown with sphalerite. Minute chalcopyrite exsolutions in sphalerite are also observed (Fig. 5). Galena, chalcocite and tetrahedrite-tennantite series members are present, as well. In some sections, chalcopyrite forms sieve-structured blasts containing inclusion of rock-forming minerals, mainly quartz. Inclusions of pyrite, cobaltite or members of cobaltite-gersdorffite series are very common (Fig. 5, 6). These are relics after the replacement of previous associations.

Occasionally, arsenopyrite is replaced by chalcopyrite (Fig. 7) or chalcopyrite forms the matrix of breccia composed of arsenopyrite fragments. The chemical composition of chalcopyrite from Ciechanowice is shown in Table 2.

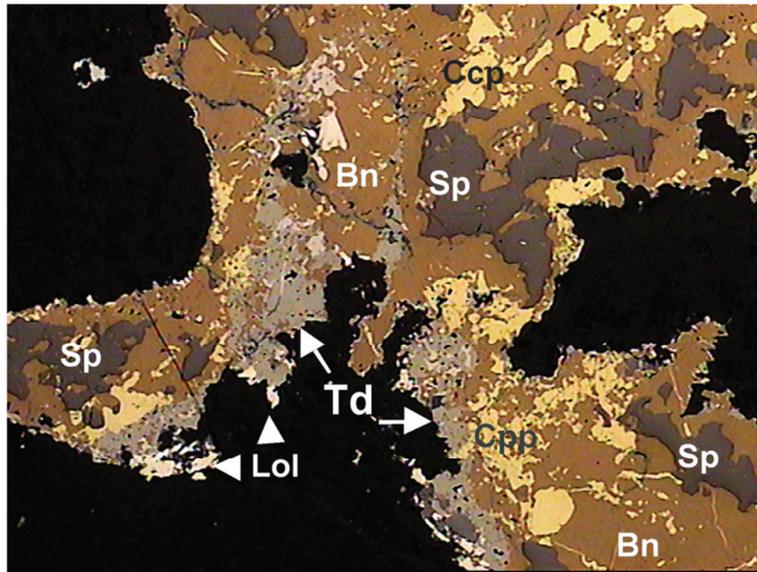


Fig. 5. Aggregates of bornite (Bn), chalcopyrite (Ccp), sphalerite (Sp) and tetrahedrite (Td) with inclusions of löllingite (Lol). Ciechanowice, sample Ciech 97 – 1. Reflected light, 1 polar.

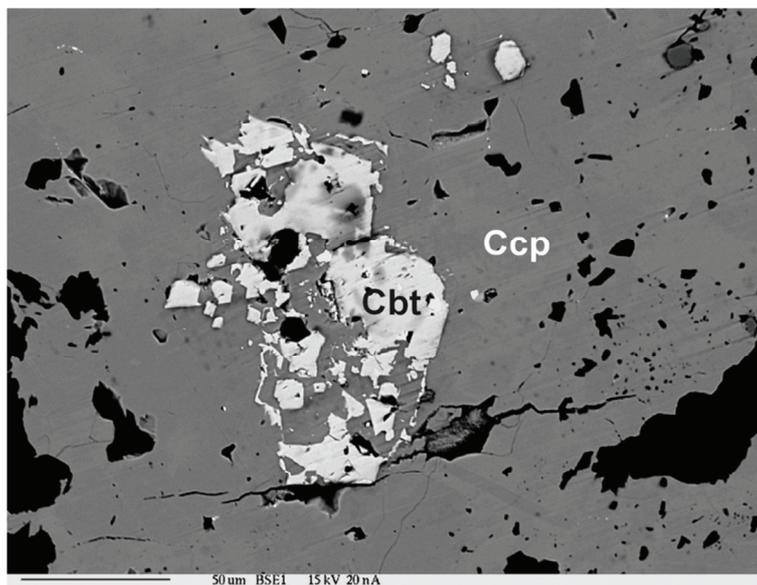


Fig. 6. Chalcopyrite (Ccp) with relics of cobaltite (Cbt) partly replaced by chalcopyrite. Ciechanowice, sample Ciech-2. BSE image.

TABLE 2

Chemical composition of selected ore minerals from the Ciechanowice field analysed by microprobe (in wt%).

	Sphalerite		Chalcocopyrite		Mawsonite		Native Bi		Bismuthinite		Wittichenite		Bornite	
	<i>n</i> =35	<i>n</i> =40	<i>n</i> =8	<i>n</i> =1	<i>n</i> =2	<i>n</i> =6	<i>n</i> =2	<i>n</i> =2	<i>n</i> =1	<i>n</i> =12	<i>n</i> =4	<i>n</i> =2		
S	32.26	32.36	34.62	34.66	29.58	0.00	18.44	19.15	25.20	28.35	27.72			
Mn	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00			
Fe	5.53	0.08	30.37	29.89	14.63	0.02	0.00	0.60	10.89	12.29	16.09			
Cu	6.01	0.05	34.33	34.92	43.11	0.00	0.15	38.02	63.17	58.92	55.85			
Zn	55.88	66.04	0.03	0.22	0.00	0.00	0.00	0.00	0.07	0.00	0.01			
As	0.00	0.01	0.04	0.03	0.00	0.00	0.00	0.00	0.02	0.01	0.03			
Se	0.00	0.04	0.00	0.00	0.05	0.00	0.06	0.00	0.00	0.00	0.00			
Ag	0.00	0.00	0.04	0.03	0.00	0.00	0.00	0.18	0.05	0.12	0.04			
Cd	0.71	0.89	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02			
In	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Sn	0.00	0.01	0.02	0.00	12.97	0.00	0.00	0.00	0.00	0.00	0.00			
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.04	0.05	0.00	0.02			
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Pb			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Bi			0.00	0.00	0.00	99.80	81.06	41.22	0.00	0.00	0.00			
<i>Total</i>	<i>100.39</i>	<i>99.46</i>	<i>99.48</i>	<i>100.01</i>	<i>100.37</i>	<i>99.82</i>	<i>99.78</i>	<i>99.21</i>	<i>99.48</i>	<i>99.72</i>	<i>99.77</i>			

Number of ions													
S	0.954	0.989	1.992	1.992	1.979	7.904	0.000	2.974	2.955	3.959	3.848	2.961	
Mn	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.094	0.001	1.002	0.971	0.980	2.244	0.001	0.000	0.053	0.983	0.958	0.987	
Cu	0.090	0.001	0.996	1.022	1.006	5.814	0.000	0.012	2.961	5.008	4.036	3.011	
Zn	0.810	0.990	0.001	0.006	0.014	0.000	0.000	0.000	0.000	0.006	0.000	0.000	
As	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.001	
Se	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.004	0.000	0.000	0.000	0.000	
Ag	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.008	0.002	0.005	0.001	
Cd	0.006	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	
In	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Sn	0.000	0.000	0.000	0.000	0.000	0.936	0.000	0.000	0.000	0.000	0.000	0.000	
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.002	0.002	0.000	0.001	
Te	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Pb			0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Bi			0.000	0.000	0.000	0.000	0.999	2.006	0.976	0.000	0.000	0.000	

n – number of analyses

Pyrite occurs in nearly all samples in which chalcopyrite is the main component but, in a few samples, it is the main or only ore mineral. It forms disseminated structures in which the pyrite crystals up to 1 mm in diameter are distributed along the foliation planes of the host rocks. Pyrite veinlets were also observed with the replacements of pyrite by chalcopyrite.

Some pyrite crystals host small inclusions of chalcopyrite occurring together with sphalerite, galena and safflorite, as well as Ti-minerals and gangues. In some samples, idiomorphic pyrite crystalloblasts form aggregates up to 10 mm in diameter. The chemical composition of pyrite is given in Table 3. Increased amounts of As (averaging 0.29wt%) are remarkable.

In some samples, intergrowths of marcasite with sphalerite resemble “rib structures”. Marcasite is a secondary ore mineral formed at the initial stage of weathering at the mine dumps.

Sphalerite is a common ore mineral seen in almost all samples, mainly as intergrowths with chalcopyrite and bornite (Fig. 5). Most sphalerite crystals contain minute exsolutions of chalcopyrite. The composition of sphalerite is characterized by variable contents of Fe (0.08-5.53wt%) and relatively low contents of Cd (0.7-1.7wt%; Table 2). Thus, two types of ZnS: with high- and low- Fe can be distinguished.

Galena occurs in the majority of samples but only in minor amounts (Fig. 8). It forms intergrowths with chalcopyrite, sphalerite and Bi minerals. Two types of galena were distinguished based on trace-element composition. The first type contains admixtures of Ag (ca 0.04-0.81wt%), Se (0.06-0.51wt%) and Bi (0.0-0.39wt%) whereas the second is free of trace elements (Table 4).

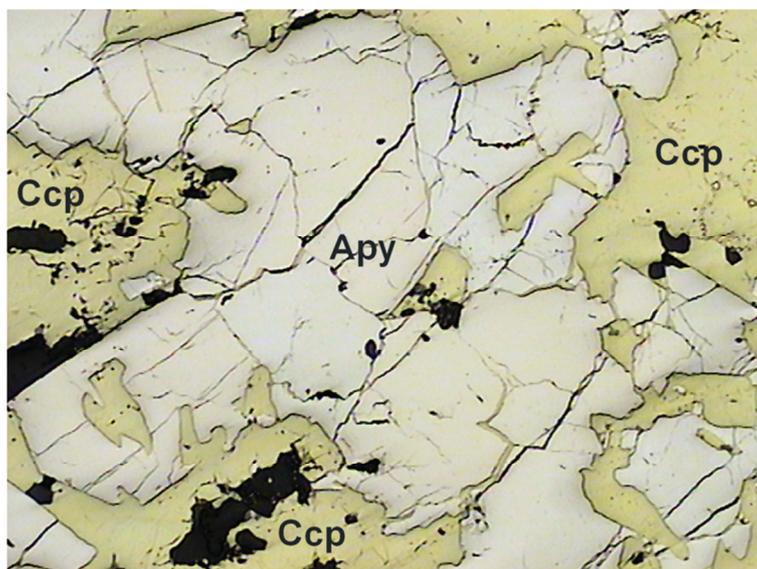


Fig. 7. Arsenopyrite (Apy) crystals partly replaced by chalcopyrite (Ccp). Ciechanowice, sample Ciech-45/1. Reflected light, 1 polar.

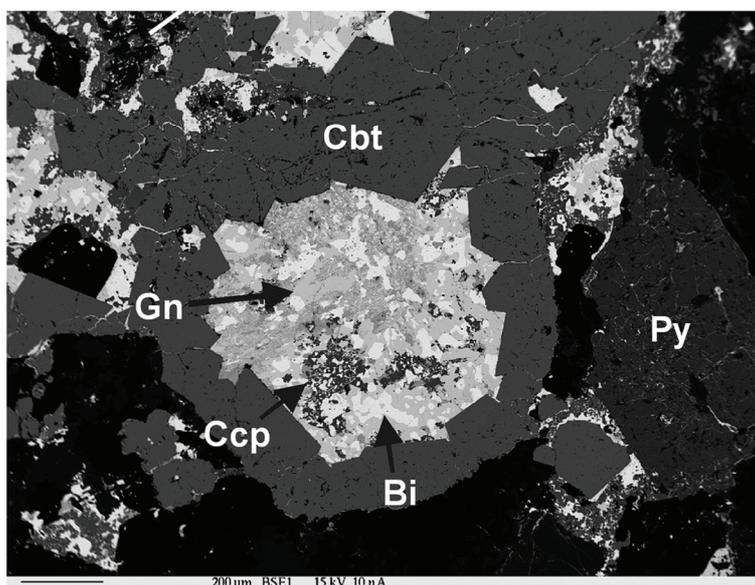


Fig. 8. Spheroidal structure of cobaltite (Cbt), filled with an intergrowth of galena (Gn), chalcopyrite (Ccp) and native bismuth (Bi), accompanied by pyrite (Py). Ciechanowice, sample Ciech-4/45. BSE image.

Members of **tetrahedrite-tennantite series** are very common and are found in majority of chalcopyrite-dominated polished sections. They form intergrowths with chalcopyrite, galena, sphalerite and native Bi (Fig. 5). Microscopic examination and the microprobe analyses reveal the presence of various members of tetrahedrite-tennantite isomorphous series but tetrahedrite prevails. They are accompanied by intermediate phases containing some admixture of Bi. Contents of Sb vary from 1.56 to 27.06wt% and those of arsenic from 1.31 to 19.50wt%. The chemical composition of these minerals is shown in Table 5.

Mawsonite ($\text{Cu}_{5.814}\text{Fe}_{2.244}\text{Sn}_{0.936}\text{S}_{7.904}$) is a rare phase found as inclusions in chalcopyrite. Because of its small crystal size, it was identified mainly by microprobe. It contains up to 15wt% Fe (Table 2).

Native Bi and bismuthinite were recorded in most polished sections but only in small amounts. Native Bi forms tiny aggregates overgrown by chalcocite, bismuthinite and, locally, by pyrite and cobaltite (Fig. 8). Microprobe analyses did not reveal detectable amounts of trace elements (Table 2).

Wittichenite was identified by microprobe analysis (Table 2) in a single sample. It occurs as an inclusion in tennantite accompanied by bornite, chalcopyrite, arsenopyrite, chalcocite and galena.

Bornite usually occurs in small amounts. It was encountered as the main ore mineral only in a single polished section (Fig. 2). It forms intergrowths with chalcopyrite, sphalerite and tetrahedrite. Microprobe analyses reveal variable, in some cases, nonstoichiometric amounts of Fe (average values from 10.89-16.08wt%; Table 2). Some grains contained increased amounts of Ag (ca 0.1wt%; Table 2).

Chalcocite was rarely observed, always in intergrowths with chalcopyrite.

Arsenopyrite ($\text{Fe}_{0.999}\text{As}_{0.975}\text{S}_{1.018}$) was observed as a dominating ore mineral in a few polished sections where it formed massive intergrowths with chalcopyrite (Fig. 7), pyrite, sphalerite and native Bi. Individual arsenopyrite crystals are usually idiomorphic and rhomboidal in cross-section. Some arsenopyrite crystals are cracked and the cracks are filled with chalcopyrite.

Members of **cobaltite-gersdorffite series** ($\text{Co}_{0.487-0.915}\text{Ni}_{0.006-0.315}\text{As}_{0.893-1.009}\text{S}_{0.989-1.108}$) occur as tiny, idiomorphic inclusions of pink color and high reflectivity in chalcopyrite. Microprobe analyses revealed both the cobaltite end-member and the minerals of intermediate compositions (Table 3). Rare spheroidal aggregates of cobaltite-gersdorffite were also seen with pyrite, chalcopyrite, native Bi, galena and chalcocite (Fig. 8).

Löllingite is a rare mineral. Its microscopic identification is difficult due to its minute crystal size. It was identified as intergrowths with bornite accompanied by tetrahedrite-tennantite members (Fig. 5).

Pyrrhotite was found only in two polished sections. It forms disseminated crystals or irregular intergrowths with pyrite, sphalerite and galena.

Rutile is a common component of amphibolites from the Miedzianka district. Usually, it forms rod-like structures with individual crystals parallel to the foliation of host-rock. Accumulations of rutile crystals also occur in chalcopyrite. In its chemical composition, SiO_2 (< 0.6wt%), V_2O_5 (0.6-0.7wt%), Nb_2O_3 (0.1-0.2wt%) and some FeO (0.2-0.3wt%) were detected. A rare variety of rutile forming idiomorphic crystals with polygonal cross-sections contains SiO_2 (0.06-0.2wt%), Nb_2O_3 (0.2-0.5wt%) and FeO (ca 0.3-1.0wt%). Locally, this rutile variety hosts tiny crystals of **cassiterite** which seem to be formed contemporaneously with TiO_2 (Fig. 9).

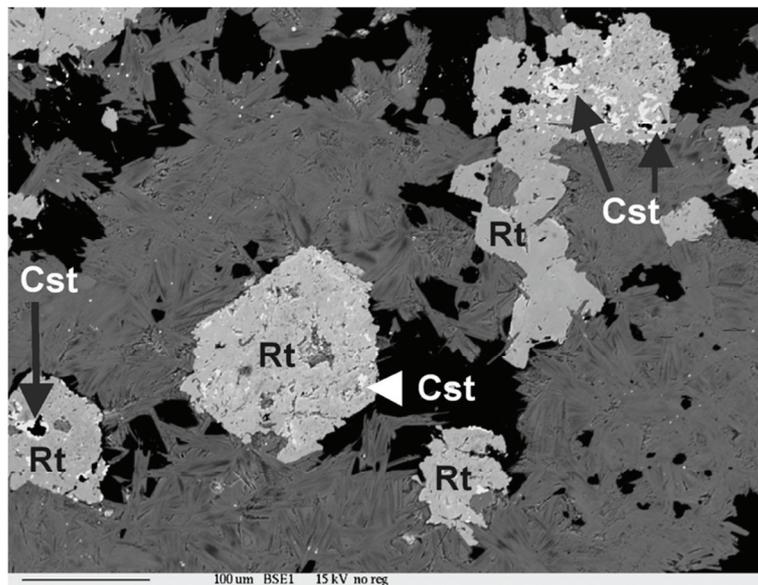


Fig. 9. Hipidiomorphic crystals of rutile (Rt) with tiny inclusions of cassiterite (Cst) in chlorite (grey). Ciechanowice, sample Ciech-112, BSE image.

TABLE 3

Chemical composition of selected ore minerals from the Ciechanowice field analysed by microprobe (in wt%).

	Löllingite-Safflorite			Arsenopyrite			Cobaltite-Gersdorffite			Pyrite				
	<i>n</i> =4	<i>n</i> =3	<i>n</i> =1	<i>n</i> =1	<i>n</i> =3	<i>n</i> =7	<i>n</i> =2	<i>n</i> =2	<i>n</i> =1	<i>n</i> =1	<i>n</i> =2	<i>n</i> =1	<i>n</i> =20	
S	1.15	0.63	3.39	0.52	1.32	1.78	8.54	20.13	19.57	19.70	21.93	19.86	19.03	52.70
Mn	0.00	0.00	0.04	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	27.17	25.42	18.92	14.44	11.33	8.62	6.56	34.48	32.02	2.81	2.90	6.60	10.43	46.32
Co	0.06	0.44	9.33	12.53	16.44	19.17	24.00	0.14	1.34	32.58	28.07	17.47	22.06	0.04
Ni	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.04	1.01	0.20	5.10	11.27	2.04	0.02
Cu	2.04	3.21	1.09	2.08	0.96	1.26	0.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	69.75	70.18	66.35	70.63	69.36	68.48	59.25	45.03	45.21	44.17	41.29	44.84	45.36	0.29
Se	0.21	0.25	0.21	0.26	0.27	0.28	0.22	0.15	0.18	0.23	0.11	0.19	0.16	0.00
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.02	0.00	0.03	0.00	0.00	0.38	0.00
<i>Total</i>	<i>100.39</i>	<i>100.12</i>	<i>99.32</i>	<i>100.46</i>	<i>99.68</i>	<i>99.61</i>	<i>99.58</i>	<i>99.88</i>	<i>99.33</i>	<i>99.72</i>	<i>99.41</i>	<i>100.23</i>	<i>99.46</i>	<i>99.37</i>
Number of ions														
S	0.069	0.038	0.205	0.032	0.083	0.111	0.494	1.018	1.001	1.016	1.108	1.017	0.989	1.979
Mn	0.000	0.000	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.936	0.887	0.658	0.513	0.408	0.309	0.218	0.999	0.940	0.083	0.084	0.194	0.311	0.999
Co	0.002	0.014	0.307	0.422	0.561	0.651	0.755	0.004	0.037	0.915	0.772	0.487	0.624	0.001
Ni	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.028	0.006	0.141	0.315	0.058	0.000
Cu	0.062	0.098	0.033	0.065	0.031	0.040	0.026	0.000	0.000	0.000	0.000	0.000	0.000	0.000
As	1.791	1.826	1.720	1.871	1.863	1.828	1.466	0.975	0.990	0.975	0.893	0.983	1.009	0.005
Se	0.005	0.006	0.005	0.006	0.007	0.007	0.005	0.003	0.004	0.005	0.002	0.004	0.003	0.000
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.005	0.000

TABLE 4

Chemical composition of galena from the Ciechanowice area analysed by microprobe (in wt%).

Galena		
	<i>n</i> =3	<i>n</i> =22
S	13.07	13.29
Mn	0.00	0.00
Fe	0.05	0.04
Cu	0.00	0.00
Zn	0.00	0.00
As	0.00	0.00
Se	0.51	0.06
Ag	0.72	0.01
Cd	0.05	0.07
In	0.00	0.00
Sn	0.00	0.00
Sb	0.02	0.01
Te	0.11	0.00
Pb	84.73	86.64
Bi	0.27	0.00
<i>Total</i>	<i>99.54</i>	<i>101.12</i>
Number of ions		
S	0.974	0.987
Mn	0.000	0.000
Fe	0.002	0.002
Cu	0.000	0.000
Zn	0.000	0.000
As	0.000	0.000
Se	0.016	0.002
Ag	0.016	0.000
Cd	0.001	0.002
In	0.000	0.000
Sn	0.000	0.000
Sb	0.000	0.000
Te	0.002	0.000
Pb	0.978	0.996
Bi	0.003	0.000

n – number of analyses

Covellite occurs as traces in the vicinity of Cu minerals. It is the product of early-stage weathering.

TABLE 5

Chemical composition of tetrahedrite-tennantite series members from the Ciechanowice field analysed by microprobe (in wt%).

Tetrahedrite-Tennantite series					
	<i>n</i> =3	<i>n</i> =2	<i>n</i> =50		<i>n</i> =2
S	23.85	24.24	24.41	26.48	27.56
Mn	0.03	0.01	0.00	0.00	0.00
Fe	1.31	1.46	1.00	1.13	1.95
Cu	37.82	38.49	38.76	41.11	43.77
Zn	6.75	6.45	6.91	7.13	5.37
As	1.31	3.59	4.13	13.95	19.50
Se	0.03	0.02	0.04	0.07	0.07
Ag	0.12	0.11	0.21	0.10	0.07
Cd	0.18	0.14	0.05	0.26	0.34
In	0.00	0.00	0.00	0.00	0.00
Sn	0.13	0.10	0.12	0.00	0.00
Sb	27.06	23.41	21.68	9.09	1.56
Te	0.01	0.00	0.00	0.00	0.05
Pb	0.00	0.00	0.00	0.00	0.00
Bi	1.28	1.75	2.74	0.00	0.00
<i>Total</i>	<i>99.87</i>	<i>99.78</i>	<i>100.05</i>	<i>99.33</i>	<i>100.25</i>
Number of ions					
S	12.099	12.168	12.361	12.661	12.572
Mn	0.009	0.004	0.000	0.000	0.000
Fe	0.381	0.422	0.290	0.311	0.512
Cu	9.682	9.749	9.905	9.918	10.075
Zn	1.679	1.587	1.717	1.671	1.201
As	0.284	0.771	0.896	2.855	3.807
Se	0.005	0.005	0.008	0.013	0.013
Ag	0.018	0.016	0.031	0.014	0.010
Cd	0.026	0.021	0.008	0.035	0.044
In	0.000	0.000	0.000	0.000	0.000
Sn	0.018	0.014	0.016	0.000	0.000
Sb	3.615	3.094	2.891	1.145	0.188
Te	0.002	0.000	0.000	0.000	0.005
Pb	0.000	0.000	0.000	0.000	0.000
Bi	0.099	0.135	0.213	0.000	0.000

n – number of analyses

6. The Przybkowice area

In the Przybkowice area, Wojciechowski and Wołkowicz (1985) described a quartz-barite vein with minor sulphides including chalcopyrite, chalcocite, bornite, covellite,

members of tetrahedrite-tennantite series and galena. The sulphides are replaced by the secondary minerals: cerussite, malachite and Fe-hydroxides.

The vein found by the present authors in the bed of an unnamed stream presumably corresponds to that described by Wojciechowski and Wołkowitz (1985) although it strikes N36W and dips at 70° to the southwest. The vein cuts metasomatically-altered greenschists. The gangues are several generations of quartz cut by barite veinlets and enclosing barite nests.

Microscopic examinations of polished sections revealed ore minerals identified earlier by Wojciechowski and Wołkowitz (1985), i.e. chalcopyrite, chalcocite, digenite, pyrite and galena. All sulphides form disseminated grains and aggregates in quartz and barite. Some aggregates may reach up to 5 cm in diameter.

Chalcopyrite, the dominant ore mineral, occurs as disseminated crystals or aggregates containing inclusions of pyrite. Chalcopyrite aggregates frequently show bluish marginal zones composed of digenite and covellite. These sulphides also fill cracks within chalcopyrite. Chalcopyrite crystals show near-stoichiometric compositions.

Chalcocite and digenite usually form intergrowths with chalcopyrite or occur as tiny, disseminated, single crystals. Microprobe analyses reveal compositions with increased amounts of Fe (ca 2.4 wt%).

Galena occurs as individual crystals or large aggregates (up to a few millimeters across) of isometric grains. These are replaced by cerussite at the margins.

TABLE 6

Ore-mineral succession in the Miedzianka district with formation temperatures of selected minerals.

rutile	_____
magnetite	? _____
cassiterite	? _____
pyrrhotite	_____
arsenopyrite	_____
löllingite-safflorite	_____
cobaltite-gersdorffite	_____
pyrite	_____
sphalerite	_____
chalcopyrite	300°C _____
chalcocite	_____
tetrahedrite-tennantite	_____
native Bi, bismuthinite	270°C _____
mawsonite	_____
bornite	_____
galena	? _____

7. Discussion

7.1. Ore-mineral succession

Microscopic observations led to the crystallization sequence of the ore minerals to be. It was supported by some microporobe analyses enabling geothermometric evaluations.

Rutile, magnetite and cassiterite are the oldest ore minerals; they crystallized at an early, oxide-ore forming stage, before prior to sulphides and sulphosalts. All of the oxides occur in complex intergrowths, e.g. cassiterite with rutile in the Ciechanowice field and with magnetite in the Miedzianka field. Cassiterite presumably crystallized under reducing conditions with Ti transported in the form of Ti^{3+} -complexes, as suggested by common, relatively high admixtures of Ti (< 2.3wt% TiO_2 ; Table 1).

The earliest, non-oxide components of ore are pyrrhotite encountered mainly in the Miedzianka western field, in the close vicinity of the Karkonosze granite, and löllingite accompanied by Co-löllingite, Fe-safflorite, arsenopyrite and cobaltite in the Ciechanowice field. Arsenopyrite that crystallized after the Fe- and Co-arsenides very rarely shows enrichment (> 1.0 wt%) in Co and Ni. Usually, contents of these elements are negligible. The crystallization sequence löllingite → Co-löllingite → Fe-safflorite → arsenopyrite → cobaltite suggests that during the early, sulfo-arsenide mineralization stage, ore minerals crystallized from fluids of high As activity with both the arsenides and sulfoarsenides stable. Increasing S contents from the older, Fe- to the younger, Co-arsenides corroborates falling As contents in the ore-forming fluids during this early stage of mineralization. Nickel is rather subordinate. It is absent from both the Fe- and Co-arsenides, concentrating only in arsenopyrite (<1.0wt%) and in cobaltite (<11.3wt%). The average contents of As (32.50(72)at%) and S (33.94(80)at%) point to the significance of S→As substitution in arsenopyrite at progressively decreasing temperatures. The coexistence of arsenopyrite with arsenides suggests that crystallization had commenced under conditions of löllingite stability and had progressed towards the crystallization of arsenopyrite with pyrrhotite until the crossing of pyrrhotite/pyrite equilibrium.

The replacement of arsenopyrite by chalcopyrite, the infilling of open spaces between euhedral cobaltite crystals by chalcopyrite and the replacement of cobaltite by chalcopyrite indicate that chalcopyrite crystallized after the arsenides-arsenopyrite-cobaltite assemblage.

The intergrowths of sphalerite and chalcopyrite, and chalcopyrite inclusions in sphalerite argue for the simultaneous formation of both minerals. Relatively low Fe contents in sphalerite in comparison with those of Cu show that the sphalerite-chalcopyrite pair crystallized after crossing the pyrrhotite/pyrite equilibrium, i.e. under the conditions of pyrite stability, as a sphalerite-chalcopyrite solid-solution. The decrease in both Fe and Cu contents in sphalerite (up to almost pure ZnS) may reflect the crystallization of sphalerite at relatively low temperatures. On the other hand, chalcopyrite commonly contains small (< 0.50wt% max) amounts of Zn which may indicate, as Scott (1983) concluded, that chalcopyrite crystallized from hydrothermal solutions of significant Zn activity at temperatures somewhat above 300°C. A similar temperature was determined by Siuda (2012) from sphalerite exsolutions in chalcopyrite. However, commonly-observed much lower Zn contents in chalcopyrite (0.20wt% to complete absence) may indicate even lower crystallization temperatures.

Minerals of the tetrahedrite-tennantite series represent an almost complete solid solution. Generally, these phases correspond to Zn-bearing varieties, in some cases enriched in Cd. Tetrahedrite contains low Bi, Ag and Sn, documenting the enrichment of the hydrothermal solutions in these elements during the later stages of ore formation. Mawsonite probably formed at this stage, as well.

Galena occurs in two varieties. The first, probably higher-temperature phase, is enriched in Ag (<0.6-0.8wt%), and in Se (0.06-0.51wt%) and Bi (0.00-0.27wt%). The second probably more common variety does not contain these elements.

Native Bi crystallized at ca 270°C, probably together with bismuthinite. A similar formation temperature for Bi minerals was determined by Siuda (2012).

Bornite crystallization at low temperatures is a result of the reaction $\text{Chp} \rightarrow \text{Bn} + \text{Py}$. Bornite varieties with higher Fe contents and of compositions close to $\text{Cu}_4\text{FeS}_{4.4}$ are probably the products of bornite transformations into chalcocite-group minerals.

In conclusion, the succession of ore minerals established here is generally consistent with that proposed by Petrascheck (1933a). The main difference concerns cassiterite; this mineral belongs with the oldest ore minerals in the Miedzianka district.

The vein at Przybkowice is located in a marginal zone of the Miedzianka district, in host rocks belonging to the Leszczyniec Unit. Hence, it should be related rather to the northern mining field, as suggested by Berg (1913).

7.2. Metallogenetic implications

The ore deposits of the Miedzianka mining district show similarities to those of the Kowary district. In both areas, older, lensoidal magnetite accumulations are followed by younger veins with polymetallic-uranium mineralization.

Differences between the Miedzianka and the Kowary ore districts concern the origin of magnetite. The Miedzianka magnetite deposit has been interpreted as contact-metasomatic, genetically related to the Karkonosze granite, whereas the Kowary magnetite deposit resembles rather the metamorphosed Lahn-Dill type (see discussion in Zimnoch 1967, 1978).

The hydrothermal, vein-type polymetallic mineralization is known from both the Miedzianka and the Kowary districts, and from other sites in the eastern metamorphic envelope of the Karkonosze granite. The authors agree with the concept of Petrascheck (1933b and references therein) who proposed a genetic relationship of this mineralization to the Karkonosze granite. The granite intrusion seems to have been the source of both the thermal energy and, at least partly, the hydrothermal solutions responsible for the formation of the Miedzianka, Kowary and other ore deposits in the eastern envelope of the intrusion. It has been suggested that quartz-sulphide veins in the Wieściszowice pyrite deposit also belong to this hydrothermal system (Oberc-Dziedzic et al. 2011).

It is interesting to note that Kanasiewicz and Sylwestrzak (1970) linked the distribution of deposits in the northern part of the Bohemian Massif (including the Sudetes) to deep tectonic zones which may have been the pathways of hydrothermal ore solutions. This concept was discussed in detail by Michniewicz (2003).

The isotopic age of ore mineralization in the Miedzianka area is still unknown. However, it may be referred to Pb/U ages of pitchblende from Kowary (265 and 70 Ma; Lis et

al. 1971) and Pb/Pb galena model ages from Czarnów (250 and 210 Ma; Legierski 1973), indicating the Variscan provenance of ore-forming solutions.

8. Conclusions

Our new data supplement existing knowledge of the ore mineralization of the Miedzianka district, especially its chemistry and the conditions of its formation.

1. Mawsonite and wittichenite are identified for the first time in the Ciechanowice field (Eastern field).
2. The geochemistry of ore minerals is examined in detail.
3. the changes in the composition of the hydrothermal ore-forming fluids are defined. An early, Ti, Fe and Sn-rich system evolved through a succession of systems characterized, in turn, by Fe-As-S, Fe-Co-As-S, Cu-Zn-S and, finally, Cu-Pb-Sb-As-Bi.
4. The well-known ore succession is supplemented by formation temperatures for some minerals resulting from geochemical considerations, namely, chalcopyrite (slightly over 300°C) and native Bi (ca 270°C).

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