New insights into the mineralization of the Czarnów ore deposit (West Sudetes, Poland)

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Abstract This paper provides new data on the mineralogy and mineral chemistry of the Czarnów ore deposit, a polymetallic vein that occurs within the eastern envelope of the Karkonosze Pluton (West Sudetes). New data are also provided on the deposits' geothermometry, mineral succession, and origins.

The Czarnów ore vein is about 500 m long, strikes SW-NE, dips 80° SE and continues to a depth of 200 m. It is hosted within the albite-mica schists, quartzofeldspathic rocks and striped amphibolites that comprise the Czarnów Schist Formation (CSF); its western part is composed of almost monomineral arsenopyrite, whereas the southwestern part locally contains a pyrrhotite lens that extends downwards. Although many types of sulphides, sulphoarsenides, sulphosalts and native phases accompanied by oxides and arsenates have been previously reported, this paper describes four minerals that have not been previously identified from the Czarnów deposit: ferrokësterite, ikunolite, bismite and pentlandite. Geothermometry data suggest formation temperatures of arsenopyrite between 551 °C and 420 °C and that of sphale- rite between about 400 °C to about 200 °C. Fluid inclusion data from vein quartz gave homogenization temperatures between 430 °C and 150 °C. Integrat on of textural and other data suggests the following primary mineral succession: early arsenopyrite and cassiterite as the high-temperature phases; then combinations of pyrrhotite, pyrite, chalcopyrite and sphalerite, all of which formed over a wide temperature range; finally, low temperature galena and Bi phases. Secondary weathering products overprint the primary sequences. Cataclasis of the first-formed arsenopyrite imply that mineralization was related to at least one tectonic event in the region. The Czarnów ore deposit probably resulted from hydrothermal activity associated with the near Karkonosze granite.

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INTRODUCTION

Czarnów is a small village located on the southeastern slopes of the Rudawy Janowickie mountain range in the West Sudetes. In the vicinity of the village are two localities that contain ore mineralization: the historical ore deposit in Czarnów; and the newly discovered, uneconomic ore mineralization in the adjacent dolomitic marble quarry in Rędziny (Fig. 1).

Mining of polymetallic vein-type ores (dominated by As minerals and containing traces of Au) at Czarnów has started during the first half of the 18th century and has continued periodically up until 1925 (Dziekoński, 1972). Between 1952 and 1955 there was intensive, but ultimately unsuccessful, exploration of the area. A reassessment of the existing ore reserves by Kłos (1955) demonstrated that proven reserves were low and, as a result, the Czarnów mine was not reopened (Banaś, 1967). Today, one can still find relics of previous mining operations: old shafts, adits and dumps, and ore minerals can still be safely collected from the dumps.

Descriptions of the geology of the Czarnów ore deposit date back to the mid-19th century and have continued sporadically into the present millenium (Websky, 1853; Fiedler, 1863; Berg, 1913; Petrascheck, 1933; Hoehne, 1934, 1941; Banaś, 1967; Zimnoch, 1985; and aspects of the gold mineralization by Mikulski, 1997, 2001).

The present paper provides new data on the mineral and chemical composition of the Czarnów ores, discusses aspects of their geothermometry and mineral succession, and offers further insight into the origin of this ore deposit.



Fig. 1. Geological sketch map of the Karkonosze–Izera Massif (after Chaloupský *et al.*, 1989; Mazur, 1995; Mazur & Aleksandrowski, 2001; Oberc-Dziedzic, 2003). Inset map: EFZ (Elbe Fault Zone), ISF (Intra-Sudetic Fault), MGH (Mid-German Crystalline High), MO (Moldanubian Zone), MS (Moravo-Silesian Zone), MT (Moldanubian Thrust), NP (Northern Phyllite Zone), OFZ (Odra Fault Zone), RH (Rhenohercynian Zone), SBF (Sudetic Boundary Fault), SX (Saxothuringian Zone), TB (Teplá–Barrandian Zone). Rectangle shows the position of the Karkonosze–Izera Massif within the Bohemian Massif

MATERIALS AND METHODS

This study is based on the analysis of approximately 50 hand specimen samples that were collected from two discused mine dumps in Czarnów and on Czarnów samples that were originally collected during the 1980s by K. Mochnacka.

Some 50 polished thin sections were prepared from representative samples and these were examined using a NIKON ore microscope. After microscopic examination, a subset of these sections were selected for electron microprobe (EMP) analysis.

Mineral chemical compositions were analyzed using the CAMECA SX 100 microprobe at the Inter-institute Analytical Complex for Minerals and Synthetic Substances at the University of Warsaw; working conditions were as follows: acceleration voltage 15 kV, beam current 20 nA, counting time 20 s and background time 10 s. The raw results were processed using PAP software (Pouchou & Pichoir, 1985). Elemental analyses employed the following standards, analytical lines and crystals: S (sphalerite, K_á, PET); Ti (rutile, K_á, PET); Cr (Cr₂O₃, K_á, PET); Mn (rhodonite, K_á, LIF); Fe (hematite, K_á, LIF); Co (Co metal, K_á, LIF); Ni (NiO, K_á, LIF); Cu (chalcopyrite, K_á, LIF); Zn (sphalerite, K_á, LIF); As (GaAs, L_á, TAP); Se (ZnSe, L_á, TAP); Nb (LiNbO₃, L_á, PET); Ag (Ag metal, L_á, PET); Cd (CdS, L_á, PET); In (InAs, L_á, PET); Sn (cassiterite, L_á, PET); Sb (InSb, L_á, PET); Te (PbTe, L_á, LIF); Ta (tantalite, M_á, TAP); W (scheelite, M_á, TAP); Pb (galena, M_á, PET); Bi (Bi₂Te₃, M_á, PET).

Geothermometry of the ore minerals was determined using arsenopyrite and sphalerite chemical compositions determined by EMP analysis and verified by textural observations. The compositions of arsenopyrite crystals were plotted on a sulphur fugacity $(\log_f S_2)$ vs. temperature (T) diagram for the Fe-As-S system (Kretschmar & Scott, 1976, as modified by Sharp *et al.*, 1985), correcting for arsenopyrite inhomogeneities (Kerestedjian, 1997). Pressure plays an insignificant role in arsenopyrite compositions in low-pressure hydrothermal deposits (Sharp *et al.*, 1985), therefore, the effect of pressure on arsenopyrite composition, as buffered by pyrrhotite and pyrite, was not calculated.

Fluid inclusion (FI) studies were carried out at the Department of Mineral Deposits and Mining Geology, Faculty of Geology, Geophysics and Environment Protection, AGH-University of Science and Technology in Kraków on samples of vein quartz collected from waste dumps. Doubly polished thin sections (200 μ m-thick)

were examined using the $50 \times$ and $100 \times$ lenses of the Linkam THMS 600 heating-freezing stage and a Nikon Eclipse E6000 microscope that had attached to it a TMS 93 module and a Linkam LNP pump. Fluid inclusion images were recorded with an Ikegami videocamera and a Linkam VTO 232 video panel; the FI system was calibrated using a special thin section that contained inclusions of pure CO_2 . Fluid inclusion sections were very rapidly frozen down to -120 °C (occasionally down to -198 °C) so as to avoid the formation of metastable phases: this enabled the presence of gases other than carbon dioxide to be revealed. The heating rates for the FI thin sections were as follows: 5-10 °C/min to room temperature (reduced to 0.5 °C close/ min to phase transformation points), then 20 °C/min to 100 °C, and 5-10 °C/min for higher temperatures. For low temperatures, the accuracy of measurement was 0.1–0.2 °C.

GEOLOGICAL SETTING

The Karkonosze-Izera Massif (KIM, Fig. 1) is the largest-scale geological feature in the West Sudetes, SW Poland. It consists of four structural units (Mazur & Aleksandrowski, 2001): the Izera-Kowary Unit, the Ještěd Unit, the South Karkonosze Unit and the Leszczyniec Unit. These four units are interpreted as elements of a nappe structure for the KIM (Mazur & Aleksandrowski, 2001). In addition, there is the Variscan Karkonosze granite, whose age has been calculated to be between 304 Ma and 328 Ma (Pin *et al.*, 1987; Duthou *et al.*, 1991; Kröner *et al.*, 1994; Machowiak & Armstrong, 2007).

The Izera-Kowary Unit is the unit that hosts the Czarnów deposit, and it is composed of ~ 500 Ma orthogneisses and mica schists (Oberc-Dziedzic *et al.*, 2010).

The eastern part of the Izera-Kowary Unit (Fig. 1)

comprises the Czarnów Schist Formation (CSF) of Teisseyre (1973). Its southern part is composed of chlorite-albite-muscovite-quartz schists and of phyllites, both of which can have intercalations of marbles, graphite phyllites, quartzitic schists, quartzofeldspathic rocks and greenschists. Further to the north, the CSF is composed of albite-mica schists, quartzofeldspathic rocks and striped amphibolites. These latter amphibolites show a withinplate geochemical signature (Winchester *et al.*, 1995) and possess a higher grade of metamorphism than do the rocks of the southern part of the CSF. This is probably due to the thermal influence of the Karkonosze granite.

The Czarnów ore deposit itself is situated in the middle part of the CSF, some 200–300 m east of the Karkonosze granite.

THE CZARNÓW ORE DEPOSIT

The abandoned Czarnów deposit comprises a single ore vein about 500 m long, striking SW-NE, dipping at 80° to SE and continuing down to a depth of 200 m or more (Kłos, 1955). The average thickness of the vein is about 40-50 cm, but lensoidal swells can locally increase the thickness to 3-4 m (Banaś, 1967; Zimnoch, 1985). According to Banas (1967), the ore vein is located at the contact between schists and silicified dolomitic marbles, and was concordant with the strike of host rocks. Kłos (1955) and Zimnoch (1985), however, reported that the vein is hosted within calc-silicate rocks embedded in mica schists. Although the vein is enveloped by a zone of disseminated ore mineralization (Banaś, 1967), the vein itself contains three parallel zones of economic-grade mineralization (Kłos, 1955). The contacts between the vein and its host rocks are, according to Banas (1967) and Zimnoch (1985), tectonic. At its southwestern edge, the ore vein is cut by the so-called Southern Fault; the vein is also cut and displaced by several, small, transversal faults (Banaś, 1967).

Three types of sulfide ore are known from the Czarnów deposit: first, and predominant, is an almost monomineral arsenopyrite ore that occurs mostly in the western part of the deposit; second, a pyrrhotite ore lens that is encountered at greater depth in the southwestern part of the deposit; and third, a galena ore lens that is found in the main adit, close to a fault zone (Zimnoch, 1985). In addition, Banaś *et al.* (1996) reported arsenopyrite ore with substantial admixtures of pyrrhotite and chalcopyrite, which perhaps represents a type of intermediate-style deposition between that of the arsenopyrite and pyrrhotite ores.

The mineralogy of the Czarnów ore deposit has been studied for over 150 years, each author successively extending the list of minerals associated with the deposit. Websky (1853) described arsenopyrite, pyrrhotite, pyrite, black sphalerite, covellite, cassiterite and tyrolite. Fiedler (1863) added hematite, and Traube (1888), when describing Czarnów ore specimens in possession of the Wrocław

(Breslau) Museum, mentioned chalcopyrite, löllingite, galena, marcasite and chrysocolla. Berg (1913) identified bornite, tetrahedrite and erythrite. Berg (1923) also identified antimonite (stibnite). Schneiderhoehn & Ramdohr (1931) found stannite; Petrascheck (1933) identified native Bi; Hoehne (1936) noted magnetite, native Cu, molybdenite and anisotropic chalcocite (digenite?) and, later, described native Sb and berthierite (Hoehne,1941). After World War II, Banaś (1967) added rodochrosite and Fe-sphalerite (the more accurate determination of the "black sphalerite" of Websky, 1853), while Zimnoch (1985) added many new phases: Bi-sulphosalts, tennantite, valeriite, cubanite, goethite, skorodite, rutile and leucoxene. In an unpublished report, Banas et al. (1996) identified bournonite, boulangerite and pyrargyrite. Finally, Mikulski (1997) discovered native Au, electrum and scheelite, all from samples of the Czarnów arsenopyritepyrrhotite ore.

Determining the chemical composition of the Czarnów minerals has also had a long history. Probably the first analysis was by Traube (1888) and was of an arsenopyrite crystal: 19.77 wt.% S; 44.02 wt.% As; 34.83 wt.% Fe and 0.92 wt.% Sb. Michałek (1962) used tradi-

tional wet chemical methods to analyse pyrite from quartz veins in the Czarnów deposit and found the following trace element concentrations: Mo (2 ppm), Ni (12 ppm), Co (15ppm), Mn (60 ppm), Cu (66 ppm), Pb (55 ppm) and As (4,960 ppm). Mikulski (1997) analysed the compositions of arsenopyrites and found Fe + Co + Ni (33.98-34.97 wt.%), As (44.10-45.66 wt.%) and S (20.34-21.46 wt.%). Mikulski (1997) also analysed native gold (Au 79-81 wt.%, Ag 18-23 wt.%) and electrum (61.7-63.9 wt.% Au, and 36.6-37.7 wt.% Ag).

From old German data, Krajewski (1947) noticed that the average grade of arsenopyrite ore was 10 wt.% As, from which a concentrate was produced grading 25–32 wt.% As, 2–4 ppm Au and 60–80 ppm Ag.

In his deposit assessment report, Kłos (1955) noted As contents in the ore ranged from 0.16 wt.% to 30.17 wt.%, accompanied by 0.1 wt.% Zn, 0.5 wt.% Pb, < 0.1 wt.% Ni and 0-41 ppm Ag. The proven reserves quoted by Kłos (1955) amounted to about 8,000 metric tons at a cutoff grade of 2 wt.% As and a minimum ore thickness of 15 cm, with a further 11,000 t of probable reserves at deeper levels.

OPTICAL MICROSCOPY, MINERAL TEXTURES AND MINERAL CHEMISTRY

Polished sections of both the arsenopyrite and pyrrhotite ore (Fig. 2A, 2B) were examined and the resultant observations confirmed many of the mineral identifications made by previous workers. New to this study, however, are four minerals not previously identified for Czarnów: pentlandite (Fe,Ni)₉S₈; ferrokësterite $Cu_2(Fe,Zn)SnS_4$; low-Se ikunolite $Bi_4(S,Se)_3$ and bismite Bi_2O_3 .

The ore minerals form a variety of structures, such as spots, nests, streaks and pseudolayers, as well massive accumulations and thin veinlets that cut through other ore structures and host rocks. In most of the samples examined herein, the ore minerals are hosted in coarse- or medium-crystalline quartz that is intergrown with chlorite, rare feldspars and carbonates (calcite). Disseminated mineralization was found in only one polished thin section from a mica schist that contained cordierite?, feldspar and tourmaline.

Arsenopyrite

Optical microscopy on the arsenopyrites generally confirmed earlier observations (e.g., Zimnoch, 1985). Arsenopyrite is the main component of the Czarnów ore deposit, and it was identified in almost all the polished sections. Usually, it forms almost monomineralic spots or veinlets and occurs as coarse, euhedral to subhedral crystals up to several millimeters across (Fig. 2A, C). Similar, but finer-grained, crystals are disseminated in the ore vein's host rocks. Commonly, aggregates of arsenopyrite are cracked and these cracks are filled with quartz and/or chalcopyrite, the latter sometimes hosting inclusions of galena and Bi phases. Some aggregates, or even individual crystals, contain fine intergrowths of chalcopyrite and/or pyrrhotite. Pyrrhotite veinlets may cut arsenopyrite crystals.

Locally, arsenopyrite aggregates form microbreccias (Fig. 2D). Within these microbreccias are occasionally found euhedral arsenopyrite crystals that can vary in size from a few micrometers to nearly 1 mm and that are cemented together with quartz. Brecciated arsenopyrite and quartz sometimes fill the cracks in large arsenopyrite crystals or its aggregates. Moreover, arsenopyrite breccias with single pyrrhotite fragments can fill fractures in quartz. Such breccias are cemented with quartz with local admixtures of Fe hydroxides.

Arsenopyrite can also form intergrowths with galena (Fig. 2C), chalcopyrite (Fig. 3A, C) pyrrhotite (Fig. 3B), cassiterite (Fig. 4A) and, locally, pyrite (Fig. 4C). Large arsenopyrite crystals normally contain only traces of other ore minerals; but sometimes, galena, chalcopyrite and Bi-minerals fill cracks within large arsenopyrite crystals (Fig. 4C). Some pyrrhotite and chalcopyrite intergrowths suggest replacement of the host arsenopyrite, which proceeded from crystal boundaries and from cracks (Fig. 3A).

Microscopic studies indicate the presence of two generations of arsenopyrite, although precise categorization is impossible due to the variability of the ore structures and textures. Nevertheless, a seemingly early arsenopyrite (I) forms large, locally cracked and/or brecciated accumulations of monomineralic crystals. A later arsenopyrite (II) is mostly euhedral and/or subhedral, unbrecciated and usually contains pyrrhotite, chalcopyrite and galena intergrowths. These observations roughly correspond to the arsenopyrite varieties of Zimnoch (1985).

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Fig. 2. (A) Arsenopyrite ore with nest-like arsenopyrite (Apy) aggregates in quartz. Sample no. 1. (B) Pyrrhotite (Po) ore. Sample no. Cz-5/3. (C) Euhedral arsenopyrite (Apy) crystals with galena (Gn) intergrowths. Back scattered electron image. (D) Arsenopyrite (Apy) matrix-type breccia cemented with quartz. Reflected light, 1N. Sample no. Cz.1. Mineral symbols after Canadian Mineralogist

The chemical composition of the arsenopyrites is shown in Table 1. There are very consistent Fe values $(33.65 \pm 0.21 \text{ at.}\%)$ but somewhat more variable amounts of As (32.79 \pm 0.44 at.%) and of S (33.45 \pm 0.48 at.%). Although arsenopyrite aggregates do not reveal admixtures of Co, Ni and Ag above microprobe detection limits (Table 1), an admixture of Se was detected (0.16 wt.% average).

Pyrrhotite

In the pyrrhotite ore, pyrrhotite crystals can form spotty, nest-like and massive structures (Fig. 2B). Pyrrhotite is commonly accompanied by euhedral arsenopyrite crystals and can contain anhedral intergrowths of chalcopyrite and pyrite. Large pyrrhotite aggregates sometimes host flame-like structures of pentlandite. Locally, pyrite forms euhedral crystals within pyrrhotite. In the monomineralic arsenopyrite ore, pyrrhotite occurs as intergrowths with arsenopyrite I and with chalcopyrite (Fig. 3B) and is here termed pyrrhotite I. Some pyrrhotite grains, however, fill cracks in arsenopyrite I aggregates and clearly replace preexisting arsenopyrite I aggregates along crystal planes and crystal edges (Fig. 3A): these are

termed pyrrhotite II. The replacement of arsenopyrite by pyrrhotite (and chalcopyrite) is a common process in the pyrrhotite ore (Fig. 3) however, the relationship between pyrrhotite II and arsenopyrite II is unclear.

Microprobe analyses (Table 1) did not reveal any significant admixtures of trace elements, although the number of analyses was low.

Chalcopyrite

Chalcopyrite was observed in almost all of the polished sections, although in highly variable amounts. Chalcopyrite usually forms spots, veinlets and disseminated crystals. Some chalcopyrite veinlets show fault displacements (Fig. 4C). Monomineralic chalcopyrite accumulations were rare, chalcopyrite usually occurring as intergrowths with arsenopyrite (Fig. 3), pyrrhotite, native Bi (Fig. 4C) and pyrite. Some polished sections showed that chalcopyrite formed the matrix for arsenopyrite breccias and such ocurrences are here termed chalcopyrite I. A clearly later generaton of chalcopyrite occur as exsolutions in sphalerite aggregates and are here termed chalcopyrite II. Secondary covellitization has also affected some of the chalcopyrites (Fig. 3C).

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Table 1

Averaged electron microprobe chemical compositions of ore minerals from the Czarnów deposit (in vol.%)

Element	Arseno- pyrite*	Pyrr- hotite*	Sphalerite				Ferrkös- terite	Chalco- pyrite	Cuba- nite	Ikunolite	Bismu- thinite	Native Bi	Galena	
	n=20	n=2	n=2	n=2	n=3	n=1	n = 1	n=10	n=8	n = 3	n=1	n=2	n=13	n=10
S	19.80	39.01	33.58	33.35	33.13	32.92	32.83	29.44	35.01	35.90	10.07	18.22	0.04	13.22
Mn			0.02		0.04	0.03			0.02	0.02				
Fe	34.70	59.85	1	8.57	6.31	4.35	0.77	8.99	30.46	40.80			0.36	
Co														
Ni														
Cu			0.25	0.03	2.19	2.50	0.53	29.02	34.44	22.94			0.14	
Zn			54.86	56.94	56.34	58.33	65.40	4.95						
As	45.35	0.07	0.04	0.01	0.02				0.03	0.02				0.02
Se	0.16							0.07			0.06			0.07
Ag								0.03		0.03	0.13			0.43
Cd			0.88	0.91	0.89	0.84	0.17	0.15		0.02				0.05
In			0.06	0.02	0.06	0.03	0.22	0.09						
Sn								26.86	0.16					
Sb													0.04	
Те											0.24	0.12		
Pb														85.79
Bi											89.52	81.20	99.79	0.05
Total	100.01	98.93	99.68	99.83	98.98	99.00	99.92	99.61	100.12	99.72	100.02	99.53	100.38	99.63
	_						Apfu							
S	1.003	0.999	1.016	1.007	1.015	1.009	0.998	3.983	2.005	3.075	2.946	2.967	3	0.985
Mn					1	1			1	1				
Fe	1.010	0.880	0.174	0.149	0.111	0.077	0.013	0.698	1.002	2.006			0.013	
Cu			4		0.034	0.039	8	1.981	0.995	0.992			5	
Zn			0.814	0.843	0.846	0.877	0.975	0.328						
As	0.984	1	1						1	1				1
Se	3							4			7			2
Ag								1		1	0.011			0.010
Cd			8	8	8	7	1	6						
In					1		2	4						
Sn								0.982	2					
Sb													1	
Те											0.018	5		
Pb														0.989
Bi											4.017	2.029	0.981	1

* - Ni and Co contents below MPA detection limit

The chemical composition of the chalcopyrites is shown in the Table 1. Small amounts of Sn (0.16 wt.%) were the only detectable admixtures.

Sphalerite

Sphalerite usually occurs as intergrowths with chalcopyrite and ferrokësterite (Fig. 4B) and with cassiterite. Only sometimes does it occur as independent aggregates of anhedral grains. Some crystals contain minute exsolutions of chalcopyrite.

Microscopic observations did not provide clear evidence for distinguishing different generations of sphalerite. However, three groups of sphalerites could be distinguished based on sphalerite geothermometry (see below). Thus, we tentatively suggest that there are three generations of sphalerite.

The chemical composition of the sphalerites (Table 1) show a highly variable Fe content, ranging from below 1 wt.% to 10 wt.%. Sphalerites intergrown with chalcopyrite have high amounts of Cu (up to 2.5 wt.%). All the analysed sphalerite grains had high Cd contents at the level of 0.8–0.9 wt.%, except for a single, low-Fe grain which had only 0.17 wt.% Cd but increased amounts of In (0.22 wt.%).



Fig. 3. (A) Arsenopyrite (Apy) replaced by pyrrhotite (Po) and chalcopyrite (Ccp). Reflected light, 1N. Sample no. Cz.A-6. (B) Arsenopyrite (Apy) replaced by pyrrhotite (Po) and pyrrhotite-chalcopyrite (Ccp) intergrowths. Reflected light, 1N. Sample no. Cz.A-6. (C) Chalcopyrite (Ccp) replacing subhedral crystals of arsenopyrite (Apy); covellite (Cv) forms inclusions in chalcopyrite. Reflected light, 1N. Sample no. Cz.E-2.

Fig. 4. (A) Cassiterite (Cst) and arsenopyrite (Apy) intergrowths. Reflected light, 1N. Sample no. Cz 1. (B) Sphalerite (Sp) and ferrokësterite (Fkt) intergrowths. Back scattered electron image. Sample no. Cz.7-1. (C) Native bismuth (Bi) and galena (Gn) in chalcopyrite (Ccp) veinlet cutting arsenopyrite (Apy) aggregate. On the right pyrite (Py) and gangues veinlet cuts arsenopyrite. Back scattered electron image. Sample no. Cz.A4-7.

	Content range[wt.%]	Mean	Apfu
Fe ₂ O ₃	0.00-2.20	0.36	0.007
MnO	0.00-0.07	0.01	
WO ₃	0.00-0.56	0.06	
Nb ₂ O ₅	0.00-0.42	0.06	
Ta ₂ O ₅	0.00	0.00	
TiO ₂	0.00-1.36	0.37	0.007
SnO ₂	95.43-100.81	98.16	0.985
Total		99.01	

Pyrite

Pyrite predominantly occurs as disseminated crystals or as intergrowths with almost all other ore minerals, with the exception of galena and the Bi phases. Together with quartz, it also forms rare veinlets cutting arsenopyrite I aggregates (Fig. 4C). Microscopic observations revealed two generations of pyrite: pyrite I is contemporaneous with chalcopyrite, as both minerals form intergrowths; pyrite II is younger than pyrrhotite, as revealed by pyrrhotite grains replaced by pyrite and accompanying marcasite (see also Zimnoch, 1985).

Galena

Small amounts of galena were observed as minute intergrowths with arsenopyrite (Fig. 2C) and with native Bi (Fig. 4C), the latter encountered in chalcopyrite veinlets cutting arsenopyrite I.

In all the analysed galena grains, Ag was present (0.43 wt.% in average, Table 1) together with traces of Se and Bi, both of which were close to the EMP detection limits.

Cassiterite

Cassiterite usually occurs as aggregates of subhedral to euhedral crystals or, rarely, as single crystals. Internal reflections revealed that some crystals were zoned. Cassiterite also forms intergrowths with arsenopyrite (Fig. 4A).

The chemical compositions (Table 2) show that the cassiterite crystals are quite pure. Only a few analyses indicated admixtures of TiO_2 (0.2 wt.% max.), Nb₂O₃ (0.17 wt.% max.) and WO₃ (0.13 wt.% max.).

Ferrokësterite

In two polished sections, ferrokësterite occurred as minute intergrowths within both sphalerite (Fig. 4B) and chalcopyrite. Its crystals are whitish, with moderate reflectance (lower than chalcopyrite, but higher than sphalerite). Other optical features could not be effectively evaluated due to the small crystal size. Ferrokësterite had not been previously identified in the Czarnów deposit, though it had been described from the adjacent Rędziny marble quarry (Pieczka *et al.*, 2006).

The chemical analyses (Table 2) revealed significant amounts of Zn (4.95 wt.% average), which corresponds to a composition of ferrokësterite of $[Cu_2(Fe,Zn)SnS_4]$. Ad-

 Table 3

 Chemical electron microprobe composition of bismite (two analyses)

	wt.%	Apfu
Fe ₂ O ₃	0.21	0.01
CuO	0.29	0.02
Sb ₂ O ₃	0.05	0.00
Bi ₂ O ₃	99.89	1.97
Total	100.44	

mixtures of Cd (0.24 wt.% max.), In (0.22 wt.% max.), Se (0.1 wt.% max.) and Ag (0.69 wt.% max.) were detected.

Bi minerals

Four Bi phases were identified in the studied samples: native Bi, bismuthinite, ikunolite and bismite.

Native Bi and bismuthinite were rare species observed in only a few samples of arsenopyrite ore. Both minerals usually occur together and form intergrowths with galena when they occur in chalcopyrite veinlets that cut large, strongly crushed arsenopyrite aggregates (Fig. 4C). The native Bi contained a small quantity of Se (0.06 wt.% max.) (Table 1). Analyses of bismuthinite revealed Te concentrations between 0.12 wt% and 0.24 wt.% (Table 1). The traces of Fe (0.36 wt.%) in the native Bi may be a background effect of the accompanying minerals.

Microprobe analyses also revealed the presence of a Bi mineral with a composition close to the low-Se member of the ikunolite $Bi_4(S, Se)_3$ -laitakarite (Bi_4Se_3) series (Table 1). This Bi mineral, considered here to be ikunolite, occurs as very fine intergrowths with native Bi and, probably, with bismuthinite: hence its optical properties could not be unambiguously determined. Ikunolite has not previously been observed in the Czarnów deposit, but it has been identified in the adjacent Rędziny marble quarry (Parafiniuk *et al.*, 2008).

Bismite (Bi_2O_3) occurs as minute crystals accompanying native Bi aggregates, and, thus, its optical properties could not be reliably determined. Bismite is accompanied by several unidentified Bi-arsenate phases. Chemical composition of the bismites is shown in Table 3. Like ikunolite, bismite has not previously been identified in Czarnów ores, but it has been found in the Rędziny marble quarry (Parafiniuk, 2003).

Pentlandite

Pentlandite is a rare phase in the Czarnów deposit. It occurs as characteristic, flame-like intergrowths of various size that are randomly distributed at the edges of large pyrrhotite crystals, and sometimes also within pyrite crystals. Pentlandite was identified by optical microscopy, but its presence has not been confirmed with chemical analyses.

Cubanite

A few cubanite grains were found as intergrowths with native Bi. Its identification was confirmed by microprobe analyses (Table 1).



Fig. 5. Sulphur fugacity (log fS) versus temperature (T) diagram (after Kretschmar & Scott, 1976 and Sharp et al., 1985) for arsenopyrite from the Czarnów ore deposit. Mineral symbols: Apy (arsenopyrite), Bn (bornite), Ccp (chalcopyrite), Enr (enargite), Fe (metallic iron), Lo (löllingite), Po (pyrrhotite), Py (pyrite), Tn (tennantite).

Marcasite

Marcasite was observed as narrow rims on, and intergrowths with, pyrite on pyrrhotite aggregates.

Ti-minerals

Small, disseminated crystals of titanite and rutile occurred within all the samples but were not studied in detail.

GEOTHERMOMETRY

The results of EMP analysis allowed us to determine the crystallization temperatures of some of the ore minerals from the Czarnów deposit (Fig. 5).

Arsenopyrite has stable Fe contents (33.65 ± 0.21 at.%), but is somewhat variable in S (33.45 ± 0.48 at.%) and As (32.79 ± 0.44 at.%). Substitution of As for S indicates that arsenopyrite crystallized under evolving thermal conditions. In theory, the initial crystallization temperature of arsenopyrite containing 33.7 at.% As and remaining in equilibrium with pyrrhotite should be 515 °C or less: however, such equilibrium with pyrrhotite could not be demonstrated for the Czarnów arsenopyrite. Nevertheless, given that arsenopyrite and pyrrhotite are the two main minerals of the Czarnów ore, it is reasonable to sug-

gest that at least part of arsenopyrite crystallized close to equilibrium with pyrrhotite at temperatures somewhat lower than 515 °C. During the crystallization of arsenopyrite, equilibrium for the pyrrhotite-pyrite pair was exceeded and late-stage arsenopyrite crystallized under conditions of pyrite stability. The final crystallization temperature of arsenopyrite containing 31.9 at.% As can be estimated as about 420 °C, assuming equilibrium with pyrite. This seems reasonable because if equilibrium had not been reached, arsenopyrite formation would have ceased at somewhat higher temperature. The lack of other As-rich ore minerals may suggest that the end of arsenopyrite crystallization was due to exhaustion of As in solution, and this took place slightly above 420 °C. Sphalerite samples had variable Fe contents: from over 17 mol.% to about 1 mol.% FeS. The earliest sphalerites are those with the highest Fe contents, and these must have crystallized under conditions of pyrite stability, not pyrrhotite, i.e., during the final stage of arsenopyrite crystallization. Crystallization of sphalerite from medium- temperature hydrothermal solutions (about 320 °C) is confirmed by exsolution textures of ferrokësterite and chalcopyrite.

Ferrokësterite crystallizes as minute inclusions in sphalerite. Applying the stannite-sphalerite geothermometer (Nakamura & Shima, 1982) and considering the chemical compositions of coexisting crystals, the crystallization temperature of this assemblage was calculated as 320 ± 5 °C. Taking into account FeS mol. contents, sphalerite crystallized over a wide temperature range, from over 400 °C to below 200 °C. It must be emphasized that the sphalerite in this study contains a low, but stable, amount of Cd (0.8–0.9 wt.%), which decreases with decreasing Fe contents, and it is practically Ag-free. This latter feature may suggest a deficit of Ag in the hydrothermal solutions at about 300 °C. Moreover, sphalerite with inclusions of chalcopyrite and ferrokësterite shows some enrichment in Cu (2.5 wt.% max.) and traces of Sn (usually below EMP detection limits). The presence of both Cu and Sn trace elements suggests that the sphalerite-chalcopyrite-ferrokësterite assemblage resulted from decomposition of a higher-temperature mineral of general formula (Zn, Cu, Sn)S.

Assuming that the Czarnów ore mineralization is comparable to that at Rędziny, the approximate temperature of galena crystallization was about 300 °C or more (Pieczka *et al.*, 2009). This lower-temperature galena contained only insignificant admixtures of Ag..

Cassiterite, formed at temperatures below 400 °C because it crystallized after the arsenopyrite. This agrees with temperature determinations of 412–285 °C for cassiterites from the Rędziny quarry (Mochnacka *et al.*, 2001). Contemporaneous crystallization of ferrokësterite and sphalerite at temperatures around 320 °C indicates that there was equilibrium of SnS/SnO₂ between the activity of sulphur and the activity of oxygen in the mineralizing hydrothermal solutions.

FLUID INCLUSIONS

Fluid inclusion thermometry was applied to samples of quartz that had been taken from ore veins fragments collected from the waste dumps. Three types of inclusions were identified.

Type 1: these include large (up to 30 μ m), mostly irregular, inclusions that may be either single or clusters of two to three individuals. Inclusions can be two-phase (V + L) or three-phase (L1 + V1 + V2) (liquid and gaseous CO₂, and H₂O vapour). Large inclusions are accompanied by small, oval individuals that are less than 10 μ m in diameter, two-phase and rich in CO2. Small inclusions occur as short rows or cellular forms. The Type 1 represent primary inclusions (as defined by Roedder, 1984), are the oldest in the studied set, and possess CO2 melting temperatures from -56.9 °C to -60.7 °C. The decrease in this temperature suggests the presence of methane. Ice melting starts between about -23 °C and -8 °C, with full melting occuring between -6.8 °C and -0.2 °C. Gas hydrate dissolves between 6.3 °C and 13.8 °C. Homogenization of CO₂ towards the gaseous phase was noticed at temperatures ranging from 8.5 °C to 26.3 °C. The temperature of full homogenization fell into a wide range (between 300

°C and 430 °C) but a large number of inclusions did homogenize towards liquid between 350 °C and 370 °C.

Type 2: these comprise single, isolated inclusions corresponding in size to those of Type 1 but are two-phase, rich in H₂O. Gaseous components constitute 30-35% of inclusion space. Rarely, Type 2 inclusions accompany those of Type 3 (below). Type 2 inclusions are also primary but younger than those of Type 1. Some of them can be categorized as syngenetic. Type 2 inclusions reveal ice melting temperatures from -2.9 °C to -0.4 °C. Full homogenization occured between 150 °C and 330 °C.

Type 3: these are small, single- or two-phase inclusions, ranging in diameter from a few to a dozen micrometers. They are distributed in rows or cover larger surfaces and are related to cracks within crystals. Type 3 inclusions are mostly secondary, though some can be regarded as syngenetic, and display the lowest range of homogenization temperatures (126 °C to 209 °C). Ice melting was observed at temperatures between -13 °C and 0 °C. As these are secondary inclusions, their homogenization temperatures were excluded from interpretations.

MINERAL SUCCESSION

Mineral paragenetic (crystallization) sequences have only rarely been attempted in the literature on the Czarnów ore deposit.

Petrascheck (1933) proposed the sequence arsenopyrite + pyrite, then pyrhotite + sphalerite, then chalcopyrite, and finally galena.

A much more detailed paragenesis was proposed by Zimnoch (1985): cassiterite – coarse-crystalline arsenopy-

rite – coarse-crystalline pyrrhotite – pyrite I – chalcopyrite I – sphalerite I – native Bi + Bi-sulphosalts – galena – tennantite – finely crystalline arsenopyrite – products of solid solution decomposition (chalcopyrite II, sphalerite II, pyrrhotite II, cubanite, valeriite) – marcasite + pyrite (formed by decomposition of pyrrhotite) – supergene minerals (chalcocite, covellite, goethite, skorodite, digenite, secondary chalcopyrite, pyrite "rosettes"). The present authors herein propose an ore mineral succession for the Czarnów ore deposit that is based upon optical microscopy of mineral intergrowths and aggregations and supported by geothermometry data (Fig. 6).

The oldest mineral in the succession is arsenopyrite I. Textures within arsenopyrite aggregates suggest there are two generations: a higher-temperature (515 °C) arsenopyrite I, and a lower-temperature (420 °C) arsenopyrite II (see above). An older generation of pyrite (pyrite I) preceeds pyrrhotite but its relationship to arsenopyrite is unclear. These three oldest minerals are followed by pyrrhotite, chalcopyrite and sphalerite. The cataclastic structures shown by arsenopyrite suggest the importance of tectonic events coeval with the crystallization process.

Pyrrhotite I forms intergrowths with arsenopyrite and probably formed at early stage of ore formation when both minerals were in equilibrium. Pyrrhotite II fills cracks in arsenopyrite I aggregates and replaces arsenopyrite I. The relationship between pyrrhotite II to arsenopyrite II is unclear.

Pyrite I is enigmatic because although it fills cracks in arsenopyrite, and so seems to be later than the cataclastic event, it also forms euhedral crystals within pyrrhotite II, which suggests that it is somewhat earlier. Pyrite II crystallized in equilibrium with arsenopyrite II at the end of FeAsS crystallization stage.

Chalcopyrite I formed somewhat after the cataclastic event as it fills cracks cutting arsenopyrite I aggregates. Chalcopyrite II occurs as an exsolution phase in sphalerite.

Cassiterite seems to be later than arsenopyrite I because no traces of cataclasis were observed. Unfortunately, the relative scarcity of this mineral precludes more detailed observations of its relationships to arsenopyrite and pyrrhotite. If one extrapolates from the nature of the cassiterite that occurs in the adjacent Rędziny marble quarry, then it can be hypothesized that this mineral crystallized at about 400 °C (Mochnacka *et al.*, 2001).



Fig. 6. Succession of ore minerals from the Czarnów ore deposit (excluding weathering phases). Crystallization temperatures [°C] are given in Arab numerals. Separate generations of minerals are given in Roman numerals. Not to scale.

Sphalerite crystallized over a wide range of temperatures, from over 400 °C for the high-Fe sphalerites – consistent with the end of arsenopyrite II crystallization when presumably some Fe was released after exhaustion of As in the system – through to about 320 °C for the sphalerite– chalcopyrite–ferrokësterite association, and down to about 200 °C.

Galena crystallization temperatures at Czarnów are inferred from analogous galenas that were analyzed from the Rędziny quarry (Pieczka *et al.*, 2009): these galenas probably crystallized at only about 300 °C. Nevertheless, galena apparently continued to crystallize at still lower temperatures, as deduced from intergrowths of galena with primary, low-temperature native Bi, bismuthinite and ikunolite.

DISCUSSION

Research on the Czarnów ore deposit can be divided into the two groups based on *in situ* versus loose sample collection. The older research, which was carried out by German geologists, as well as the later investigations by Banaś (1967) and, partly, by Zimnoch (1985), were based upon samples collected directly from the operating mine. Subsequent researchers, however, including the authors of this paper, have had to be content with studying loose samples collected from waste dumps: hence, detailed locality data remains unknown or hypothetical (e.g., arsenopyrite ore *versus* pyrrhotite ore, ore vein *versus* contactmetasomatic rocks).

About 150 years of studies on the Czarnów ores has demonstrated the presence of an abundant assemblage of sulphides, sulphoarsenides, sulphosalts and native phases. This paper adds four more, hitherto unrecognised, phases from the Czarnów ores: pentlandite, ferrokësterite, ikunolite and bismite.

The optical features and chemical composition of

ferrokësterite generally agrees with data published by Kissin & Owens (1989) and with data on ferrokësterite from the Rędziny quarry (Pieczka *et al.*, 2006) but detailed measurements of optical properties could not be made. Data for ikunolite were consistent with that published by Parafiniuk *et al.* (2008).

Microscopic observations, supported by geochemical data, provide evidence for a diverse assemblage of ore minerals and also offers insight into their succession (Fig. 6).

The oldest minerals in succession is arsenopyrite I which crystallized at about 515 °C and was accompanied by small amounts of pyrrhotite I when both minerals were in equilibrium. These minerals formed the early, high-temperature pulse of mineralizing solutions and were followed by an unidentified tectonic event that caused the cataclasis of arsenopyrite I. Insignificant amounts of pyrite I and chalcopyrite I, although later than the brecciation, can also be ascribed into this early pulse. However, detailed relationships between arsenopyrite I and pyrite I re-

main unclear. The mineralizing solutions were rich in Fe, As and S.

The next mineralizing pulse, at the temperature about 400 °C, included lower-temperature arsenopyrite II, pyrrhotite II, pyrite II, chalcopyrite, higher-temperature sphalerite and traces of cassiterite. It seems that arsenopyrite II and pyrite II crystallized in equilibrium. The position of chalcopyrite at this stage is doubtful, as the authors did not find sufficient evidence for distinguishing separate generations of CuFeS. At the end of this pulse the mineralizing solutions became depleted in As but enriched in Zn and Sn.

The final mineralizing pulse (from about 320 °C down to 200 °C) precipitated medium- and low-temperature sphalerites with some exsolution of chalcopyrite II, galena, Bi minerals and ferrokësterite. Late calcite veinlets might have formed from even lower temperature solutions (Hoehne, 1941; Banaś *et al.*, 1996). At this stage the mineralizing solutions became enriched in Bi and Pb.

The two latter stages of mineralization were accompanied by quartz, which crystallized over a wide temperature range, from about 430 °C down to about 150 °C.

The mineral succession shown above documents more generally the evolving nature of the mineralizing solutions from an early, high temperature Fe-As-S association, through a medium-temperature Fe-Cu-As-S association, to a low-temperature Zn-Pb-Bi-Sn association.

The crystallization temperatures determined herein are consistent with data by Mikulski (2001) for both the ore minerals and for the quartz. Furthermore, the crystallization temperature of native Bi (about 270 °C) reported by Zimnoch (1985) fits with our data.

Mikulski (1997) raised some doubts concerning the applicability of the arsenopyrite geothermometer when arsenopyrite was intergrown with other minerals: we analyzed arsenopyrite aggregates that were either free from intergrowths or that had only minute inclusions of other sulphides which themselves were outside the analytical zone of the EMP beam. The chemical data confirmed the purity of the arsenopyrite grains (admixtures of Se only), and demonstrated that the Czarnów arsenopyrite grains met the criteria set out in Kretschmar & Scott (1976) for accurate geothermometry.

The origin of the Czarnów deposit is still a matter of debate. Berg (1913) interpreted it as a skarn deposit, noting the deposit's location in the contact aureole of the Karkonosze granite where there are known skarns. Petrascheck (1933, 1934) and Zimnoch (1985) considered Czarnów to be a hydrothermal vein deposit, still related to the Karkonosze granite. Banaś (1967) suggested that the Czarnów ore resulted from "complicated polymetamorphic processes". Later, Banaś *et al.* (1996) proposed a two-stage formation process in which most of the ore formed via contact metamorphism by the Karkonosze granite, followed by later hydrothermal depositions. Finally, Mikulski (1997) compared the Czarnów ores to analogous ores from the Bohemian Massif and proposed that the metals of the Czarnów deposit resulted from primary, volcano-sedimentary processes.

Because it was impossible to examine in situ ore-host rock relationships and, equally, arsenopyrite ore-pyrrhotite ore-galena ore relationships, only the most general genetic considerations can be drawn. Based on the totality of the evidence to date – ore structures seen in hand specimen; ore textures in polished thin sections; ore mineralogy; and mineral geochemistry – we propose that the Czarnów ores were formed by hydrothermal solutions. Ore formation apparently started just prior to an unidentified tectonic episode, as documented by the cataclasis of the older arsenopyrite I, and lasted until the final low-temperature quartz (and/or calcite) precipitated from residual solutions depleted in base metals, sulphur and arsenic.

In the marble quarry at Redziny, about 2 km away and which also belongs to the Izera-Kowary Unit, is a similar, yet more diverse, ore mineral assemblage (Pieczka & Gołębiowska, 1997 and references therein). Whereas the Czarnów deposit is dominated by arsenopyrite, the Rędziny deposit contains cassiterite and Bi minerals, a fact that may reflect a local variability in the chemistry of the basement rocks from which the metals and other elements might have been hydrothermally scavanged, as proposed by Mikulski (1997). Perhaps both the Czarnów and the Rędziny ore deposits belong to the same hydrothermal cell system, which was driven by the thermal energy of the Karkonosze granite and was structurally controlled both by local tectonics on the scale of deposit itself (Kłos, 1955; Banaś, 1967; Zimnoch, 1985) and by the regional- scale Leszczyniec shear zone (Mikulski, 2001).

According to the local categorization of ore deposits that are hosted within the metamorphic envelope of the Karkonosze granite (Mochnacka, 2000), the Czarnów deposit belongs to the so-called stage III, *i.e.*, vein- or stockwork-type deposits that have a strong tectonic signature.

The age of ore formation is controversial. The only isotopic age determinations are from Czarnów ore minerals (Legierski, 1973) using the Pb–Pb model applied to galena, which gave ages of 250 Ma and 210 Ma. However, these results were criticized by Vaněček *et al.* (1985) as too young. In fact, the time gap between the isotopic age of crystallization of the Karkonosze intrusion (328–305 Ma; Pin *et al.*, 1987; Duthou *et al.*, 1991; Kröner *et al.*, 1994; Machowiak & Armstrong, 2007) and the galena ages (250–210Ma; Legierski, 1973) may rise some doubts concerning the duration of hydrothermal cell. Perhaps a long circulation period for the mineralizing solutions could produce a much larger ore deposit than those known from the granite itself and from its metamorphic envelope.

CONCLUSIONS

New mineral, textural, geochemical, fluid inclusion, and geothermometric data on the Czarnów ore deposit allow for some general statements. First, the minerals pentlandite, ferrokësterite, ikunolite and bismite are reported for the first time from Czarnów. Second, thermochemical analysis revealed that crystallization temperatures of the ore minerals were within the range of 515 °C down to about 200 °C; fluid inclusion analysis showed that the quartz crystallized between 430 °C to 150 °C. Third, microscopic observations of ore structures and textures allowed a mineral succession to be constructed that developed from a high-temperature arsenopyrite I-pyrrhotite I association down to the low-temperature crystallization of galena, (low-temperature) sphalerite, ferrokësterite and Bi minerals. Fourth, the high-

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