Original paper

Polymetallic mineralization in Ediacaran sediments in the Żarki-Kotowice area, Poland

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Abstract. In one small mineral vein in core from borehole 144-Ż in the Żarki-Kotowice area, almost all of the ore minerals known from related deposits in the vicinity occur. Some of the minerals in the vein described in this paper, namely, nickeline, hessite, native silver and minerals of the cobaltite-gersdorffite group, have not previously been reported from elsewhere in the Kraków-Lubliniec tectonic zone. The identified minerals are chalcopyrite, pyrite, marcasite, sphalerite, Co-rich pyrite, tennantite, tetrahedrite, bornite, galena, magnetite, hematite, cassiterite, pyrrhotite, wolframite (ferberite), scheelite, molybdenite, nickeline, minerals of the cobaltite-gersdorffite group, carrollite, hessite and native silver. Moreover, native bismuth, bismuthinite, a Cu- and Ag-rich sulfosalt of Bi (cuprobismutite) and Ni-rich pyrite also occur in the vein. We suggest that, the ore mineralization from the borehole probably reflects post-magmatic hydrothermal activity related to an unseen granitic intrusion located under the Mesozoic sediments in the Żarki-Pilica area.

Key-words: Małopolska Block, ore mineralization, cobaltite, nickeline, wolframite

1. Introduction

All bore-holes in the Żarki-Kotowice area were drilled during the last two decades of the last century (Fig. 1). Several drillings intersected Mesozoic sediments and youngest Precambrian strata. The average depth of the Mesozoic profiles is ca 500 m. Only the

deepest rock complexes situated below 500 m were recognized as Ediacaran sediments. After a long interval, a new deep research bore-hole (ZW-1) was drilled in 2008 in the area. The total length of the drill core is 800.3 m of which 332.3 m constitute Precambrian rocks.

In almost all core samples, ore mineralization is evident. The first preliminary ore investigation took place during examination of the core (Wołkowicz et al. 1992). Studies of the material were continued by Markowiak and Habryn (2003) and Lasoń and Markowiak (2008). The main results of these investigations were descriptions of the visible zonation of the rocks caused by metasomatic mineral changes and of the ore mineralization (Markowiak, Habryn 2003).
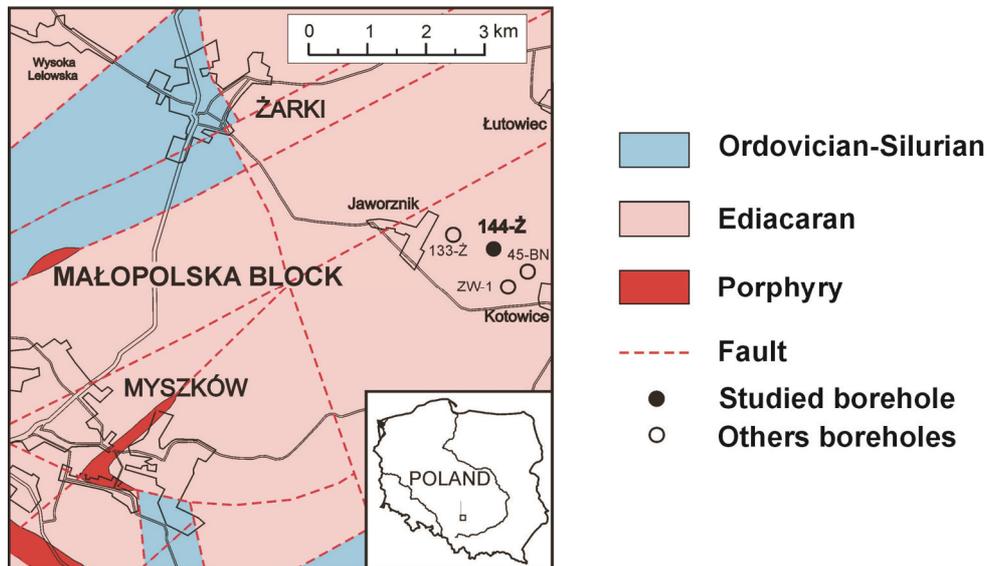
Fig. 1. Location of the 144-Ż borehole in the Małopolska Block.

2. Geological setting

The main structural element of the area studied is the Kraków-Lubliniec tectonic zone. It is a regional fault that was active many times during its geological history (e.g. Żaba 1999). The faulted rocks are Precambrian sedimentary complexes. This tectonic zone, most active from Cambrian- to Permian times (Buła 2000; Buła et al. 1997; Żaba 1999), separates the Małopolska Block from the Upper Silesian Block. Polymetallic mineralization occurs along the contact between the blocks. Ore concentrations are related to small territories, so called "districts". The 144-Ż bore hole is located near Żarki in the western part of the Małopolska Block (Fig. 1).

Ediacaran sediments in the western part of the Małopolska Block are dominated by reddish/brownish- or grey/greenish clastic rocks. They are represented by claystones and fine-grained polimict conglomerates. The rocks show features characteristic of low-grade metamorphism reflecting diagenesis and anchimetamorphic processes. An intrusion of

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granite into these rocks caused widespread alternation. The altered rocks, originally claystones, mudstones and sandstones, are almost identical in their chemical- and mineralogical compositions, and in their textural- and structural features, to similar rocks from the Mo-W-Cu deposit in Myszków formed after emplacement of a similar intrusion (Truszel 2001). The wall-rock mineral composition and rock structure were changed on a large scale. The alternations are visible as changes in the rock color. Black-coloured rocks dominate out to 800 m from the intrusion (biotitization). Outside, up to 1500 m, the color changes to gray and greenish.

In the ZW-1 borehole, intense veining is observed, with the concentration of veins ranging from a few up to tens per meter of drill core. Most of the veins are less than 3 mm thick. The veins are filled with gangue minerals such as quartz, feldspar, calcite, chlorite, sericite (muscovite), biotite and barite. Dispersed in the gangue are magnetite, hematite, wolframite (ferberite), cassiterite, ilmenite, rutile, sphen, pyrite, pyrrhotite, marcasite, chalcopyrite, bornite, sphalerite, galena, molybdenite, scheelite, Bi-minerals (native bismuth, bismuthinite, wittichenite, aikinite and others) argentite, pyrite-melnikovite, arsenopyrite and anglesite (Lasoń, Markowiak 2001; Markowiak, Habryn 2003). Ore minerals are also present in the country rocks.

Alterations due to K-feldspar metasomatism, sericitization, chloritization, epidotization and argilization are all evident in the Ediacaran sediments. The hydrothermal changes are related to the ore veins. No magmatic rocks were affirmed by the drillings made in the Żarki-Kotowice area. However, ore mineralization and metasomatic changes can be evidence of magmatic activity and granitoid emplacement - as in the case of the ore deposit in the Myszków area. An extensive gravity anomaly does suggest the presence of a magmatic body between Pilica and Żarki (Cieśla et al. 1984).

Geochemical- and petrographical investigations of the 144-Ż borehole show that it intersects the marginal part of a porphyric mineralization zone (Lasoń, Markowiak 2001). The secondary alternations seen in the Żarki Area, and the mineral association of the part enriched in ore minerals, are almost the same as in nearby mineralised areas, e.g. Pilica (Harańczyk 1983), Myszków-Mrzygłód (Ślósarz 1994) and in the Zawiercie Area (Górecka 1978; Harańczyk 1983). These various occurrences of mineralisation may have a genesis connected with the Variscan cycle that is common to all (e.g. Oszczepalski et al. 2010).

3. Analytical techniques

At the Faculty of Earth Sciences, University of Silesia, polished samples were examined using a NIKON E600 POL optical microscope and a Philips XL30 ESEM/TMP scanning electron microscope equipped with EDS (EDAX type Sapphire) detector was used for preliminary mineral-phase identification. Microprobe analyses of minerals and BSE photography were carried out using a CAMECA SX-100 electron microprobe at the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances in Warsaw.

The analytical conditions for analysis of metallic phases were: accelerating voltage 15 kV, beam current 20 nA, counting time 6 seconds on samples and standard. The counting time ranged from 10-20 seconds on both sample and standard. Analytical lines (and standards) used were: TeLα (PbTe), MnKα (Rhod), FeKα (Fe_2O_3), CuKα (Cpy), ZnKα (Sph), AsLα (GaAs), SeLα (ZnSe), SKα (Spha), PbMα (PbS), BiMα (Bi_2Te_3), AgLα (pure

metal), CdLα (CdS), InLα (InAs), SnLα (Cass), NiKα (NiO), CoKα (CoO), CaKα (Woll), WMα (CaWO$_4$), MoLα (MoS$_2$) and SbLα (InSb).

4. Results

The main feature of the ore mineralization is a network of veins. As noted above, the numbers of veins range from a few up to tens per meter of core. A typical ore vein is <3 mm thick. The vein forming minerals are mainly quartz, chlorite, alkali feldspar, muscovite-biotite aggregates and barite.

One of the most interesting of the ore veinlets occurs in the metaclaystone rich part from the core at a depth of 498.6 m. The veinlet cuts a fine-grained host rock rich in quartz, carbonates, biotite and chlorite and with apatite and zircon as the only accessories. The total amount of ore minerals in the vein ranges between 25-30vol.%. Obvious alternation extends for a few millimeters from the vein contact (Fig. 2).

Fig. 2. Section of the studied drill core (borehole 144-Ż, depth 498.6 m). In the lower part of the core, an ore vein with light metasomatic aureole is visible.

Ore minerals in the veinlet comprise all previously-known minerals from the Kraków-Lubliniec area, and some new minerals not noted before. These minerals are chalcopyrite, pyrite, sphalerite, Co-bearing pyrite, marcasite, tennantite and tetrahedrite, bornite, galena, magnetite, hematite, cassiterite, pyrrhotite, wolframite (ferberite), scheelite, molybdenite, nickeline, a mineral phase belonging to the cobaltite-gersdorffite solid solution, carrollite, hessite and native silver. In addition, bismuth, bismuthinite, a Bi-rich sulfosalt with copper and silver (cuprobismutite?) and Ni-bearing pyrite were noted, as well as ilmenite in the metasomatic aureole. Some minerals reported in this paper, i.e. nickeline, hessite, native silver and the cobaltite-gersdorffite phase have not been noted before in the Kraków-Lubliniec area.

One of the earliest minerals to crystallize was a wolframite member with a very low manganese content. It is ferberite with the chemical composition ($Fe_{0.83-0.84}$, $Mn_{0.14-0.15}$)WO_4 (Table 1) and a well-defined bireflectance and anisotropy. The lack of internal reflections is due to the presence of Fe in the structure. All wolframite grains are elongate (<250 µm) and thin (<a few µm). Wolframite found as inclusions in quartz is mostly replaced by scheelite (Fig. 3).

TABLE 1

WDS composition in wt% and crystal-chemical formulae (4 O^{2-}) of wolframite

	1	2	3	4	5	6	7
W	60.32	60.14	60.32	60.46	60.61	60.40	60.41
Fe	15.39	15.24	15.39	15.29	15.03	14.96	15.18
Mn	2.64	2.76	2.78	2.45	2.54	2.53	2.72
O	20.93	20.87	20.97	20.88	20.87	20.79	20.91
Σ	99.29	99.03	99.47	99.10	99.07	98.70	99.24
W^{+6}	1.00	1.00	1.00	1.01	1.01	1.01	1.01
Fe^{+2}	0.84	0.84	0.84	0.84	0.83	0.82	0.83
Mn^{+2}	0.15	0.15	0.15	0.14	0.14	0.14	0.15
O^{-2}	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Σ	5.99	5.99	6.00	5.98	5.98	5.98	5.99
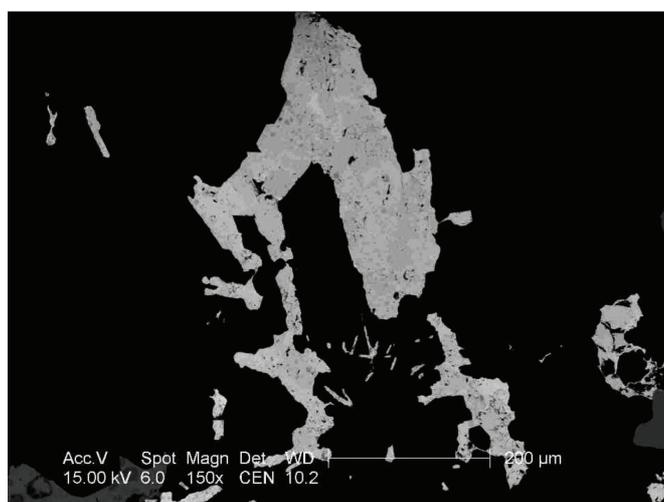
Fig. 3. BSE image of wolframite (ferberite) aggregates (lighter spots) almost totally replaced by scheelite (darker spots).

Scheelite observed in reflected light displays colorful internal reflections. Oxides and hydroksyoxides of iron occur between scheelite grains. The scheelite composition is shown in Table 2.

TABLE 2

WDS composition in wt% and crystal-chemical formulae (4 O^{2-}) of scheelite

	1	2	3
W	63.83	63.88	63.78
Ca	13.88	13.82	13.97
Fe	0.09	0.03	0.01
Mn	0.00	0	0
O	22.23	22.20	22.234
Total	100.05	99.94	100.00
W^{+6}	0.999	1.001	0.999
Ca^{+2}	0.997	0.994	1.004
Fe^{+2}	0.005	0.002	0.000
Mn^{+2}	0.000	0.000	0.000
O^{-2}	4.000	4.000	4.000
Σ	6.001	5.997	6.003

One of the rare mineral phases present is molybdenite. It occurs as very thin and small flakes included in quartz. Optical identification was confirmed by electron microprobe analyses. In the core from a depth of 514.8 m, overgrowths of molybdenite and wolframite (Markowiak, Habryn 2003) are indicative of the simultaneous growth of these two minerals.

Bismuthinite occurs as rare isometric grains in quartz. Electron microprobe analyses reveal the presence of Cu, Bi, S and Ag in some parts of the crystals. The analyses may suggest the local presence of cuprobismutite as small lamellae in the bismuthinite. A few grains of native bismuth as inclusions in chalcopyrite were also noted.

The main ore mineral is chalcopyrite characterized by amoeba-like grains <2 mm in diameter and with visible anisotropy. Galena and sphalerite are the most common sulphide inclusions in the chalcopyrite. In some instances, bornite (secondary?) forms thin coronas on chalcopyrite grains.

In the chalcopyrite grains, a lighter mineral phase with high relief was noted. The color of this mineral is similar to that of pyrite. The habit of the grains is hipautomorphic and they are isotropic. They are cracked and filled by secondary chalcopyrite (Fig. 4A, B). EMP investigation reveals the presence of carrollite. Carrollite was noted by Harańczyk (1983) in the NE area of the Upper Silesian Unit.
All of the analyzed grains have similar chemical compositions (Table 3).

The general chemical formula of the carrollite is ($Cu_{(0.940 - 0.899)}$, $Fe_{(0.101 - 0.060)}$) ($Co_{(1.870 - 1.600)}$, $Ni_{(0.127 - 0.049)}$, $Fe_{(0.321 - 0.060)}$) S_4. All of the analyzed grains belong to the Co-rich end-member. The Fe content is higher than Co and Ni in all.
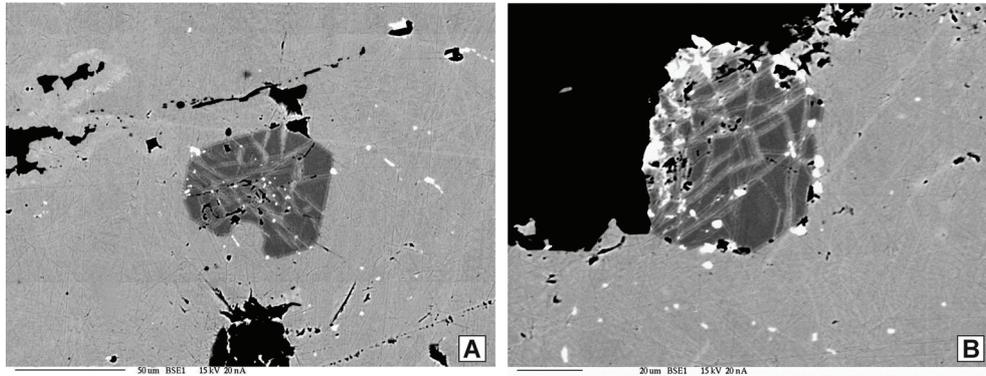
Fig. 4. (A, B) BES image of cracked carrollite crystal (dark grey) in chalcopyrite (light grey). The cracks are filled by chalcopyrite. The white dots are galena.

TABLE 3

WDS composition in wt% and crystal-chemical formulae (4 S^{2-}) of carrollite

	1	2	3	4	5	6	7	8	9	10	11	12
Fe	3.80	3.20	3.60	5.95	6.93	6.88	3.73	3.16	3.56	5.95	6.84	6.76
Co	34.74	35.68	34.89	30.55	31.14	30.37	34.06	35.26	34.55	30.55	30.76	29.84
Ni	0.92	1.02	0.96	2.41	1.27	1.49	0.90	1.01	0.96	2.41	1.26	1.46
Cu	18.88	18.50	18.77	19.31	18.88	19.18	18.51	18.28	18.58	19.31	18.65	18.85
S	41.49	41.53	41.41	41.48	41.54	41.23	42.32	42.50	42.04	42.60	42.23	42.27
Σ	99.85	99.96	99.65	99.72	99.79	99.17	99.54	100.23	99.70	100.84	99.75	99.21
Cu^{+2}	0.92	0.90	0.91	0.94	0.92	0.94	0.88	0.87	0.89	0.92	0.89	0.90
Fe^{+2}	0.08	0.10	0.09	0.06	0.08	0.06	0.12	0.13	0.11	0.08	0.11	0.10
Σ M^{+2}	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Co^{+3}	1.82	1.87	1.83	1.60	1.63	1.60	1.75	1.81	1.79	1.56	1.59	1.54
Ni^{+3}	0.05	0.05	0.05	0.13	0.07	0.08	0.05	0.05	0.05	0.12	0.07	0.08
Fe^{+3}	0.13	0.08	0.11	0.27	0.30	0.32	0.09	0.06	0.09	0.24	0.26	0.27
Σ M^{+3}	2.00	2.00	2.00	2.00	2.00	2.01	1.88	1.92	1.93	1.92	1.91	1.88
S^{-2}	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Σ	7.00	7.00	7.00	7.00	7.00	7.01	6.88	6.92	6.93	6.92	6.91	6.88

Explanations: M^{2+} position – Cu^{2+} position, M^{3+} position – Co☐N^{3+} position

Another pyrite-like mineral enclosed in chalcopyrite is a phase from the cobaltite-gersdorffite group which occurs as xenomorphic grains up to 150 μm in size. The analyzed crystals are characterized by variable Co, Fe and Ni. The Cu content is relatively low (Beziat et al. 1996; Table 4). The general chemical formula of this phase is (Co$_{(0.716 – 0.635)}$,Ni$_{(0.182 – 0.121)}$,Fe$_{(0.169 – 0.149)}$,Cu$_{(0.013 – 0.008)}$)As$_{(1.009 – 0.919)}$ S$_{(1.081 – 0.991)}$.

TABLE 4

WDS composition in wt% of mineral from the cobaltite-gersdorffite group. All analyses were calculated according to the sum of $(As+S)_{\Sigma=2}$

	1	2	3	4	5
Co	22.94	22.04	22.70	24.85	23.95
Ni	6.65	6.55	5.96	4.25	6.69
Fe	5.70	5.80	5.60	5.07	5.79
Cu	0.51	0.51	0.32	0.50	0.03
As	44.25	45.35	45.22	45.86	44.94
S	19.04	19.60	19.71	19.20	19.21
Total	99.11	99.87	99.54	99.75	100.63
Co	0.657	0.615	0.632	0.697	0.678
Ni	0.191	0.184	0.167	0.121	0.190
Fe	0.172	0.171	0.165	0.150	0.173
Cu	0.014	0.013	0.008	0.013	0.001
As	0.997	0.995	0.991	1.011	1.001
S	1.003	1.005	1.009	0.989	0.999
Σ	3.035	2.983	2.972	2.979	3.042

TABLE 5

WDS composition in wt% of nickeline. All analyses were calculated according to the sum of $(As+S)_{\Sigma=1}$

	1	2	3
Ni	41.84	42.01	41.25
Co	0.24	0.29	0.33
Fe	1.81	1.84	2.46
Cu	0.14	0.00	0.00
As	55.10	54.34	55.82
S	0.69	0.84	0.20
Total	99.83	99.33	100.09
Ni^{+2}	0.942	0.953	0.935
Co^{+2}	0.005	0.007	0.008
Fe^{+2}	0.043	0.044	0.059
Cu^{+2}	0.003	0.000	0.000
As^{-2}	0.972	0.965	0.991
S^{-2}	0.028	0.035	0.009
Σ	1.993	2.003	2.002

Nickeline, a rare component, occurs as very small xenomorphic grains with the characteristic salmon color. The nickeline displays bireflectance and strong anisotropy. The chemical composition is very stable. Fe, Co and Cu contents are small (Table 5). The general chemical formula of this phase is $(Ni_{(0.949-0.947)}, Fe_{(0.045-0.042)}, Co_{(0.008-0.006)}, Cu_{0.003})(As_{(0.994-0.972)}, S_{(0.028-0.006)})$.

Iron oxide, with the optical features of hematite, occasionally occurs as inclusions in the chalcopyrite. Rhombic cassiterite crystals may mark hematite-chalcopyrite junctions (Fig. 5, 6).
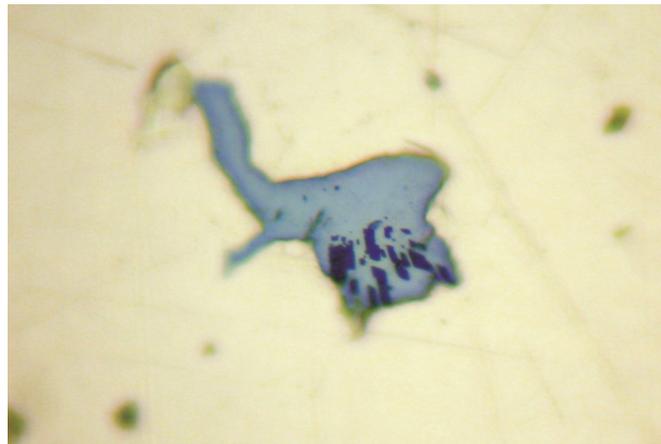
Fig. 5. Hematite inclusion in chalcopyrite with enclosed cassiterite crystals. Reflected light, 750x, immersion.
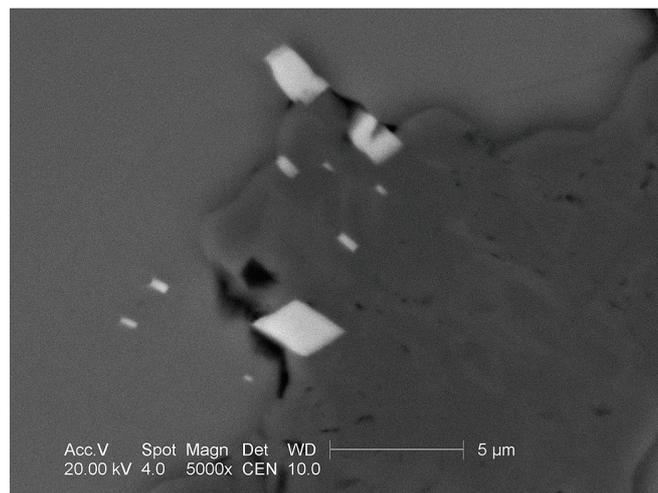
Fig. 6. Automorphic crystals of cassiterite on the junction between hematite (dark phase) and chalcopyrite (light phase). BSE image.

Pyrite of pure FeS$_2$ composition is the second most common mineral in the rocks. It occurs as separate crystals of cubic habit (Fig. 7) with the faces of some showing the typical striations.

Within aggregates of chalcopyrite, small, xenomorphic grains of pyrite with characteristic internal structure are sporadically present. These may reflect different centers of growth. Higher Co is characteristic of marginal parts (Fig. 8). Though, generally, all pyrite crystals are without Ni substitution, a weak Ni zonation is seen in a few. Profiles of Co and Ni variation in the pyrite are shown on Figures 9A, B and 10A, B, C.
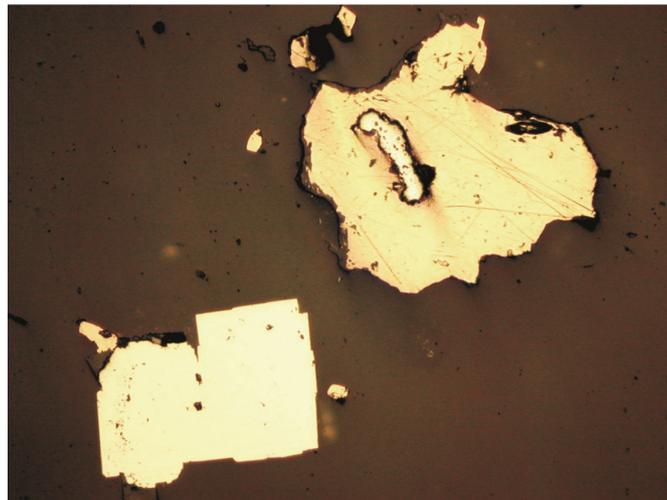
Fig. 7. Automorphic pyrite crystal (lower part) and chalocpyrite crystal (upper part) with Co-rich pyrite inclusion. Reflected light, 210x, immersion.
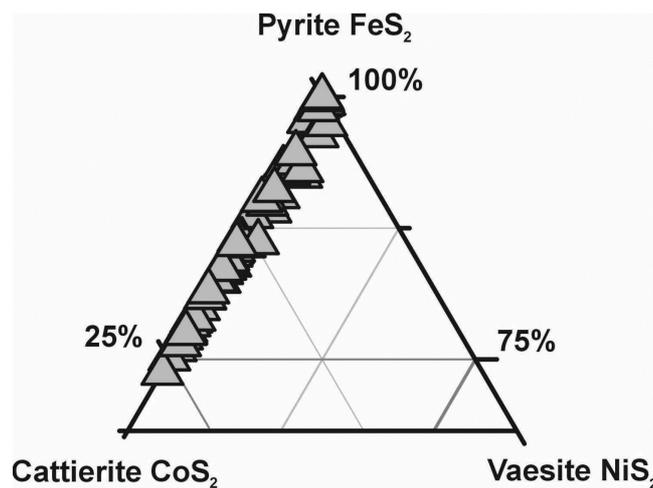
Fig. 8. Ternary projection of minerals from FeS$_2$ – CoS$_2$ – NiS$_2$ solid solution. 112 analytical points plotted.
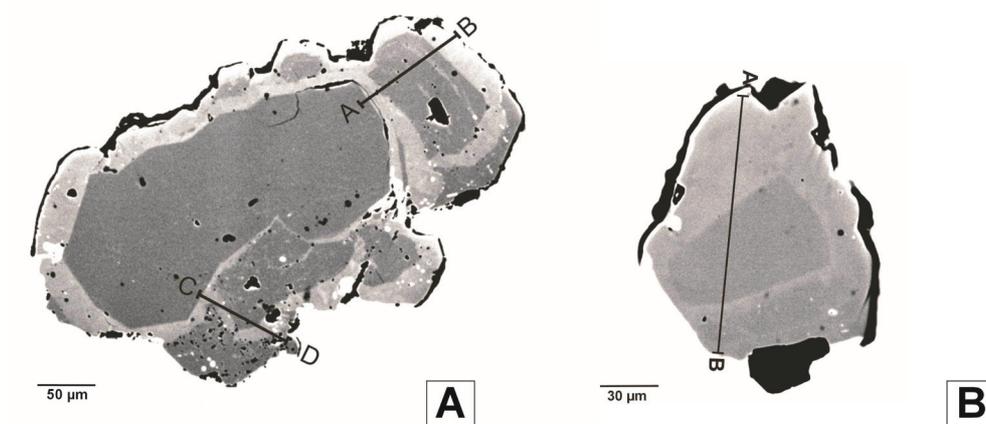
Fig. 9. Co-rich pyrite grains. (**A**) Profile lines A-B and C-D on pyrite grain. (**B**) Profile line A-B on a small pyrite grain. BSE image.
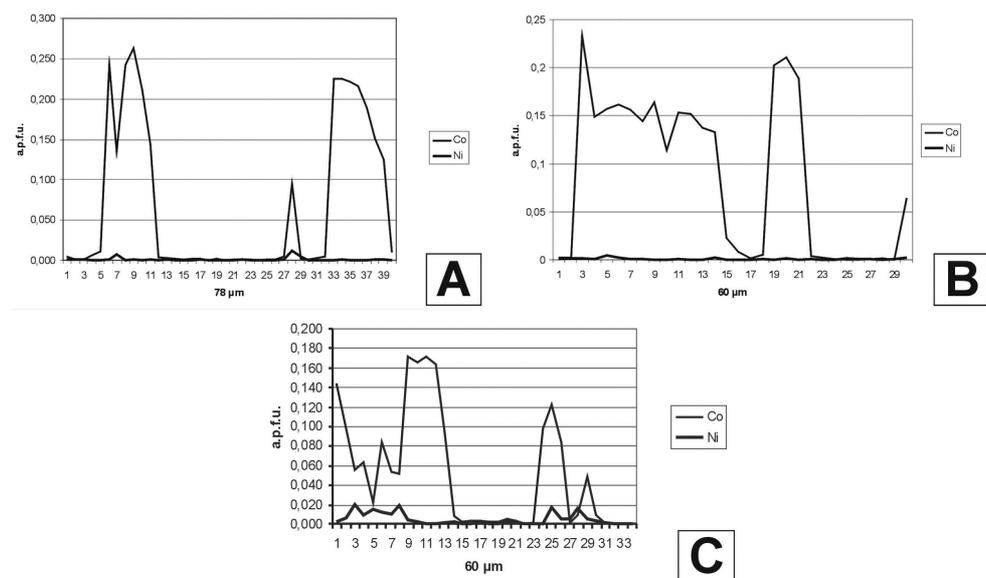
Fig. 10. Diagrams showing Ni and Co distribution in pyrite grains. A-B (**A**) and C-D (**B**) profiles are taken from Figure 9A and profile A-B (**C**) from Figure 9B.

Hessite (Ag_2Te) occurs as very small inclusions in chalcopyrite (Fig. 11; Table 6). The inclusions are similar in appearance to galena. Though subject to interference from chalcopyrite, electron microprobe analyses permit the calculation of Ag/Te = 2:1.

The rarest mineral components of the rocks belong to the tetrahedrite group. They form, together with chalcopyrite and galena, irregular overgrowths (Fig. 12). They are represented only by tetrahedrite and tennantite phases.

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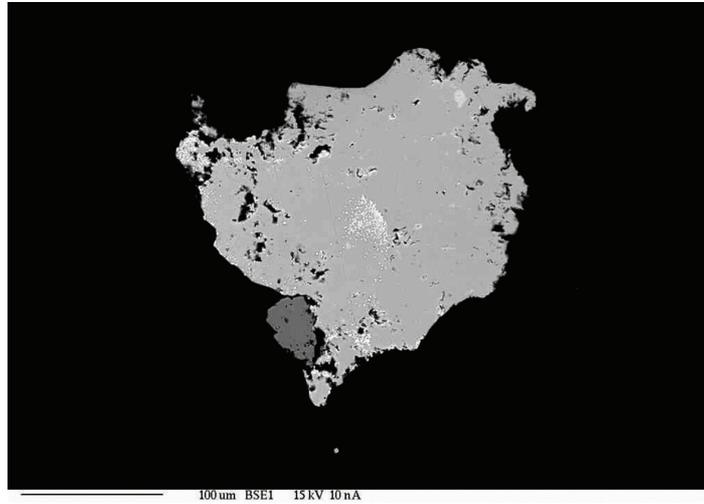
Fig. 11. BSE image of chalcopyrite grain with hessite inclusions (light dots).

WDS composition in wt% of hessite included in chalcopyrite. All analyses were calculated according to the sum of $(Te+S)_{\Sigma=1}$

	1	2
Ag	62.68	63.04
Te	37.11	36.98
Cu	0.09	0
Fe	0.01	0.01
S	0.02	0.01
Total	99.92	100.05
Ag^+	1.994	2.014
Te^{-2}	0.998	0.999
S^{-2}	0.002	0.001
Cu^+	0.005	0.000
Fe^{+2}	0.001	0.001
Total	2.999	3.015

5. Discussion

The first mineral phases to crystallize were probably the wolframites with chemical compositions similar to ferberite. The position of molybdenite in the mineral sequence is not clearly understood. Molybdenite flakes, seen only in quartz, are strongly deformed.
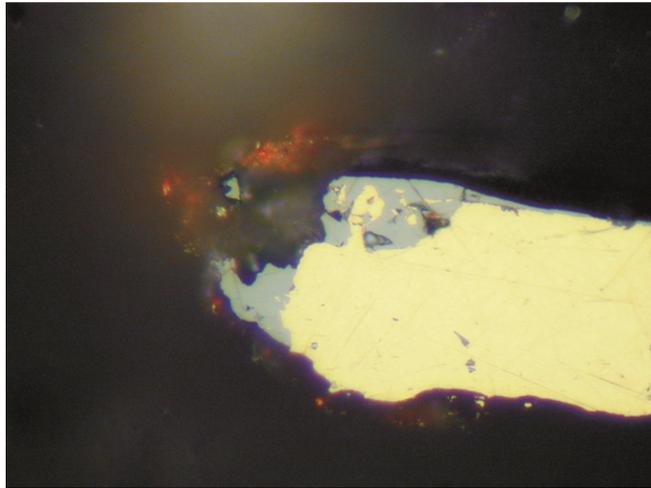
Fig. 12. Tennantite - tetrahedrite minerals (grey blue) replaced by chalcopyrite. Reflected light, 460x, immersion.

Similar textures in the same drill core serve to suggest that the molybdenite crystallized simultaneously with ferberite. Afterwards and/or during the same time interval, the bismuth-rich minerals formed. Next, the crystallization of cobaltite-gerdsorffite minerals, nickeline, carrollite, Co-rich pyrite and chalcopyrite occurred, with the last enclosing all of the Co- and Ni-rich minerals mentioned. Younger minerals such as galena, sphalerite, tennantite and tetrahedrite are present both as inclusions in chalcopyrite and as independent grains. Tellurium minerals, e.g. the hessite enclosed in chalcopyrite, relate to the later stages of mineral growth (Mikulski et al. 2009). Autmorphic crystals of pyrite lacking Co and Ni, and bornite overgrowths on chalcopyrite, crystallized last of all. Scheelite is a secondary phase after decomposition of primary wolframite.

A very similar polymetallic ore mineral association with Te-Bi-Ag-Pb minerals has been reported from the 144-Ż borehole by Mikulski et al. (2009) and, also, from the Pilica area by Harańczyk (1983). It has been recognized as aposcarn stockwork-type mineralization (Ślósarz 1994). Veins of light-gray quartz enclose wolframite that is paragenetic with scheelite, pyrite, chalcopyrite, sulfosalts and Bi- and Te-rich other minerals. According to Harańczyk (1983), the quartz veins contain a few ppm of Au. A similar situation has been described from the Smoleń IG-1 drill core from Pilica (Slósarz 1994).

The mineral association in the 144-Ż core differs from that in the Smoleń IG-1 core in that it is characterized by the presence many minerals richer in Co and Ni. It is in the former core that minerals such as gersdorfite, nickeline Co-rich pyrites were first noted from the Cracov-Lubliniec Area (Muszyński 1991).

The secondary scheelite described from a few veins is a result of ferberite alternation. The presence of primary scheelite as described by Harańczyk (1983) and Ślósarz (1994) was not definitively confirmed. The wolframite transformation to scheelite is labile. In some cases, the only secondary phase is very pure crystalline scheelite.

Ore mineral bearing high-temperature quartz veins from cores from the Będkowska Valley show similar mineralization features (Harańczyk 1983). There, the main mineral is grey/greenish Au bearing quartz with chloride. In addition to small amounts of wolframite, pyrrhotite, chalcopyrite, black sphalerite and pyrite, traces of Bi- and Ti-rich minerals also occur in the veins. Though gold was also reported by Mikulski et al (2008) from the Będkowska Valley, our study to date has not confirmed the mineralization in the Żarki-Kotowice area to be Au-bearing.

6. References

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