MINERALOGIA POLONICA
Vol 23, No 2 — 1992

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HYDROTHERMAL MINERALIZATION PHENOMENA IN KARNIOWICE TRAVERTINE NEAR CRACOW

Abstract. Ore mineralization in Karniowice travertine occurs predominantly within the forms of hydrothermal karst and only in subordinate amounts in fissures and pores of this rock. Ore mineral association consists of pyrite, marcasite, galena, chalcopyrite, sphalerite, tetrahedrite, tennantite, bornite, bravoite-villamaninite, siegenite, gersdorffite (?), antimonite (?). They are accompanied by calcite, quartz and barite. Taking into account mineral and chemical composition, this mineralization shows some similarity with the Miedzianka type deposit in the Holy Cross Mts.

INTRODUCTION

Karniowice travertine occurs at the area of about 7 sq.km. between Dulowa, Karniowice and Filipowice, west of Cracow. This is a calcareous plate showing variable and small thickness (2-8 m), overlying discordantly sandstone series of productive Carboniferous complex of the Upper Silesian Coal Basin. It is overlain by Myślachowice conglomerates filling erosional troughs (Siedlecki 1954, 1958; Lipiarski 1969). The rock in question is a limestone of travertine type, containing numerous floral and faunal remnants, determining its Lower Autunian age (Lipiarski 1971). This is, unquestionably, a freshwater sediment in a lake with abundant vegetation, causing precipitation of calc tufa (Gąsiorowski et al. 1986). This basin was supplied with Ca-rich waters flowing from the Dębnik anticline (Skórska 1959). There are different opinions concerning the origin of these waters. They were supposed to be cold karst waters (Siedlecki 1954) or thermal, juvenile ones coming from hot springs related with Permian volcanism (Goetel 1921, *fide* Siedlecki 1954).

Ore mineralization phenomena in Karniowice travertine in the form of malachite traces were reported already by Zaręczny (1894) and more detailed data in this subject are due to Lipiarski and Zakrzewski (1970, 1971). These authors have distinguished two associations of primary ore minarals. The first is represented by chalcopyrite, pyrite, marcasite, whilst the second — by galena, sphalerite, pyrite and gersdorffite. In their opinion, this mineralization is epigenetic, being associated with red and white calcite, in fissures and pores of travertine. As possible sources of mineral substance these authors suggest alternatively:

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a) hydrothermal ascending solutions;

b) secretional processes, leading to concentration of originally dispersed ore components in calc tufa;

c) infiltration descending solutions, transporting mineral substance from overlaying porphyric tuffs.

Field and microscopic observations of the present author (Czerny 1983) are consistent with hydrothermal nature of these processes, which resulted in mineralization within the travertine. Chemical composition of ore minerals was determined by Zakrzewski (1984) using microprobe method.

FORMS OF MINERALIZATION

There are three forms of occurrence of ore minerals in the Karniowice travertine:

A) point concentrations of goethite in synsedimentary pores;

B) coatings and incrustations of goethite and malachite in fissures;

C) nesty aggregates and incrustations of goethite and malachite within karst caverns.

Traces of mineralization of A and B type in the travertine are observed in numerous places (mainly near Karniowice) but the richest one, representing all the above types, occurs only in outcrops situated in the upper part of eastern branch of Dulowskie Jary ravine (Fig. 1). The main outcrop (10 m long and 2-3 m high) was renovated in about 1980 by landslide. We observe here massive creamy-gray limestone, arenaceous in lower part and pinkish to haematite-red in the upper one. The upper surface of travertine plate is subjected to strong karsting (grikes and clints of fossial Permian karst). It is covered by a complex of variegated clays (up to 2 m thick), containing pebbles of Carboniferous limestones and fragments of travertine, as well as by loess layer (1 m thick). In the bottom of travertine plate there occur gray-pinkish, poorly compact arcosic sandstones, locally containing intercalations of quartzy gravel.

Apart from surface karsting, we observe — in upper part of this outcrop — numerous forms of underground karst: irregular caverns, tubes and channels. The cross-section of tubes and caverns are oval or circular, being up to 30 cm in diameter. As follows from their morphological features, they were formed under phreatic conditions. Caverns are filled, to different degree (some even wholly), with internal sediments. These sediments or walls of karst caverns are covered by crystalline calcite, forming druses. Calcitic crustifications are accompanied by concentrations of goethite and malachite (locally silicified) and barite rosettes. Moreover, calcite druses are overgrown by euhedral galena crystals. Field observations allow to determine the succession of deposition of minerals and to present typical profiles of substances filling the karst forms in question (Fig. 2). These profiles, though slightly differing in the top and bottom parts of caverns, can be correlated.

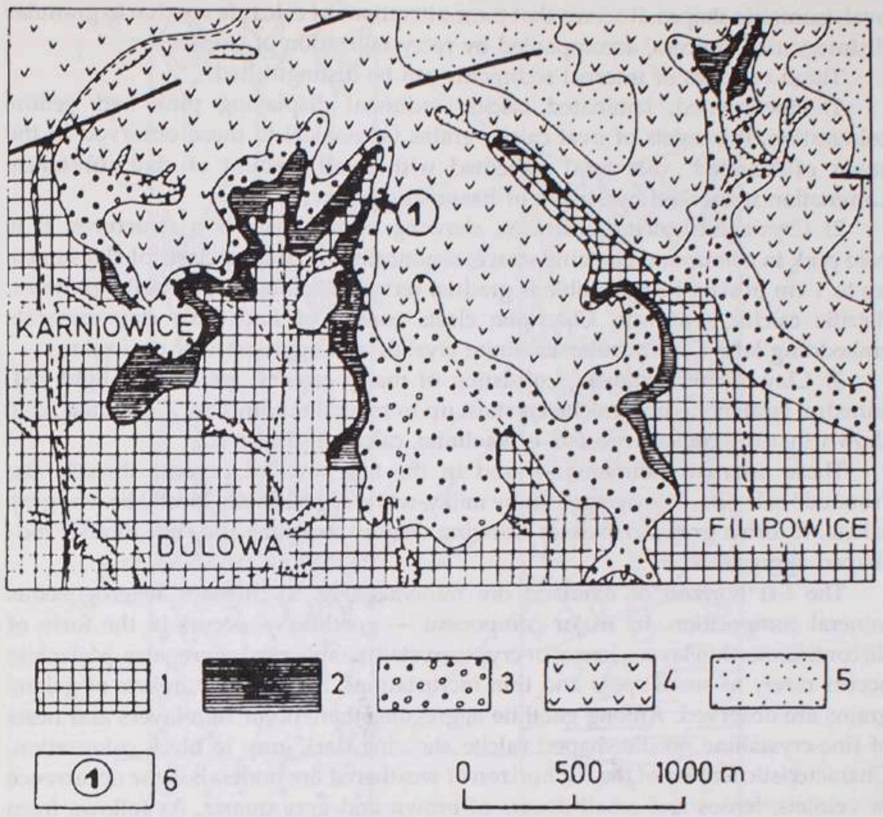

Fig. 1. Geological sketch map of the Karniowice region (after Alexandrowicz et al. 1971): 1 — Carboniferous — sandstones and shales; 2 — Lower Permian — Karniowice travertine; 3 — Lower Permian — Myślachowice conglomerate; 4 — Lower Permian — porphyric tuffs; 5 — Triasic — marls, limestones; 6 – the outcrop of travertine in Jary Dulowskie ravine

Fig. 1. Szkic geologiczny okolic Karniowic (według Alexandrowicza i in. 1971): 1 — Karbon — piaskowce i łupki; 2 — Perm dolny — martwica karniowicka; 3 — Perm dolny — zlepieniec myślachowicki; 4 — Perm dolny — tufy porfirowe; 5 — Trias — margle, wapienie; 6 — odsłonięcie martwicy w Jarach Dulowskich

CHARACTERISTICS OF SUBSTANCES FILLING THE CAVERNS

The walls of caverns are covered by thin layer (2-3 mm) of granular and scattering "sanded" travertine. As follows from microscope observations, the transition from fine-crystalline "fresh" to "sanded" calc tufa is continuous and gradual (Phot. 1). In this zone calcite grains are slightly larger and tend to have oval, isometric shapes. It seems that these alterations of calc tufa are due to granular disintegration process, accompanied by recrystallization of calcite.

Three varieties of internal sediments can be distinguished:

1) Fine-grained, laminated calcitic sediment displaying pink and yellow colouration. It consists of oval calcite grains (analogical to those observed in the zones of "sanded" calc tufa) cemented with small amount of clay substance. Lamination is marked by stripes of haematitic pigment.

2) Crystalline calcitic sediment, showing no sedimentation structures. It is pale pink in colour and contains scarce, chaotically distributed clasts of claystones, up to 1 cm in size. Fairly visible is gradual recrystallization of primarily granular, detritic calcitic sediment. Claystone clasts consist of fine flaky clay minerals embedding larger, vermicular kaolinite crystals and aggregates of chalcedony.

3) Clay-calcitic sediment, consisting of marly cement, embedding light red, euhedral (scalenohedral) calcite crystals, up to several mm in size. X-ray data have shown that the cement consists of kaolinite, calcite and quartz.

These internal sediments — and in the top parts of caverns directly the "sanded" calc tufa — is overgrown by milky-white or yellowish, locally brown-gray calcite. It forms granular masses showing chaotic structure and, but locally, rod-shaped aggregates.

The I-st horizon of oxidized ore minerals (Fig. 2) displays heterogeneous mineral composition. Its major component — goethite — occurs in the form of discontinuous thin layers, lenses or cryptocrystalline spherical aggregates. Malachite occurs rarely as small spots and thin incrustations. Sporadically, relicts of galena grains are observed. Among goethite aggregates there occur thin layers and nests of fine-crystalline needle-shaped calcite showing dark gray to black colouration. Characteristic feature of the I-st horizon of weathered ore minerals is the occurrence of veinlets, lenses and small druses of brown and gray quartz. As follows from microscope observations, primary components of ore mineralization were aggregates of ore minerals and needle-shaped calcite. These substances were, subsequently, subjected to silicification, accompanied by partial oxidation of ore minerals. Silicification front at the boundary calcite-quartz is marked by stripes of ferruginous substance, whilst in quartz we observe considerable amounts of small goethite needles. They are forming a delicate net, often showing the shape of primary ore minerals.

In the profiles of the top parts of caverns, the I-st horizon of ore mineralization is represented by characteristic cover of yellow calcite, coloured by goethite admixture. This variety of calcite is accompanied by barite, occurring in rosette-tabular aggregates, consisting of milky-white crystals, up to 3 cm in size (Phot. 2). In this zone we may observe poor silicification phenomena.

Yellow calcite and, in bottom part of caverns the I-st horizon of oxidized ore minerals, are overgrown by calcitic cover, 2-5 cm thick, developed in druses filling karst caverns. In lower part it is pink, finely rod-shaped and radial calcite and above — white, transparent, thick prismatic calcite, containing single growth zone, haematite-red in colour.

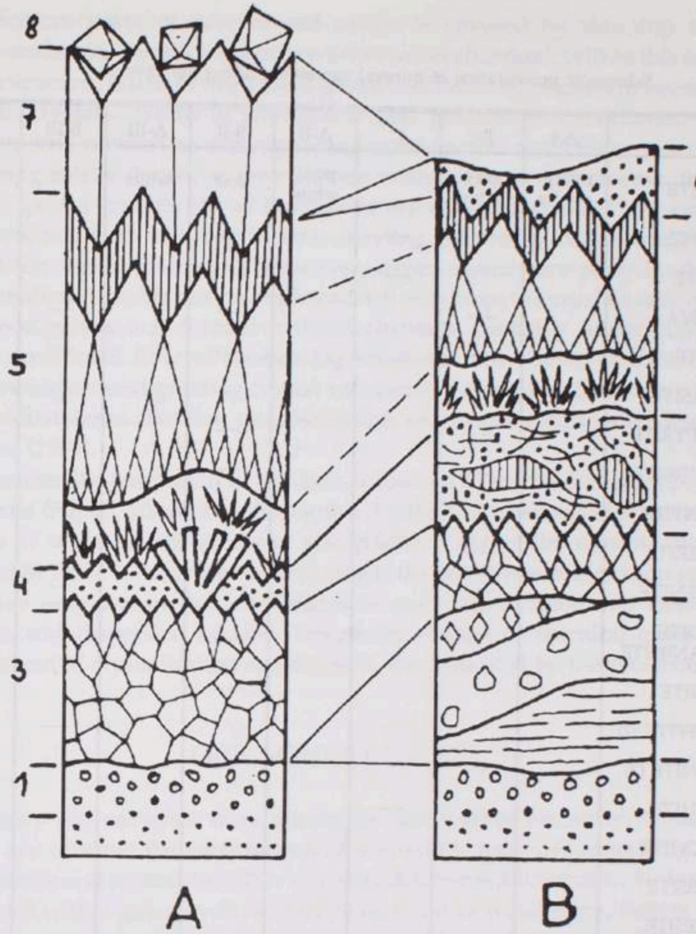

Fig. 2. Schematic profile of mineral forms filling the caverns: A — profile of top parts of caverns; B — profile of bottom parts of caverns; 1 — "sanded" travertine cover; 2 — internal sediments; 3 — milky-white calcite; 4 — I-st mineralization horizon (nesty aggregates of goethite, gray calcite and quartz, in the tops of caverns — yellow calcite and barite); 5 — tripartite calcite cover: in the bottom — pink calcite, in the middle — white, transparent calcite, in the top — red calcite zone; 6 — II-nd horizon of ore mineralization (goethite-malachite incrustation); 7 — druses of white calcite; 8 — III-rd horizon of ore mineralization (euhedral galena crystals).

Fig. 2. Schematyczne profile utworów wypełniających kawerny: A — profil stropowych części kawern; B — profil spągowych części kawern; 1 — powłoka martwicy „zmurszałej"; 2 — sedymenty wewnętrzne; 3 — kalcyt mleczno-biały; 4 — I poziom mineralizacji kruszcowej (gniazdowe nagromadzenia goethytu, kalcytu szarego i kwarcu, w stropie kawern — kalcyt żółty i baryt); 5 — trójdzielna powłoka kalcytowa: w dole — kalcyt różowy, w środku — kalcyt biały, przeświecający, w górze — zona kalcytu czerwonego; 6 — II poziom mineralizacji kruszcowej (naskorupienie goethytowo-malachitowe); 7 — druzy kalcytu białego; 8 — III poziom mineralizacji kruszcowej (euhedralne kryształy galeny).

Table 1

Schematic presentation of mineral succession filling the caverns

	A-I	B-I	C	A-II	B-II	A-III	B-III	D
CALCITE	milky--white	gray, yellow		pink, white	red	white		
QUARTZ			--					
BARITE			--					
GALENA		--			--		--	
PYRITE		--			--		--	
MARCASITE					--			
CHALCOPYRITE		--			--			
TETRAHEDRITE		--			--			
TENNANTITE					--			
SPHALERITE		--			--			
Cu-SIEGENITE		--			--		--	
BRAVOITE--VILLAMANINITE					--		--	
BORNITE					--			
GERSDORFFITE (?)							--	
ANTIMONITE (?)		--			--			
GOETHITE			--					--
MALACHITE								--
CERUSSITE								--
ANGLESITE								--
COVELLITE								--
CHALCOCITE								--
DIGENITE								--
SMITHSONITE								--
JAROSITE								--

Explanations of symbols:
A-I, A-II, A-III – stages of barren, calcitic mineralization
B-I, B-II, B-III – stages of ore mineralization
C – stage of silicification and partial oxidation of ore minerals
D – weathering stage of ore minerals

In bottom parts of caverns red calcite is covered by thin (up to 5 mm) goethite-malachite layer (II-nd horizon of ore mineralization). Within this association there occur scarce relicts of fine galena grains and radial aggregates of needle-shaped marcasite crystals. Traces of smithsonite and jarosite were evidenced by X-ray diffractometric method as accompanying goethite and malachite.

Among calcite druses, mainly on side walls and topes of caverns, there occur euhedral galena crystals (III-rd horizon of ore mineralization). They are 2 mm–1 cm (sometimes even to 4 cm) in size, showing commonly octahedral habit or its combination with cubic forms. However, larger crystals are platy in shape. This transformation of habit can be explained by anisotropy of crystallization environment since galena was formed in karst channels, probably under conditions of intense, directional flow of ore-bearing solutions. The stream of these solutions, when flowing around growing crystal was causing diversification of rate of growth of individual faces. Similar transformation of crystal forms was described by Grigoriev (1981).

Characteristic succession of minerals, observed in the profiles of deposits filling the caverns (Fig. 2), allowed to distinguish 3 phases of barren calcitic mineralization, 3 phases of ore mineralization and a silicification stage. The mineral succession is presented in Table 1. Particularly interesting is the position of silicification stage which was active only within the I-st horizon of ore mineralization and caused partial oxidation and dispersion of ores. Temporary change of chemical composition of solutions and of crystallization conditions is also indicated by the presence of barite.

ORE MINERALIZATION

Primary ore minerals were altered by weathering processes. Consequently, actually we observe the associations of secondary minerals containing relicts of galena, pyrite and marcasite. Other minerals determined occur as inclusions (10–100 μm in size) within galena which is more resistant to weathering. Relicts of galena grains are surrounded by fine-crystalline cerussite and, less abundant, anglesite. At the boundary of galena and cerussite, in specific cementation microzone, we observe concentration of numerous fine grains of covellite, less abundant chalcocite and, sporadically, digenite.

Galena of the I-st mineralization horizon often contains chalcopyrite and tetrahedrite inclusions. They are always euhedral, often developed in grains of complex, zonal structure, whereby concentric zones contain alternating both minerals (Phot. 3). Tetrahedrite distinguishes by white-gray colour with weak heather tint and slightly higher reflectivity ($R \approx 34\%$). Less common are euhedral grains of pyrite, sphalerite and an isotropic mineral showing $R \approx 45\%$ and pale yellow colour with pinkish tint. These features correspond to minerals of linnaeite-siegenite-polydymite group (Phot. 4). Moreover, individual very fine grains of strongly anisotropic, white-gray mineral occur which was preliminarily defined as antimonite(?).

Relicts of galena of the II-nd mineralization horizon, apart from the above mentioned minerals, also contain relatively large anhedral tennantite inclusions (Phot. 5) and single bornite grains. Tennantite, partly altered into covellite, is characterized by gray colour with olive tint when examined in reflected light.

Haematite-red variety of calcite contains numerous fine grains of ore minerals: pyrite, sphalerite and chalcopyrite. There were also observed pyrite inclusions displaying interesting inner structure (Phot. 6). It is characterized by zones of a darker mineral, isostructural with pyrite. Similar zonal structure of crystals of the pyrite-bravoite series is described by Ramdohr (1969).

Within euhedral crystals of galena of III-rd mineralization horizon there occur inclusions of pyrite, siegenite, mineral defined as bravoite and single grain of mineral representing gersdorffite-ullmannite-willyamite series(?).

Detailed microprobe data on the occurrence of siegenite and minerals of the pyrite-bravoite-villamaninite series in galena from Karniowice travertine were published by Zakrzewski (1984). It was shown by this autor that Cu-bearing Ni-Co-Fe bisulfides of pyrite structure and zonal structure displaying variability of chemical composition, ranging from cupriferous pyrite (2.9 wt. % Cu) through cupriferous bravoite to villamaninite $Cu_{0.36}Ni_{0.46}Co_{0.14}Fe_{0.04}S_2$. Cupriferous siegenite has, following Zakrzewski, the mean composition $Cu_{0.31}\ Ni_{1.46}\ Co_{1.18}\ Fe_{0.05}S_4$ and was probably formed by transformation process of bisulfides.

The contents of some trace elements in euhedral galena crystals from the III-rd mineralization horizon were determined using AAS method. This analysis was carried out by means of Pye Unicam apparatus. The obtained data indicate that the galena in question contains: 255 ppm Cu, 150 ppm Ni, 55 ppm Co, 170 ppm Fe, 60 ppm Zn, 40 ppm Ag, 185 ppm Sb, 3 ppm Cd, and 4 ppm Mn. Moreover, spectrochemical analysis has shown that this mineral contains about 300 ppm As, <3 ppm Bi, < 10 ppm Tl, < 1 ppm Mo, and less than 300 ppm Ba. The above trace element assemblage differs from that of galena from Triassic Zn-Pb deposits. The occurrence of traces of Cu, Ni, Co, Fe, Sb and As can be explained by the presence of inclusions of pyrite, bravoite, siegenite and a mineral of gersdorffite group. Low concentrations of Ag and Bi indicate that this galena has crystallized from relatively cold, epi- or telethermal solutions.

CONCLUSIONS

Primary mineralization in the Karniowice travertine was formed due to the flow of ore-bearing solutions through the system of karst cavities. On the other hand, traces of mineralization in fissures and pores of this rock are connected with infiltration of solutions from caverns, being secondary in character. It should be emphasized that the margins of fissures containing goethite incrustations consist of "sanded" travertine. Traces of goethite and malachite found in the cement of underlaying sandstones were also formed due to infiltration of solutions from caverns.

The shapes of caverns indicate them to be formed under phreatic conditions where intense hydrodynamic water flow took place. The stage of formation of karst is strictly connected with the phase of filling the caverns with internal sediments. This conclusion is based on the similarity of clastic carbonate components of sediments with the products of granular disintegration occurring on the walls of caverns — in the zones of "sanded" travertine. It is supposed that evolution of karst forms was connected not only with dissolution of calcium carbonate by CO_2-enriched waters, but also with specific disaggregation process of limestone. The transition from sedimentation stage of clastic deposits to that of crystallization of carbonates and ore minerals is also continuous. Clay-calcitic variety of sediments is supposed to represent the product of intermediate stage. It is, thus, supposed that karsting, sedimentation and mineralization processes are mutually connected by common factor — the flow of mineralized thermal waters.

Hydrothermal origin of mineralization in the Karniowice travertine is supported both by its polymetallic character (Cu, Fe, Ni, Co, Pb, Zn, Sb, As, Ba), stadial evolution (Tab. 1) and common zonal structures of ore minerals.

The age of mineralization — determined by the age of caverns — is younger than that of lithification stage of travertine but older from the stage of development of forms of surface karst and covering the carbonate plate by variegated clays (weathering products of Myślachowice conglomerate and porphyric tuffs). Consequently, the age of mineralization in question can be defined as Lower Permian and correlated with the period of melaphyric to porphyric volcanism accompanying Saalic tectonic stage.

It is generally accepted that Permian volcanism in the environs of Cracow was not accompanied by ore mineralization (Bukowy 1961). It is supposed that hot magmatic solutions, connected with basic volcanites and being rather poor in dissolved metals, just within caverns developed in travertine found convenient conditions for deposition of small amounts of ore minerals. In Filipowice, about 1 km SE from the outcrops of travertine in the Jary Dulowskie ravine melaphyric lava flows were found in artificial outcrops. They are overlaying Carboniferous sandstones or a thin layer of silicified pebbles of Myślachowice conglomerate (Oberc and Parachoniak 1962). Fairly intense calcitization and silicification phenomena are observed within melaphyre rocks (calcite and chalcedony veinlets, calcite and quartz druses in amygdules). On the other hand, one cannot reject Goetel's suggestion on thermal origin of waters flowing into the lake where the travertine in question was formed (*fide* Siedlecki 1954). It is supposed that these solutions could later cause the formation of karst forms and mineralization in travertine.

The above described mineralization is, in many respectes, comparable with that of the Miedzianka type distinguished in Holy Cross Mts. (Rubinowski 1971). Among common features we have to mention: a) similar epithermal and polymetallic character (symptomatic co-occurrence of Cu, Fe, Co, Pb, Zn, As and Ba minerals); b) nearly the same assemblage of trace elements in galena; c) similar Lower Permian age and connection (?) with subsequent Variscan magmatism. Less evident is, suggested by Górecka (1972), relation of the mineralization in question with post-Variscan mineralization of Cu-Mo porphyry ores, found in Paleozoic series of Cracow-Myszków zone. It is generally accepted (Ślósarz 1979, 1982) that the final mineralization stages of this type are manifested by barite-fluorite and calcite-quartz veins containing traces of ore minerals (pyrite, marcasite, chalcopyrite, galena, sphalerite).

Acknowledgement. The author gratefully acknowledge Prof. Andrzej Manecki for helpful advice and discussion.

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EXPLANATIONS OF PHOTOGRAPHS

PHOT. 1. Recrystallization and granular disintegration of travertine at the walls of caverns (right side of photograph). Transmittant light, crossed nicols, magn. 60×.

PHOT. 2. Platy barite crystals overgrown by calcite. Transmittant light, crossed nicols, magn. 6×.

PHOT. 3. Euhedral tetrahedrite crystal growing concentrically over chalcopiryte grain. Reflected light, magn. 120×.

PHOT. 4. Siegenite inclusions in galena. Reflected light, magn. 120×.

PHOT. 5. Anhedral tennantite grain in galena. Reflected light, magn. 120×.

PHOT. 6. Zonal crystals of pyrite-bravoite series. Reflected light, magn. 240×.

Jerzy Czerny

PRZEJAWY MINERALIZACJI HYDROTERMALNEJ W MARTWICY KARNIOWICKIEJ W OKOLICACH KRAKOWA

S t r e s z c z e n i e

Mineralizacja kruszcowa w martwicy karniowickiej (fig. 1) występuje głównie w obrębie form krasu hydrotermalnego, w towarzystwie sedymentów wewnętrznych i krustyfikcji kalcytowych. W podrzędnych ilościach kruszce obecne są w szczelinach i porach martwicy. Na podstawie obserwacji kolejności nawarstwiania się składników zestawiono profile utworów wypełniających kawerny (fig. 2). Mineralizacja miała charakter stadialny (tab. 1). Lista minerałów kruszcowych obejmuje piryt, markasyt, galenę, chalkopiryt, sfaleryt, tetraedryt, tennantyt, bornit, bravoit, siegenit, gersdorffit(?), antymonit(?). Towarzyszą im kalcyt, kwarc i baryt. Mineralizacja ta jest wieku permskiego i być może związana jest z gorącymi roztworami pomagmowymi pochodzącymi z nieodległych przestrzennie i czasowo wylewów law melafirowych (Filipowice). Pod względem składu mineralnego i chemicznego mineralizacja wskazuje pewne podobieństwo do wyróżnianego w Górach Świętokrzyskich polimetalicznego okruszcowania typu Miedzianki.

OBJAŚNIENIA DO FOTOGRAFII

FOT. 1. Rekrystalizacja i dezintegracja granularna martwicy na ścianach kawern (prawa strona fotografii). Światło przechodzące, nikole skrzyżowane, powiększenie 60×.

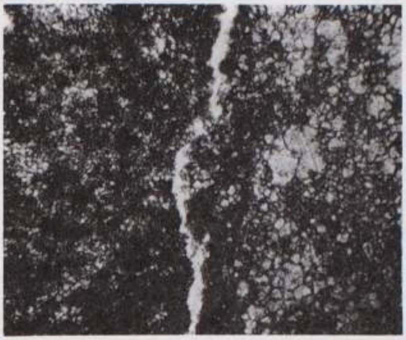
FOT. 2. Tabliczkowe kryształy barytu obrośnięte kalcytem. Światło przechodzące, nikole skrzyżowane, powiększenie 6×.

FOT. 3. Idiomorficzny tetraedryt obrastający koncentrycznie ziarno chalkopirytu. Światło odbite, powiększenie 120×.

FOT. 4. Wrostki siegenitu w galenie. Światło odbite, powiększenie 120×.

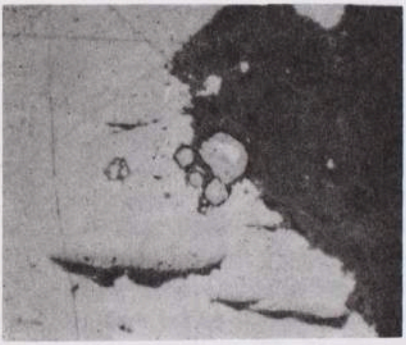
FOT. 5. Ksenomorficzne ziarno tennantytu w galenie. Światło odbite, powiększenie 120×.

FOT. 6. Kryształy szeregu piryt-bravoit o budowie zonalnej. Światło odbite, powiększenie 240×.



1

2



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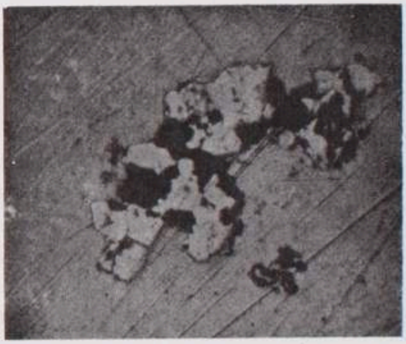
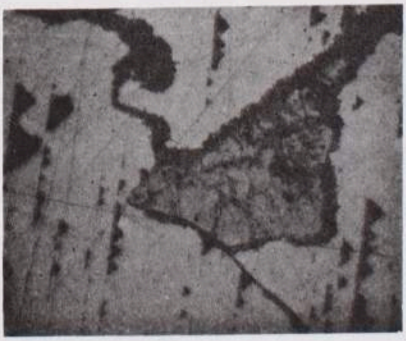
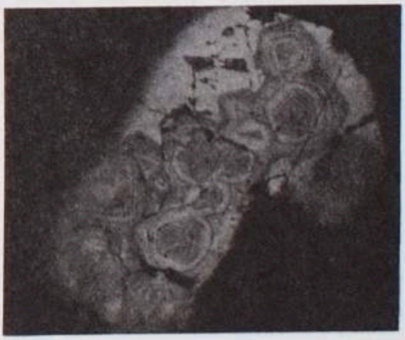


4



5



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