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Sulfide minerals from the barite-flourite deposit at Stanisławów in the Kaczawa Mts, Lower Silesia

ABSTRACT: Microscope studies of the sulfides associated with the barite-fluorite deposits exposed at the Stanisławów mine in the Kaczawa Mts, Lower Silesia, yielded their different origin and formation time when compared with sulfides precipitated during the Variscan mineralization cycle, whereas the barite-fluorite ore assemblage with sulfides developed in the post-Variscan (Saxonian) cycle.

INTRODUCTION

The paper presents results of studies of sulfide minerals associated with the barite-fluorite mineralization in the Stanisławów mine in the Kaczawa Mts, Lower Silesia (see Text-fig. 1), as well as of sulfides occurring in the wall rocks of the deposit. Specimens used for the studies have been collected since 1965 in the underground mine and from boreholes pierced in 1964/65 and 1977/79. For these studies, the reflected light microscopy methods were applied with the completion of the other special mineralogical and geochemical methods.

GEOLOGIC SETTING AND MINERALOGY OF THE DEPOSIT

The barite-fluorite deposit at Stanisławów occurs in the Lower Paleozoic rocks of the NE part of the Kaczawa metamorphic area (cf. Jerzmański 1965; Teisseyre 1957, 1967; Paulo 1972; Kowalski 1977, 1980).

Wall-rocks of the deposit consist of various schists, diabases and subordinate keratophyres (cf. Text-fig. 1). This rock complex is cut by numerous veins of Tertiary basalts. The latter are frequently found in the immediate contact of the barite-fluorite deposit.

Metamorphic rocks of the Mt. Chełmiec regional unit to which the Stanisławów area belongs, are altered, cut with faults, and locally brecciated along the latter structures. The faults and other tectonic zones developed the best in the NW-SE and weaker in WNW-ESE and **NE-SW** directions.

The barite-fluorite deposit at Stanisławów formed within the deep NW-SE tectonic zone occurring in the middle-western part of the Mt.

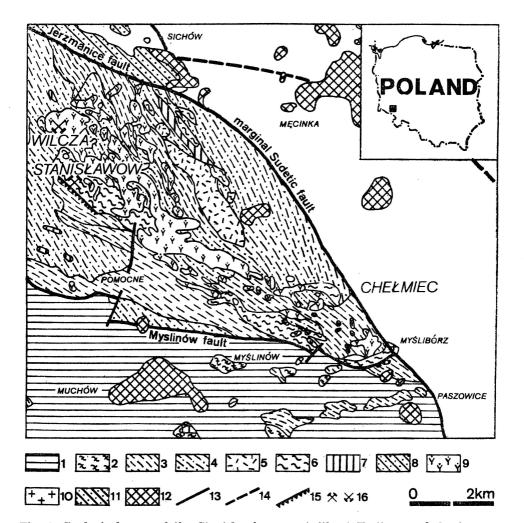


Fig. 1. Geological map of the Stanisławów area (without Tertiary and Quaternary

I. Geological map of the Stanisławów area (without Tertiary and Guaternary deposits (after Jerzmański 1965, supplemented by Kowalski 1977)
UPPER CAMBRIAN: 1 — greenstones, 2 — sericite-chlorite schists. ORDOVICIAN:
3 — quartz-sericite schists with intercalations of conglomerate-bearing quartzites,
4 — sericite schists, 5 — epidote schists, 6 — chlorite schists. SILURIAN: 7 — quartzites and silica shales, 8 — graywacke-clayey shales, 9 — diabases. OTHERS:
10 — Strzegom granite, 11 — Rotliegende deposits, 12 — Tertiary basalts, tuffs and basalt breccias, 13 - faults and overfolds, 14 - probable boundary of the Strzegom intrusion under the Tertiary and Quaternary cover, 15 - barite-fluorite vein nearly Stanisławów, 16 - mines (working and abandoned)

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Chełmiec unit, and crossing all the rocks distinguished in the unit. Processes of brecciation, alteration and secondary mineralization developed intensively in this zone. All the resulting rocks are of bright-red colour. The tectonic zone is usually 40—60 m thick, although locally it reaches 100 and more metres. The barite-fluorite deposit at Stanisławów is considered (Kowalski 1977, 1980) as a part of extensive hydrothermal mineralization developed in the discussed zone and known in the other regions of the Kaczawa Mts (Paulo 1973).

The deposit is a steep vein with the strike 140° and mean dip about $70-75^{\circ}$ SW. It has recently been contoured with boreholes at the distance about 1200 m and down to depth about 650 m, and with underground mining galleries situated at the levels of 900 and 220 m.

The thickness of the vein is usually 1—3 m, but in lenticular parts it reaches 6—8 m. Sometimes it contains inclusions of the barren wall--rocks which cause its ramification; locally the vein interrupts abruptly, is cut and transplaced with transverse faults, or its thickness diminishes gradually to nil. The distinct connection of the vein morphology with the wall-rock type is apparent. Although the wall-rocks are commonly strongly brecciated, if they consist of diabases and metadiabases, the rock/vein contacts are sharp and vein boundaries are very distinct. Contrary, barite-fluorite mineralization penetrates deeply wall--rocks consisting of schists and thus it forms ores of both vein-type and rock breccia cemented with barite and fluorite.

It was suggested (Kowalski 1977, 1980), that this mineralization, similarly to the mineralization in the Erzgebirge (Baumann 1968) formed in the two mineralization cycles: Variscan and post-Variscan (Saxonian). During the Variscan cycle of the Permian-Carboniferous age, under action of hydrothermal solutions connected with the Karkonosze and Strzegom granitoids, metamorphic rocks of the Kaczawa Mts altered in the intensive processes of carbonatization, silicification, chloritization, albitization, pyritization, and formation of numerous quartz- and/or siderite-polymetallic deposits. During the younger, post-Variscan cycle, the hematite-barite-fluorite deposits formed bearing also siderite and scarce amounts of sulfides, like those known in the Mt. Chełmiec unit at Wilcza and Stanisławów (cf. Text-fig. 1). Consequently, the Stanisławów deposit is regarded as of hydrothermal origin formed after the Lower Triassic and before the Upper Cretaceous, and a deep-seated magmatic chamber would be the source of hydrothermal solutions. The deposit developed within the old tectonic zone renewed during transverse folding of the Kaczawa region. Within the Stanisławów deposit, the four essential barite-fluorite parageneses and assemblage of the weathering-zone barites are recognizable (cf. Kowalski 1977, 1980).

I. Coarse-crystalline, tabular barite, strongly impregnated with iron oxides with small amount of siderite, poor in fluorite and bearing only traces of sulfides, mostly colloform pyrite and marcasite; this barite is very strongly structurally deformed.

II. Fluorite-quartz bearing sulfides, and occurring mostly in strongly brecciated wall-rocks; minerals are also crushed, and cemented with the later barite.

III. Medium- and coarse-grained barite-fluorite-siderite bearing sulfides.

IV. Medium- and coarse-crystalline barite, frequently laminated with fluorite, quartz, and strongly silicified.

The distinguished parageneses of the Stanisławów deposit are very simi¹ar to those known in the Thuringian Forest (Werner 1966).

At the Stanisławów deposit, two distinct stages of mineral formation may be distinguished:

— the older one of the paragenesis I of barite with hematite and siderite, almost without sulfides;

— the younger one of the parageneses II—IV of barite with fluorite, siderite and sulfides.

Subsequently, the ore-forming processes caused final silicification and weathering and recrystallization of the earlier mineral assemblages.

SULFIDE MINERALS

Wall-rocks and barite-fluorite mineralization in the Stanisławów deposit bear following sulfides which are microscopically discernible: pyrite, marcasite, chalcopyrite, galena, tetrahedrite, sphalerite, wurtzite, native bismuth, digenite, bornite, chalcocite, covellite.

Sulfides commonly found in the wall-rocks, *i. e.* mostly pyrite plus subordinate chalcopyrite and rare marcasite, are disseminated or they occur in the tiny veinlets. The minerals are associated with carbonates (mostly ankeritic dolomite, calcite, dolomite and rarer siderite), hematite, titanium oxides (leucoxene), quartz, albite.

Pyrite usually forms euhedral grains up to few millimeters in size, commonly bearing inclusions of gangue minerals (Pl. 5, Fig. 2). Chalcopyrite sometimes has dendritic habit (Pl. 1, Fig. 3). Studies performed by Karwowski (*in preparation*) reveal that certain dendritic chalcopyrites bear inclusions of mineral of optical features of valeriite or mackinawite (Pl. 1, Fig. 4), which do not display pattern typical of exsolution phenomena.

Sulfides associated with the hydrothermal barite-fluorite mineralization occur either as more than ten-centimeter nest-type aggregates or as disseminated grains. Sometimes they form veinlets cutting the earlier mineral associations of the deposit. Ore veins and veinlets thus are the latest mineral associations of the deposit and ores usually are of colloform structure.

On the basis of the composition of sulfide aggregates, forms of their occurrence and shape, relations between sulfides and barite-fluorite,

three essential sulfide parageneses developed in the deposit, often overlapping each other:

I. The oldest sulfide paragenesis consists of chalcopyrite, galena, pyrite, marcasite, tetrahedrite, native bismuth. This association is genetically and with origin time connected with crystallization of the main minerals of the deposit: barite-fluorite of the II, III and IV mineral parageneses.

II. The later sulfide paragenesis includes sphalerite, wurtzite, galena, pyrite and marcasite. These minerals most commonly occur in crushed parts and healed fractures of the ore series forming tiny veinlets with typical colloform structures.

III. Sulfide paragenesis consisting of colloform pyrite and marcasite. Those sulfides concentrated in zones of crushing and brecciation in the barite-fluorite assemblage and in pockets along the vein/wall-rock contact.

Mineral composition of the I sulfide paragenesis is quite varied and one may observe the change of quantitative relations between minerals at different levels of the deposit. This assemblage occurs both as coarse--crystalline aggregates usually in the marginal parts of the vein and as tiny agglomerate dispersed in the barite-fluorite vein and in the interstices of the main minerals of the deposit. Minerals of this paragenesis also group in later veinlets.

Chalcopyrite and galena prevail in coarse-crystalline aggregates reaching sometimes few centimeters in diameter. Usually one of the two sulfides occupies most of the aggregate, without any observable regularity in this feature. Galena commonly crystallized in cube habit, but some large chalcopyrite agglomerations contain relics of collomorphic structures. Pyrite, often euhedral, associated with galena and chalcopyrite, and in deeper part of the deposit also with marcasite (Pl. 5, Figs 1, 3 and 4; Pl. 7, Fig. 2). Occasionally marcasite and pyrite form rounded, radial aggregates embedding chalcopyrite or galena (Pl. 5, Fig. 4).

Coarse-crystalline aggregates of the I sulfide paragenesis commonly bear scarce amounts of tetrahedrite and sphalerite, which form small inclusions or veinlets in the main sulfides, or rims around their larger grains.

Galena prevails over chalcopyrite in minute agglomerate dispersed in the barite-fluorite vein; the agglomerations are also relatively rich in tetrahedrite (Pl. 4, Figs 1—3 and 4), sometimes forming intergrowths with chalcopyrite (Pl. 7, Fig. 3). Assemblage of the fine sulfide agglomerate includes moreover sphalerite (Pl. 3, Fig. 3; Pl. 4, Figs 1—4) pyrite and marcasite (Pl. 3, Fig. 4; Pl. 4, Figs 1, 3 and 4; Pl. 7, Fig. 3). Those sulfides also frequently occur as separate grains trapped in barite and fluorite or inside interstices of non-sulfide minerals.

In the deeper parts of the deposit (about 400 m) richer in fluorite and quartz (II paragenesis F/Q), also minute grains of native bismuth were found inside galena crystals (Pl. 1, Fig. 1) and native bismuth microinclusions in tetrahedrite; both galena and tetrahedrite belong to the I sulfide paragenesis. Galena bearing bismuth inclusions co-occurs most frequently with chalcopyrite and marcasite.

Recognition of the mineral sequence within the I sulfide paragenesis is difficult. Probably iron sulfides crystallized as the earliest minerals. Variable forms of sulfides of the I paragenesis suggest the pulsating regime of the deposit formation at Stanisławów and crystallization of the defined mineral assemblages during time intervals which are to be specified. The possibility of redeposition of minerals during the deposit formation is also acceptable. Mineral composition of the II sulfide paragenesis includes only sulfides of zinc, iron and lead; other minerals known from the paragenesis I were not found.

Minerals of the II sulfide paragenesis have colloform structures similar to those known from the Silesia-Cracow zinc-lead deposits (Harańczyk 1965). Zinc sulfides prevail here (Pl. 2, Figs 3-4; Pl. 3, Figs 1-2) represented both by sphalerite and wurtzite (Pl. 2, Fig. 4). Wurtzite was identified by X-ray powder method and by transmitted light microscopy. It usually occurs in the laminated or concentric-radial blendes (Pl. 2, Fig. 3). Galena distributes accordingly to the colloform structure of zinc blende, frequently forming laminae alternating with zinc blende laminae.

Colloform iron sulfides, mostly pyrite, occur essentially within galena laminae (Pl. 3, Figs 1—2). Sulfides of the paragenesis II often overlap the mineral assemblages of the sulfide paragenesis I.

Iron sulfides of the paragenesis *III* occur as cement in brecciated parts of the deposit and as small, up to 2.5 cm thick veinlets cutting the barite-fluorite vein.

Colloform structures of iron sulfides (Pl. 2, Figs 1-2; Pl. 8, Figs 1-4) consist of pyrite and marcasite lamellae identified under microscope, as well as of finely-dispersed black-green loose substance, which is gray under ore microscope and of low reflectance, difficult for precise determination.

In immersion microscopy, tiny (about 0.1 μ m in size) grains of iron sulfide were found in lamellae of loose substance, cemented with unidentified dark matrix. By X-ray powder studies those lamellae revealed presence of pyrite and marcasite plus small amount of unreliable geothite. Reflectance of lamellae of the loose substance varies within certain ranges and reportedly it depends on the crystallinity degree of iron sulfides.

Quantitative pyrite/marcasite ratio in colloform aggregates changes significantly. In some parts of veinlets recrystallization processes caused formation of euhedral pyrite grains often bearing relics of the primary colloform structures. Likewise, large grains of marcasite used to be found.

Colloform structures of iron sulfides display variable outline (Pl. 2, Figs 1-2; Pl. 8, Fig. 1). Sometimes veinlets of colloform iron sulfides are fractured or cataclased, and fragments of the veinlets are moved aside (Pl. 8, Fig. 3), and next cemented with colloid iron sulfide substance. This proves the existence of rock movements during precipitation of the described minerals.

SECONDARY POST-SULFIDE MINERALS

Location of the barite-fluorite deposit in the tectonic zone is favourable to water migration which is the main factor in weathering and formation of secondary minerals. Intensity of these processes decreases with depth: the weathering and alterations are best developed down to the depth 200 m, although they are recognizable down to 400 m. Secondary processes cause formation of minerals typical of the oxidation, carbonatization and cementation zones. Weathering developed in various degree in different parts of the deposit, depending mostly on local permeability of rocks, and resulting mostly in the appearance of manganese and/or iron oxides-hydroxides (Bolewski & al. 1969, Chrostowska 1970).

The alteration of sulfide minerals is to be characterized as follows:

Chalcopyrite is frequently replaced by covellite on the grain edges and along thin fractures (Pl. 7, Fig. 4) up to complete disappearance of chalcopyrite. The zones with abundant covellite have deep blue-black colour. Iron from chalcopyrite may be either completely removed or fixed in secondary pyrite trapped in covellite or iron hydroxides surrounding covellite aggregates.

Chalcopyrite also alters by different way, being replaced by bornite rims on the grain sides or in the center of chalcopyrite grains by bornite parallel lamellae (Pl. 7, Figs 1—2). Subsequently, bornite alters into isotropic pink-bluish substance being a reaction zone between bornite and chalcocite (Pl. 7, Figs 1—2). Chalcocite is usually the final product of chalcopyrite alteration accompanied by complete removal of iron.

Sometimes, the occurrence of digenite inside chalcocite grains was observed (Pl. 7, Fig. 2), and moreover, in the outer cores of the altering minerals the mixture of digenite and bornite used to be observed (Pl. 1, Fig. 2). Under such conditions also cuprite sometimes occurs with bornite.

In the shallow parts of the deposit chalcopyrite is oxidized with precipitation of colloform iron hydroxides and complete copper removal.

Tetrahedrite is in general more resistant to the secondary processes, and only occassionally its alteration into covellite was observed.

Copper carbonates, malachite and azurite, formed relatively rarely, probably from solutions circulating in the ore zone, as it appears from acicular euhedral crystals of those minerals, and from their occurrence in fractures apart of copper sulfides.

Relatively best-known post-galena mineral in the surface deposit zone is pyromorphite (Jerzmański & Kornaś 1970), occurring in porous barite, in the post-galena voids as small columnar crystals or minute greenish aggregates.

Galena alterations yielded also cerussite (Pl. 6, Fig. 3) and anglesite (Pl. 6, Fig. 4). Cerussite is more common and it forms coarse-crystalline aggregates, whereas rarer anglesite occurs in compact masses. Both minerals were identified by optical and X-ray methods.

Pyrite (Pl. 6, Fig. 2) and marcasite (Pl. 6, Fig. 1) often were found in the weathering zone, however, they commonly oxidize altering into iron hydroxides.

CONCLUSIONS

The differences between sulfides formed in the wall-rocks and those occurring with barite and fluorite at Stanisławów are apparent both in composition of mineral assemblages, and in their morphology. Sulfides in wall-rocks consist mostly of pyrite, and only in subordinate amounts of chalcopyrite and marcasite.

Sulfides associated with barite and fluorite include pyrite, marcasite, chalcopyrite, galena, tetrahedrite, sphalerite, wurtzite, native bismuth, digenite, bornite, chalcocite and covellite. Wall-rock sulfides are usually clearly crystalline, but sulfides of the vein deposit have frequently colloform structures; this feature is especially typical of pyrite and marcasite.

In the Stanisławów deposit three essential sulfide assemblages (parageneses) were distinguished.

In the spatial distribution of the four distinguished barite-fluorite parageneses down to the depth 600 m, one may ascertain the following features.

Parageneses II (fluorite-quartz) and III (barite-fluorite-siderite) are developed mostly in the deep parts of the deposit, without horizontal variations. These assemblages bid the greatest fair to the commercial fluorite resources.

Paragenesis I (coarse-crystalline barite with hematite) is connected with the moderate depths and relatively frequently it occurs with the paragenesis IV of laminated barite with fluorite.

Distinguishing two stages of barite-fluorite mineralization at Stanisławów, it is stated that sulfides genetically are connected with barite and fluorite of the second stage, *i. e.* with parageneses II—IV.

Sulfides of the first paragenesis are contemporaneous with barite and fluorite mainly of the II and III parageneses. The second sulfide assemblage is usually connected with the IV barite-fluorite paragenesis. Colloform iron sulfides present very late mineral generation that formed after origin of the essential part of the deposit. They impregnate the brecciated assemblages and occur in the marginal pockets in the ore/wall-rock contacts. The discussed pyrite and marcasite frequently are found in barite of the paragenesis I.

Crystallization temperatures of fluorite determined by fluid inclusion homogenization method (Kowalski 1980, Blankenstein 1980, Chojecka 1980) range from 160 to 310° C for the hydrothermal barite and fluorite deposit at Stanisławów. The highest temperatures were obtained for fluorite of the *II* fluorite-quartz paragenesis.

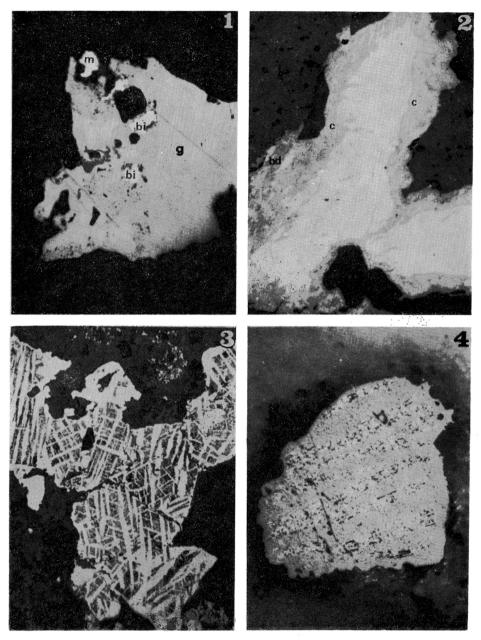
Sulfides occupy in general 0.3-0.5% of the barite-fluorite ore from Stanisławów, although locally they are more abundant. Sulfides, mainly of lead and zinc, do not seem to become an additional raw material to be exploited. However, they are the component which should be considered during dressing processes of the barite-fluorite ores.

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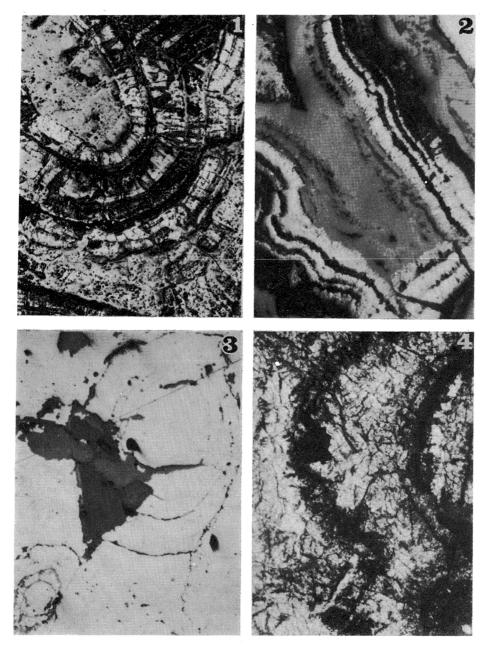
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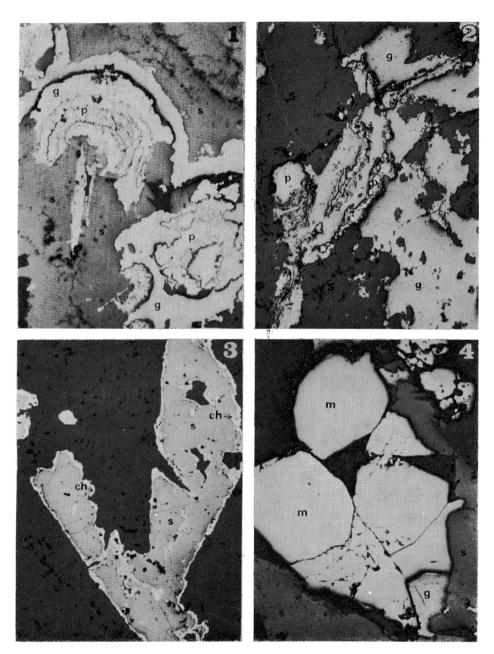
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- 1 Native bismuth (bi) in galena (g) occurring with marcasite (m) and traces of chalcopyrite; reflected light, one nicol, $\times 760$
- 2 Replacement of chalcopyrite (white) by chalcocite (c) and digenite-bornite mess (bd); reflected light, one nicol, $\times 300$
- 3 Dendritic chalcopyrite; reflected light, one nicol, imes 760
- 4 Valeriite (mackinawite ?) in chalcopyrite; reflected light, nicols oblique, $\times 300$



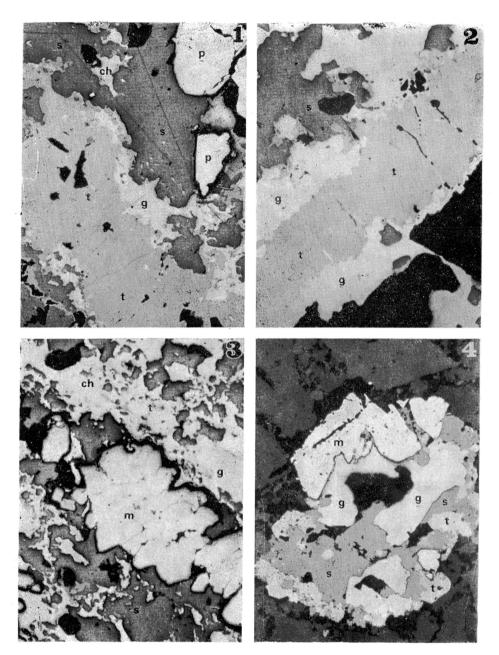
- 1 and 2 Colloform structures of iron sulfides; reflected light, one nicol, 1 is taken imes 75, 2 imes 150
- 3- Concentric structure of zinc blende; reflected light, one nicol, imes 300
- 4 Colloform structure of wurtzite; transmitted light; nicols oblique, ×75



- Colloform aggregates of zinc blende (s), galena (g) and iron sulfides (p); reflected light, one nicol, ×300
 Colloform aggregates of iron sulfides (p) in galena (g) embedded by zinc blende (s); reflected light, one nicol, ×300
 Sphalerite (s) with chalcopyrite inclusions and surrounded with chalcopyrite (ch); reflected light, one nicol, ×300
 Coarse-crystalline marcasite (m) overgrown with sphalerite (s) and galena (g); reflected light, one nicol ×150

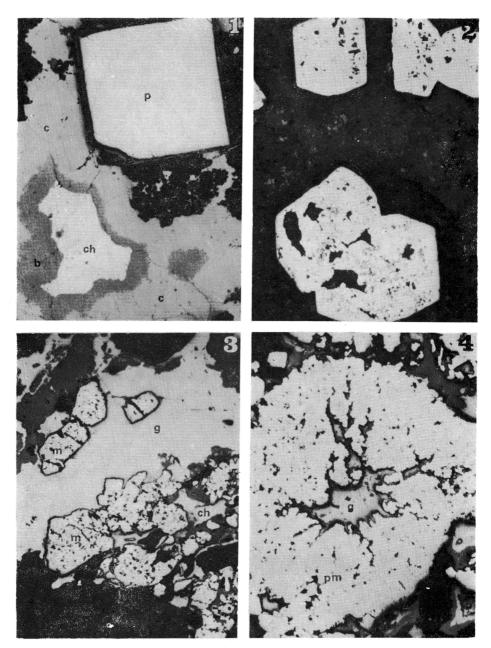
- reflected light, one nicol, $\times 150$

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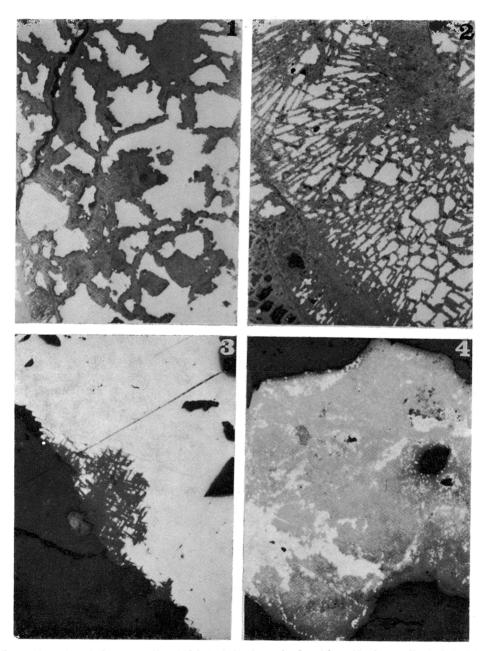
- 1 Tetrahedrite (t) and galena (g) surrounded with sphalerite (s) bearing in-clusion of chalcopyrite (ch) intergrown with pyrite (p); reflected light, one nicol, imes300
- a) A state of the transformation of tra
- reflected light, one nicol, ×3000

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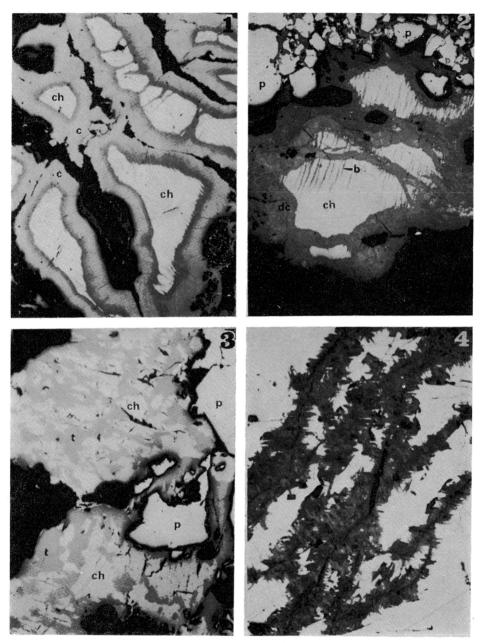


- Euhedral pyrite (p) associated with chalcopyrite (ch) partly altered into bornite (b) and chalcocite (c); reflected light, one nicol, ×300
 Euhedral pyrite grains with inclusions of barren minerals; reflected light, one nicol, ×150
 Marcasite (m) surrounded with galena (g), sphalerite (s) and chalcopyrite (ch); reflected light, one nicol, ×300
 Radial aggregate of pyrite and marcasite (pm) bearing galena grain (g); reflected light, one nicol ×300

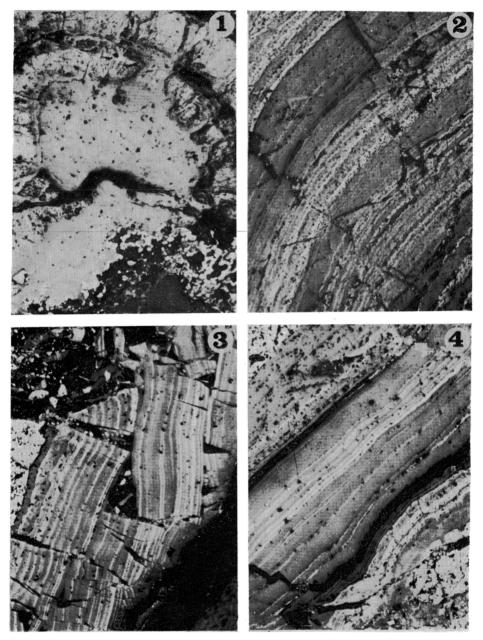
- reflected light, one nicol, $\times 300$



- 1 -Alteration of marcasite (*white*) into iron hydroxides (*dark*); reflected light, one nicol, $\times 300$
- 2 Alteration of vein pyrite (*white*) into iron hydroxides (*dark*); reflected light, one nicol, $\times 300$
- 3 Galena (white) replaced by cerussite (gray); reflected light, one nicol, ×300
 4 Cerussite-anglesite pseudomorph (pale-gray) with galena relics (white); reflected light, one nicol, ×300



- Chalcopyrite (ch) partly altered into bornite (dark gray), and subsequently into chalcocite (c); reflected light, one nicol, $\times 30$ 1 -
- 2 Replacement of chalcopyrite (ch) by bornite (b), next being altered into digenite-chalcocite (dc) mixture; the aggregate is surrounded with iron hydroxides (dark gray) in which pyrite (p) is present; reflected light, one nicol, $\times 300$
- 3 Intergrowths of chalcopyrite (ch) with tetrahedrite (t) associated with pyrite (p); reflected light, one nicol, $\times 300$
- 4 Replacement of chalcopyrite (white) by covellite (gray); reflected light, one nicol, $\times 300$



- Colloform structures of iron sulfides with visible tiny pyrite grains (white); 1 reflected light, one nicol, $\times 150$
- Colloform, laminated structure of iron sulfides; reflected light, one nicol, 2 $\times 150$
- 3 Cataclased veinlet of colloform iron sulfides; reflected light, one nicol, $\times 150$ 4 Veinlet of colloform iron sulfides; reflected light, one nicol, $\times 150$

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MINERAŁY SIARCZKOWE W ZŁOŻU BARYTOWO-FLUORYTOWYM W STANISŁAWOWIE W GÓRACH KACZAWSKICH

(Streszczenie)

W wyniku badań przeprowadzonych głównie w świetle odbitym, stwierdzono wyraźne różnice w składzie mineralnym i wykształceniu siarczków stowarzyszonych z mineralizacją barytowo-fluorytową w złożu Stanisławów w Górach Kaczawskich oraz siarczków występujących w skałach osłony tego złoża (*patrz* fig. 1 oraz pl. 1—8). Siarczki skał osłony powstały w czasie rozwoju procesów pomagmowych cyklu mineralizacyjnego waryscyjskiego, natomiast mineralizacja barytowo-fluorytowa wraz z siarczkami jest rezultatem procesów hydrotermalnych cyklu powaryscyjskiego (saksońskiego).

Wśród siarczków osłony stwierdzono głównie piryt, podrzędnie chalkopiryt, a rzadko markasyt. W paragenezach barytowo-fluorytowych stwierdzono galenę, chalkopiryt, piryt, markasyt, sfaleryt, wurcyt, tetraedryt i bizmut rodzimy, oraz bornit, chalkozyn, digenit i kowelin. Siarczki paragenez barytowo-fluorytowych wyraźnie różnicują się w trzech zespołach mineralnych i genetycznie przywiązane są do drugiego aktu mineralizacji barytowo-fluorytowej (por. Kowalski 1977, 1980).

W strefach wietrzenia złoża stwierdzono szereg wtórnych minerałów charakterystycznych dla stref utleniania, karbonatyzacji i cementacji, takich jak: tlenki i tlenowodorotlenki manganu i żelaza, piromorfit, kupryt, malachit, azuryt, cerusyt, anglezyt, bornit, chalkozyn, digenit oraz kowelin.