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## Sphalerite origin in the Olkusz mining district: a fluid inclusion model

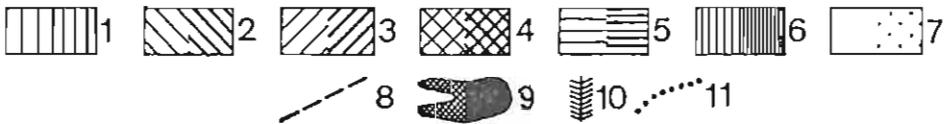
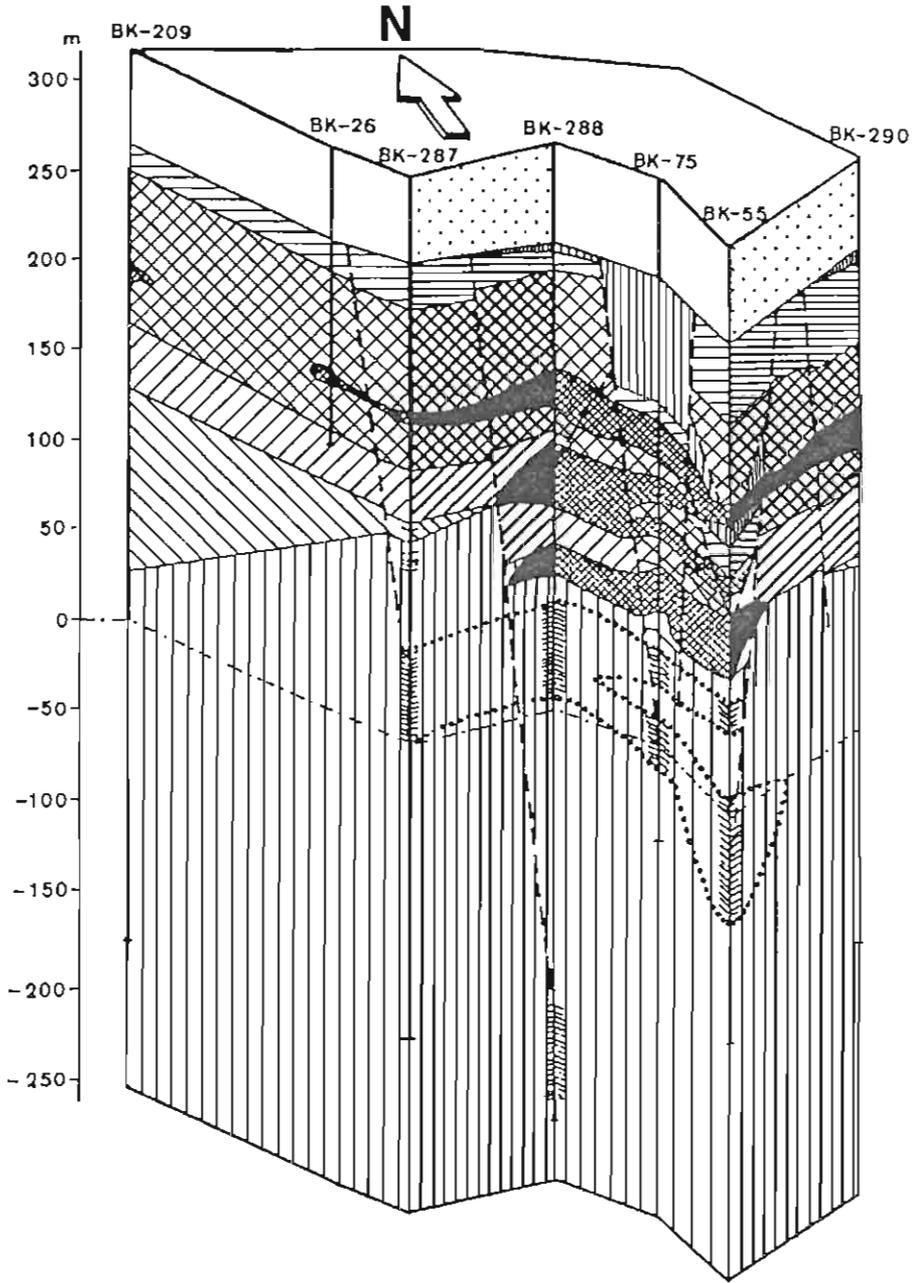
The zinc and lead ores occurrences in the Olkusz district, their structures and attribution to various host rocks, are presented. The course of sphalerite crystallization in cycles starting from oversaturated solutions to relatively diluted ones is evidenced. Fluid inclusion studies in sphalerite yielded the data on the organic-aqueous, inhomogeneous nature of the parent fluids, Th ranging from 130 to 90°C and vertical thermal gradient of the ore-forming fluids, from 6 to 10°C per 100 m. A direct genetic connection of the Zn-Pb ores hosted by Paleozoic and Mesozoic beds is concluded.

### INTRODUCTION

The Klucze deposit area, where the research has been done, lies within the Olkusz mining district at the distance of ca. 3 km north of Pomorzany mine. A detailed elaboration of this deposit has been published by E. Górecka (1991, 1993). The investigation results presented in this paper have been extended by an analysis of the fluid inclusion data studied in sphalerite.

The first data on fluid inclusions in the Silesian-Cracow ores, namely in sphalerites, was published by T. Gałkiewicz (1965, 1967) who quoted the visual homogenization temperatures (Th) estimations by N. P. Ermakov achieving 120°C. Next, E. Roedder (1976) made a series of Th determinations resulting in Th values of 100-120°C.

The following more extensive studies of the specimens, mainly from the Bytom and Chrzanów districts, yielded Th ranging from 92 to 138°C. Hydrocarbon-aqueous type of fluids was recognized with the aqueous phase of the total salt concentration from



nil to 22 wt.% NaCl equiv. and  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , plus possibly  $\text{HCO}_3^-$  as the main ions (Ł. Karwowski et al., 1979; A. Kozłowski et al., 1980).

New investigations on fluid inclusions (A. Kozłowski, 1991a, b, 1992), mostly in the Olkusz and Chrzanów districts, confirmed the Th ranges obtained earlier and yielded a new information on the origin of inclusions in sphalerite, and the values along the vertical extent of the ore mineralization.

The possibility to observe the sphalerite mineralization in an extensive geological cross-section of the Mesozoic and Paleozoic beds was of great importance for genetic considerations of zinc and lead ore deposits.

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### DISTRIBUTION OF ORE MINERALIZATION

The Zn-Pb mineralization, recognized in the drilling cores, varies strongly in its distribution (Fig. 1). The most abundant ore mineralization has been observed in the Lower Muschelkalk (mainly in the ore-bearing dolomites), in the Roethian dolomites and in the Upper Devonian limestones. The number and thickness of the ore-bearing zones in the individual drilling cores range from one to more than ten ore intervals and from some centimetres to several tens metres of the total ore mineralization extent in the Triassic and Devonian beds. The maximum depth of the mineralization ranges usually from 320 to 370 m, rarely reaching about 500 m (e.g. in the borehole BK-288).

In the area under discussion, the intensive ore mineralization is distinctly connected with the density of the disjunctive tectonic structures; the further from those structures, the poorer the mineralization. Generally, an intensive disjunctive Variscan and Alpine tectonics, and karst phenomena are important factors influencing the forms of ore mineralization.

In the Mesozoic beds, the ore bodies lie horizontally and form more or less elongated lenses and nests. These features concern mostly the ores in the Muschelkalk carbonate rocks where the ore-bearing dolomites represent the main host for Zn-Pb mineralization. In the Roethian dolomites, the ore nests of smaller horizontal extent than in the ore-bearing dolomites are characteristic. The ore bodies occurring in the Roethian beds sometimes are connected with the ore bodies in the Paleozoic complex. Generally, however, the bodies do not show any continuation and they are often separated by the screening rocks, e. g. of the Permian or Lower Triassic age. In the

Fig. 1. Blockdiagram presenting the distribution of Zn-Pb ores in Mesozoic and Paleozoic beds

1 — Upper Devonian; 2 — Lower Permian; 3 — Lower Triassic; 4 — Middle Triassic; 5 — Upper Triassic; 6 — Upper Jurassic; 7 — Quaternary; 8 — dislocation zone; 9 — ore body; 10 — ore zone; 11 — presumed ore mineralization extent in Devonian beds

Blokdiagram przedstawiający rozmieszczenie rud Zn-Pb w utworach mezozoicznych i paleozoicznych

1 — dewon górny; 2 — perm dolny; 3 — trias dolny; 4 — trias środkowy; 5 — trias górny; 6 — jura górna; 7 — czwartorzęd; 8 — strefa dyslokacyjna; 9 — ciało kruszcowe; 10 — strefa okruszcowana; 11 — przypuszczalna granica zasięgu okruszcowania w utworach dewonu

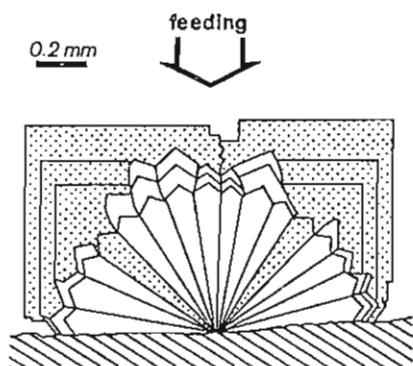


Fig. 2. Scheme of the geometric selection of sphaferite fibres as crystallization nuclei for growth of euhedral sphaferite crystals

Schemat doboru geometrycznego włókien sfalerytowych jako zarodków krystalizacji automorficznych kryształów sfalerytu

Upper Devonian limestones, the ores are connected with deep dislocation zones. Steeply dipping lenses and chimneys are predominant forms there.

A few types of ore structures may be distinguished in the Mesozoic and Palaeozoic carbonate-hosted deposits, namely: ore fillings of cavities, ore cement of carbonate breccias, replacement of host rocks by ore minerals and brecciated ores. A continuous transition from one to another type of the structures was often observed.

#### MORPHOLOGICAL TYPES OF THE SPHALERITE OCCURRENCES

The ores of the deposit are represented by zinc, lead and iron sulfides, accompanied by carbonates, mainly calcite, and barite. Small amounts of chalcopyrite have also been observed. Due to the macro- and microscopic investigations, different mineral assemblages containing ZnS can be distinguished, occurring with variable intensity in the Mesozoic and Palaeozoic beds (E. Górecka, 1993). The ores display granular and collomorphic structures.

Among the granular ores, sphaferite occurs as isolated, often euhedral zonal grains or their aggregates with dispersed very fine pyrite cubes (Pl. I, Fig. 8). There occur also granular aggregates displaying concentric-banded microtexture. The cores are built of the microcrystalline or radial ZnS covered with bands of euhedral ZnS crystals with very small grains of pyrite (Pl. I, Fig. 9). Shell-blende is typical of the collomorphic ores (Pl. II, Figs. 10, 11). There exists a distinct trend of idiomorphism and the size of crystals increase toward the marginal parts of the encrustations. The shell-blende is built of sphaferite in its microcrystalline, fibrous and isometric crystals habit. The aggregates form either parallel or concentric (spherulitic) light and dark bands. Crystals are oriented perpendicularly to their growth surface. Fibrous ZnS often underlies sphaferite of drusy character that forms the outermost band of the shell-blende. Structural etching of the collomorphic aggregates has proved that the ends of ZnS fibres on the outer surface of the spherulitic aggregates possibly acted as crystallization nuclei of the sub- and euhedral sphaferite crystals of the outer band. Transition from the fibrous aggregates to the euhedral ones was probably connected with a geometric selection (Fig. 2). This phenomenon is caused by the orientation of

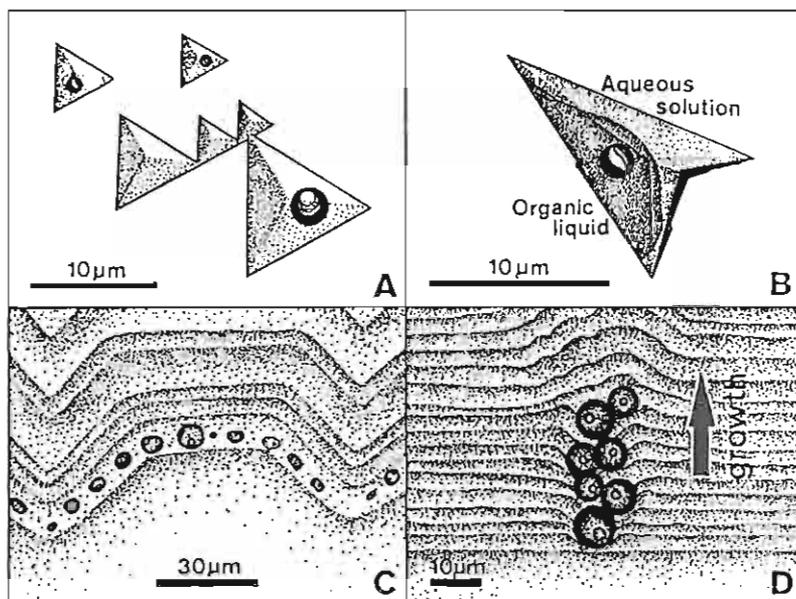


Fig. 3. Primary gas-liquid inclusions in sphalerite

A — a group of inclusions with tetrahedral habit filled by aqueous solution bearing shrinkage bubbles; B — an inclusion with the filling of heterogeneous trapping, consisting of aqueous solution and organic matter, and bearing the shrinkage bubble; C — organic matter inclusions formed along the growth zone of a sphalerite crystal; D — a group of the organic matter inclusions formed along the growth direction of a sphalerite crystal  
Pierwotne inkluzje gazowo-ciekłe w sfalerycie

A — grupa inkluzji o pokroju tetraedycznym wypełnionych roztworem wodnym z pęcherzykami kontrakcyjnymi; B — inkluzja z wypełnieniem heterogenicznego pochodzenia, składającym się z roztworu wodnego, substancji organicznej i pęcherzyka kontrakcyjnego; C — inkluzje substancji organicznej ułożone zgodnie ze strefami wzrostu sfalerytu; D — grupa inkluzji substancji organicznej rozwiniętych zgodnie z kierunkiem wzrostu kryształów sfalerynu

the crystal lattice of the nuclei in relation to the direction of delivery of parent solutions. The geometric selection was already recognized by G. G. Laemmlein (1973) for chalcedony and quartz, and the transition from fibrous spherulitic aggregates to euhedral crystals was related to a decrease in concentration of mineral-forming solution.

In the area discussed, the granular sphalerite prevails in the Paleozoic and Roethian beds. The banded variety is most abundant in the Lower Muschelkalk ore-bearing dolomites.

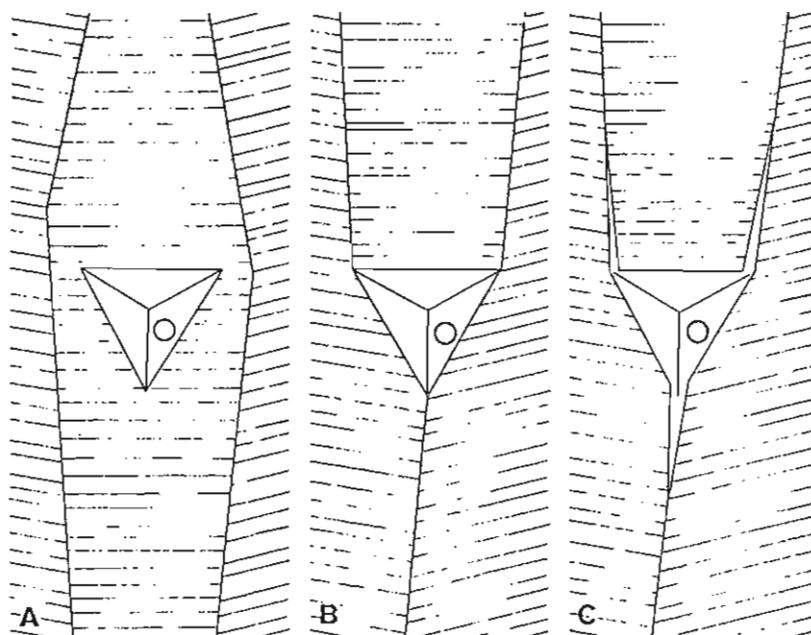


Fig. 4. Intra- (A) and intercrystalline (B) fluid inclusions in fibrous sphalerite; the latter inclusion can easily leak on homogenization run (C)

Wewnątrz- (A) i międzykrystaliczna (B) inkluzja fluidalna w pręcikowym sfalerycie; ta ostatnia może łatwo utracić hermetyczność podczas homogenizacji (C)

## FLUID INCLUSIONS

The studies of fluid inclusions have been performed by use of the routine methods in double polished sections; Th determinations were made by means of the immersion method with an objective 90 x (Ł. Karwowski et al., 1979; A. Kozłowski, 1991a).

Fluid inclusions occur in the studied sphalerites rarely, from 1 to 30 inclusions per cubic millimetre, and their dimensions are small, from 1 to 5  $\mu\text{m}$ , exceptionally to 20  $\mu\text{m}$ . A number of inclusions was too small to recognize their fillings. Primary fluid inclusions occurred as single ones (Fig. 3B), in groups (Fig. 3A and D) or in planes according to growth zones (Fig. 3C).

Primary fluid inclusions were found either inside crystals (intracrystalline inclusions) and thus the measured Th were reliable, or between crystals (intercrystalline inclusions). In this case the increasing pressure during the homogenization run might have caused the inclusion stretching and pulling the fluid in fractures between crystals (Fig. 4). In this case the measured Th could be distinctly higher than their true values. Hence, one should avoid Th measurements on the intercrystalline inclusions.

The secondary inclusions were not numerous and frequently they occurred along straight-line trails (Fig. 5). In such case their genetic attribution was simple. However,

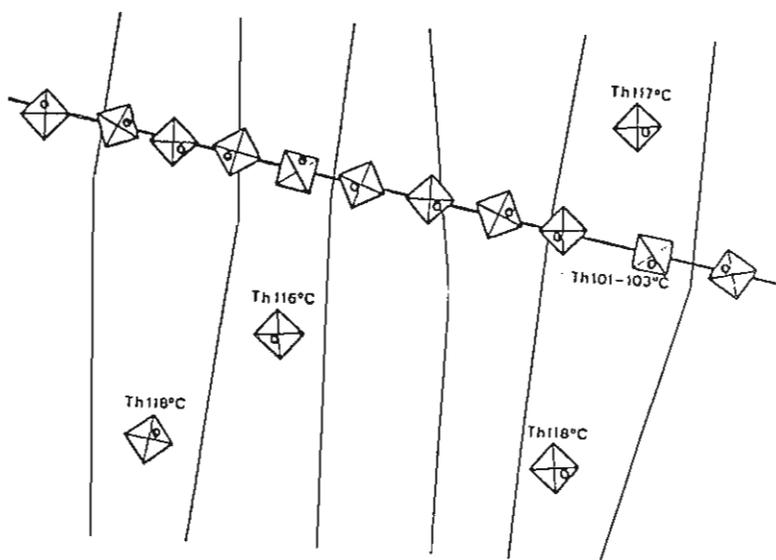


Fig. 5. Scattered primary inclusions and a straight-line trail of the secondary inclusions  
Rozrzucone pierwotne inkluzje i prostoliniowe ułożenie inkluzji wtórnych

not rarely a fracture in the polycrystalline aggregate, following the grain boundaries and cleavage planes in the mineral grains, displayed a complicate zig-zag pattern (Fig. 6). Thus, individual secondary inclusions in such zig-zag trail might have been erroneously considered as isolated primary inter- or intracrystalline inclusions. Because sphalerite has perfect cleavage according to rhombic dodecahedron, i.e. there are six different cleavage planes in each crystal, this results in many possible changes of the fracture direction. A wrong recognition of the inclusion genetic type may lead to establishing of incorrect Th ranges for primary and secondary inclusion generations.

It is necessary to indicate that relatively large primary inclusions, achieving  $20\ \mu\text{m}$  or more, were found in sphalerite crystals of euhedral habit. Those crystals formed due to either slow growth from diluted solutions on the apices of the sphalerite fibres as on crystallization nuclei, or recrystallization of the fine-grained sphalerite. The crystals might form not in main course of the ore formation process but during periods of its inhibition between the subsequent pulses of the ore-forming solution inflow.

The inclusions had essentially two types of the habit: more or less similar to the regular tetrahedrons or globular (Fig. 3). Seemingly the inclusion morphology is related to the inclusion filling. There were found inclusions filled with salt aqueous solutions (tetrahedral, Fig. 3A), liquid hydrocarbons (globular, Fig. 3C and D) and liquid hydrocarbons plus salt aqueous solutions jointly (mainly tetrahedral, Fig. 3B). Almost all inclusions large enough to distinguish their filling, contained shrinkage bubbles. Inclusions bearing daughter minerals, c. g. halite, were not found; this

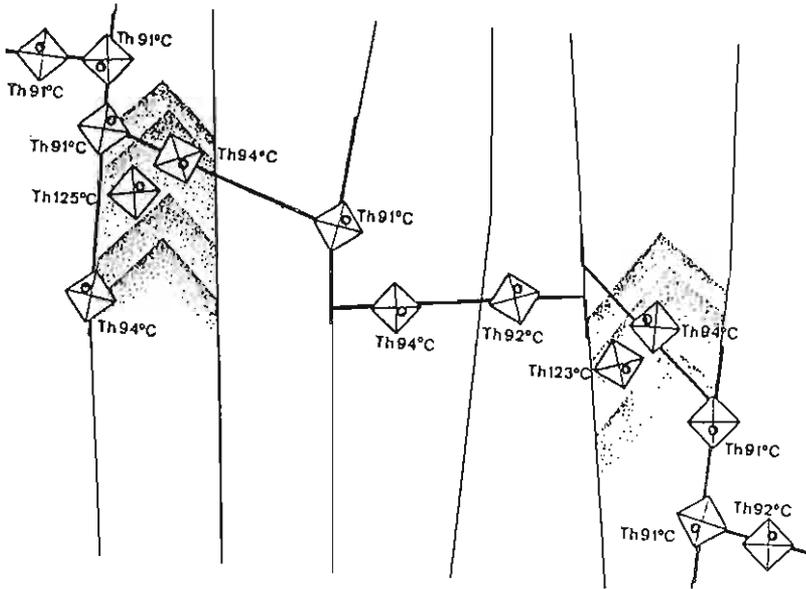


Fig. 6. A zig-zag trail of secondary inclusions and two primary inclusions attributed to the growth zones of sphalerite

Inkluzje wtórne ułożone wzdłuż linii lamanej i dwie inkluzje pierwotne w strefach wzrostu sfalerytu

indicates that salt concentrations in parent solutions were lower than 26 g NaCl equiv. per 100 g water.

The variable water solution/hydrocarbon ratio in fluid inclusions suggests the heterogeneous parent medium of sphalerites: aqueous liquid contained dispersed droplets of liquid hydrocarbon. The existence of such droplets is evidenced by accretional groups of globular hydrocarbon inclusions in sphalerite (Fig. 3D). Such inclusions cannot form due to concentration increase of hydrocarbons dissolved in aqueous solution to achieve the oversaturation point and hydrocarbon exsolution caused by the approaching face of the growing crystal. Such accretional inclusion groups form by adhesion of several oil droplets floating in water phase on a growing crystal. Contrary, oil inclusions in one growth zone (Fig. 3C) may appear due to both the local exsolution caused by the growing crystal and general presence of the immiscible droplets in the matrix liquid.

### HOMOGENIZATION TEMPERATURES

Homogenization temperatures (Th) were measured for more than 200 inclusions. Homogenization of gas bubble and liquid occurred always in liquid phase. Homogenization of two liquid phases: aqueous solutions and hydrocarbons was never observed.

Th of primary inclusions of aqueous solutions in sphalerite from the studied samples range from 90 to 130°C. These values are the best approximation of the origin

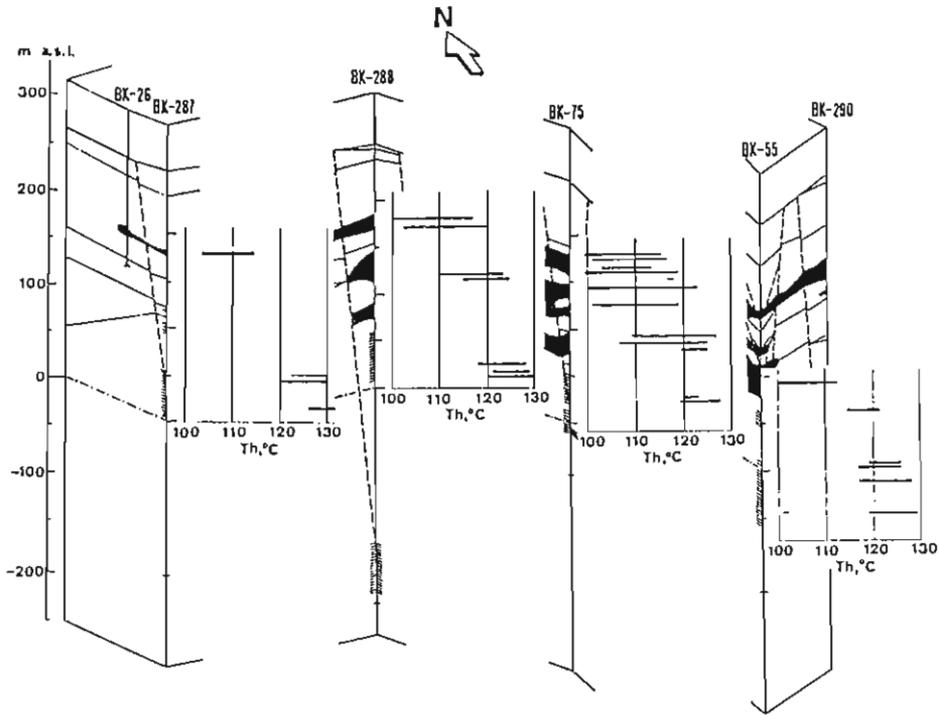


Fig. 7. Homogenization temperature ranges of primary inclusions in sphalerite versus sampling depth on the background of the geological and ore bodies contours of the blockdiagram presented in the Fig. 1  
 Zakresy temperatur homogenizacji inkluzji pierwotnych w sfalerycie dla próbek pobranych na różnych głębokościach, naniesione na tle konturów blokdiagramu przedstawionego na Fig. 1

temperatures of the studied mineral parageneses. Secondary inclusions of the aqueous filling yielded Th values from 80 to 119°C, proving an activity of fluids down to somewhat lower temperatures. Inclusions filled by water solution and organic liquid homogenized at 124–89°C, what means the disappearance of the gas bubble. Liquid organic matter filled inclusions homogenized at 119–87°C.

Homogenization temperatures of primary inclusions with aqueous filling increase distinctly, though not very regularly, with the increasing depth of sampling (Fig. 7). This feature has been found in all the systematically sampled drillings. Any difference in inclusion fillings was not found in ores hosted by rocks of various age (Triassic, Permian, Devonian) and Th values showed only the above mentioned regularity.

The Th ranges for primary water-filled inclusions in sphalerite from the same depth level are distinctly larger for small depths (23–12°C) than for greater depths (11–5°C, cf. Fig. 7). This suggests either cooling or mixing of the ascending fluids, or both. Such feature would be more difficult to explain for descending solutions heated by warmer country rocks.

The upper Th range versus the sampling depth yielded even more distinct pattern of the temperature evolution of the ore-forming fluids (Fig. 7). The average inclination of the line: maximum Th versus depth, is very similar for all the sampled drillings and ranges from 6 to 10°C per 100 m of the depth difference. This value in a first approximation may be accepted as the thermal gradient of the parent solutions during ore deposit formation.

Differences in Th of inclusions in different sphalerite varieties, sampled at the same depth, were not significant except for the recrystallized and late euhedral ones. The latter sometimes yielded Th much lower than the other varieties.

### FINAL REMARKS

The presented research result, including the studies on fluid inclusions, point to a genetic connection between Zn-Pb ores from the Mesozoic and Paleozoic beds, and relatively narrow time interval of their formation. The ores were formed in few inflow pulses of ore-forming solutions. The ores crystallized from true solutions in presence of other ions and in the conditions of a distinct oversaturation and rapid nucleation (cf. E. Roedder, 1968; Chu-Tuan-Nha, J. Kubisz, 1973). Rhythmic growth of the sulfides on the host rock and variation in iron sulfide polymorphism and habit of crystals (granular and fibrous) prove periodic changes in chemical composition and pH of the environment.

Further studies, especially the chemical ones, are necessary to draw conclusions on source of the ore-forming solutions. Such studies are in progress in the co-operation with the scientists from USGS Denver, and the results will be presented in a separate paper.

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Andrzej KOZŁOWSKI, Ewa GÓRECKA

#### GENEZA SFALERYTU W KRUSZCACH REJONU OLKUSKIEGO — MODEL OPARTY NA BADANIACH INKLUZJI FLUIDALNYCH

##### Streszczenie

W pracy scharakteryzowano występowanie rud cynku i ołowiu w regionie olkuskim. Zwrócono uwagę na genetyczny związek rud występujących w skałach mezozoicznych i paleozoicznych oraz na stosunkowo krótki czas tworzenia się tych rud. W trakcie ich powstawania kilkakrotnie mogły występować cykle krystalizacji z roztworów bardzo stężonych (sfaleryt promienisto-pręcikowy) przez roztwory coraz bardziej rozcieńczone (sfaleryt hlp- i automorficzny). Ta cykliczność wiązała się prawdopodobnie z pulsacyjnym dopływem roztworów mineralotwórczych. Omówione zostały cechy inkluzji gazowo-ciekłych występujących w różnych odmianach sfalerytu oraz rozkład temperatur homogenizacji inkluzji pierwotnych zawartych w granicach od 130 do 90°C. Wykazano, że płytsze poziomy mineralizacji charakteryzują się szerszym interwalem temperatur homogenizacji tych inkluzji (23-12°C), głębsze natomiast — znacznie węższym (11-5°C), co może sugerować stygnięcie wód wstępujących wraz z ewentualnym mieszaniami się z wodami chłodniejszymi. Pionowy gradient temperaturowy roztworów został oceniony na 6-10°C na 100 m.

PLATE I

Fig. 8. Sphalerite crystals containing very fine pyrite inclusions (black dots). Borehole BK-75 (Upper Devonian); reflected light, nicols crossed

Kryształy sfalerytu, w których występują bardzo drobne wrostki pirytu (czarne kropki). Otwór BK-75 (dewon górnym); światło odbite, nikole skrzyżowane

Fig. 9. Concentric-banded sphalerite aggregate; the inner core consist of microcrystalline sphalerite, the outer zone comprises subhedral sphalerite crystals associated with pyrite (black grains). Borehole BK-75 (Roethian); reflected light, nicols crossed

Agregat sfalerytowy o budowie koncentryczno-pasmowej; jądro agregatu buduje mikrokrystaliczny ZnS, strefa zewnętrzna jest wykształcona w postaci hipautomorficznych kryształów ZnS, którym towarzyszy piryt (czarne ziarna). Otwór BK-75 (ret); światło odbite, nikole skrzyżowane

Scale bars on all photos — 0.5 mm

Odcinki skali na wszystkich zdjęciach odpowiadają 0,5 mm



Fig. 8



Fig. 9

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PLATE II

Fig. 10. Shell-blende on dolomite: spherulites of fibrous sphalerite surrounded by subhedral sphalerite crystals (dark brown). Borehole BK-75 (Lower Muschelkalk; ore-bearing dolomites); reflected light, nicols crossed

Blenda skorupowa narastająca na dolomicie: sferolity włóknistego sfalerytu otoczone pasmem hipautomorficznych kryształów sfalerytu (ciemno-brązowe). Otwór BK-75 (wapień muszlowy dolny; dolomity kruszczońskie); światło odbite, nikole skrzyżowane

Fig. 11. The same as Fig. 10. Borehole BK-75 (Middle Muschelkalk — Diplopora Dolomites)

Jak na Fig. 10. Otwór BK-75 (wapień muszlowy środkowy — dolomity diploporowe)



Fig. 10



Fig. 11

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