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Origin of Zn-Pb ores in the Olkusz and Chrzanów districts: A model based on fluid inclusions

ABSTRACT: Fluid inclusion studies in sphalerite from early-stage Zn-Pb mineralization, hosted by Devonian, Triassic and Jurassic carbonate beds in the Olkusz and Chrzanów ore districts, Silesian-Cracow region (southern Poland), yielded homogenization temperatures (*Th*) from 80 to 158°C with the upper range higher in the south of the region and lower in the north. Vertical thermal gradient of the parent fluids was 6 to 10°C, and the ore crystallization temperature ranges varied from < 10°C at deep levels to 25°C at shallow levels. The peculiarities of formation of primary and secondary fluid inclusions from organic-matter-bearing water-dominated medium, position of the inclusions in crystals, features of secondary inclusions, the inclusion refilling phenomena, their bearing on recrystallization of ores, and *Th* distribution in single fissure fillings were considered. The ore-forming fluids were liquid-hydrocarbon-bearing aqueous solutions of Na-Ca-Cl type with lower Ca contents in the south and higher Ca contents in the north of the region. The ore-forming fluids had salinities from nil to *c.* 23 wt. % of NaCl equivalent. Three types of fluids were recognized: (1) low-to-moderate salinity *versus* high *Th*, (2) high salinity *versus* moderate *Th*, and (3) low salinity *versus* low-to-moderate *Th*, attributed to ascending fluids, formation brines, and meteoric descending waters, respectively. The three fluids mixed during ore precipitation. Mobilization of the fluids (ascending and partly formation brines) is linked with folding and uplift of the Carpathians to the south of the ore region. A comparison of the Silesian-Cracow deposits with the Mississippi Valley-type ones is presented.

INTRODUCTION

The origin of the carbonate-hosted sulfide Zn-Pb ore deposits, occurring in the Silesian-Cracow region, southern Poland (*see* Text-fig. 1), has been attempted to explain on the basis of mineralogical (*e.g.* HARAŃCZYK 1962, 1963), sedimentological (SMOLARSKA 1968a, b, 1974; EKIERT 1976; GRUSZCZYK 1977), tectonic (GÓRECKA & *al.* 1992, JAROSZEWSKI 1993, KIBITLEWSKI 1993, KIBITLEWSKI & JAROSZEWSKI 1993), structural (BOGACZ, DŻUŁYŃSKI & HARAŃCZYK 1970; DŻUŁYŃSKI 1976; DŻUŁYŃSKI & SASS-GUSTKIEWICZ 1980), geochemical (*e.g.* HARAŃCZYK 1965, 1979) and isotope (ZARTMAN & *al.* 1979, CHURCH & VAUGHIN 1992, HARAŃCZYK 1993, LEACH & *al.* 1996) studies. The proposals for ore substance accumulation process ranged from sedimentary mechanisms (*e.g.* KONSTANTINOV 1993), as inferred from experimental works (*cf.* FERGUSON & *al.*

1975), to orthohydrothermal activity (Gałkiewicz 1971). A number of interesting studies was performed in the weathering zone of the sulfide ores (*see e.g.* Kubisz 1958; Kubisz & Żabiński 1958; Żabiński 1958a, b, 1960).

The previous fluid inclusion investigations have given a general outline of the temperatures of the ore origin and chemical composition of the ore-forming solutions (*see* references *in* Kozłowski & Górecka 1993). This study aimed to determine the parametres of crystalization of the very earliest ore sequence, as reflecting the original features of the ore-forming fluids. Thus, the results of the studies of all the redeposited, altered, so-called metasomatic and hydrothermal karst ores have not been included to this report.

For reason of the availability of the samples for studies, only two ore districts: the Olkusz, and the Chrzanów one (Text-fig. 1), became the area of

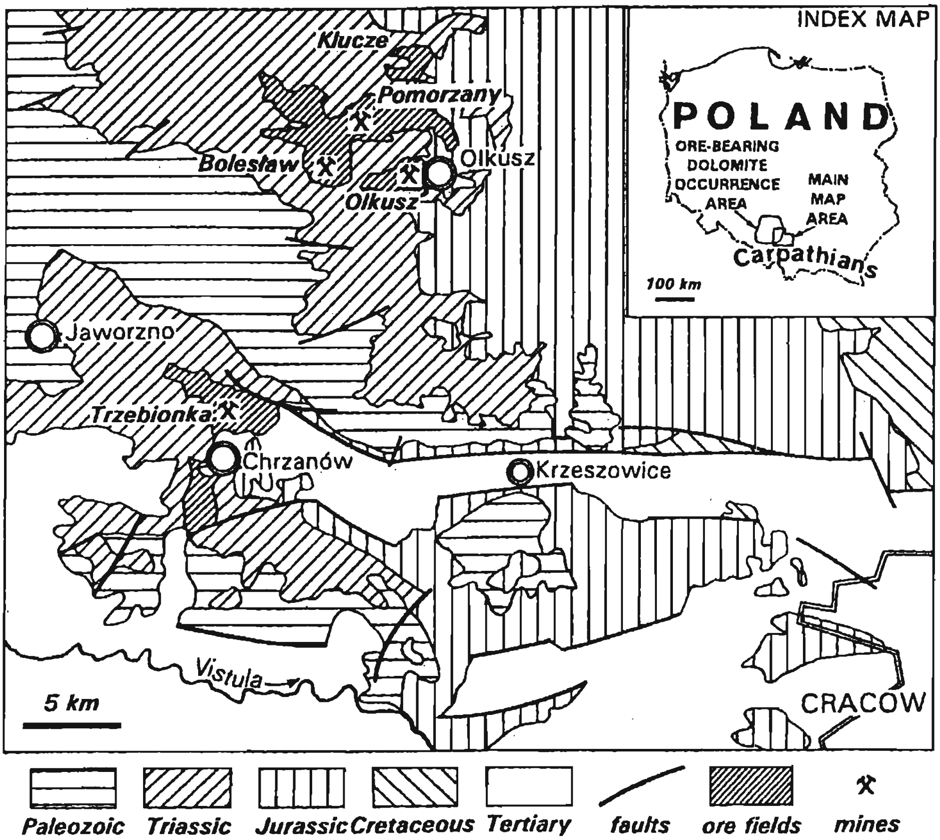


Fig. 1

Geological sketch-map of the Olkusz and Chrzanów districts and location of the sampled mines and ore fields (main map taken *from* Górecka 1993a, Fig. 9, *modified*; the area of the ore-bearing dolomite *from* Narkiewicz 1993) the present study. The third one, the Bytom district, was not considered in this project, because all its mines are presently abandoned and the samples preserved in various collections do not yield a systematic sequence. The strictly systematic sampling was one of the most important guidelines of the material selection for this study.

The zinc and lead mineralization occurring in the Zawiercie, Myszków and Mrzygłód areas (GÓRECKA 1972, GÓRECKA & NOWAKOWSKI 1979, KARWOWSKI 1988) was not investigated in this project.

GEOLOGIC SETTING

The Silesian-Cracow zinc and lead ore deposits occur in the border zone of the Bohemian massif (*see* Fig. 1 *in* GÓRECKA 1993a). The geologic structure of this ore region, called the Cracow-Myszków zone, includes two tectonic-sedimentary complexes: (*i*) Paleozoic rocks of block-folded tectonics, eroded to various depth and displaying pre-Permian/Permian surface relief with remarkable denivelations, afterwards covered by (*ii*) nearly horizontally resting Mesozoic sediments with patches of Tertiary rocks. The Paleozoic complex was intruded by small bodies of magmatic rocks of various age, but apparently mainly connected with Variscan orogeny, as summarized by GÓRECKA (1993a).

Among the Paleozoic rocks, in the context of ore mineralization investigated in this study, of interest are the platform-type, mainly carbonate sediments of Devonian age, covered discontinuously by Carboniferous beds and/or Permian clastics and pyroclastics, with a gap in the Permian and lowermost Triassic.

A stratigraphic gap finished either in the Lower Triassic (sandy and shaly, partly continental Buntsandstein and/or carbonate Roet with evaporite intercalations), or locally in the Middle Triassic (Muschelkalk), when in the Silesian-Cracow region the uniform epicontinental, mainly carbonate sedimentation started (ŚLIWIŃSKI 1969). The Lower Muschelkalk series is composed of limestones, partly or completely dolomitized. The Middle Muschelkalk sequence consists of dolomites, locally with conglomerates and gypsum in its uppermost part; the Upper Muschelkalk is developed as clays, limestones, dolomites, marls and conglomerates. The Upper Triassic (Keuper) is a sequence of dolomites and clays with gypsum and anhydrite, marls and clastic sediments, truncated by an erosion surface. The total thickness of the Triassic sequence is variable and may achieve *c.* 150-200 m. More detailed data on the geologic setting of the Silesian-Cracow ores has concisely been presented by BOGACZ, DŻUŁYŃSKI & HARAŃCZYK (1970).

The Triassic sequence was covered by the Middle Jurassic (Callovian) sandy-limestone beds, and then by the Upper Jurassic limestone sequence.

Post-Jurassic denudation removed partly the Jurassic sediments. The Mesozoic unit was weakly folded and cut by faults during post-Variscan, apparently mostly Alpine orogenic events. The faults frequently followed the older disjunctive tectonic pattern (GÓRECKA 1993a, b, *and* references quoted there). From its southern edge the Silesian-Cracow region is bordered by the Fore-Carpathian Depression filled with the Miocene sedimentary sequence developed from clastics through limestones to evaporites. Carpathian flysch mountainous chain of Alpine orogeny occurs further to the south (*see* Text-fig. 1).

The "ore-bearing dolomite" (Pl. 1, Fig. 1) is a term to determine saccharoid (often coarse) metasomatic, mainly post-limestone dolomite. It is usually darker than the host rocks (limestone, or primary, *i.e.* early diagenetic dolomite) and its contacts with the host rocks are discordant to their bedding; relics of the host rocks are frequent in the ore-bearing dolomite. The origin of the "ore-bearing dolomite" was extensively discussed (*e.g.* TRACZYK 1965; ŚLIWIŃSKI 1969; BOGACZ & *al.* 1972, 1975; PAWŁOWSKA & SZUWARZYŃSKI 1979; KRZYCZKOWSKA-EVEREST 1990; BĄK 1993; NARKIEWICZ 1993), and most of the authors attributed its formation to epigenetic dolomitization of limestones and, to a lesser extent, recrystallization of early diagenetic (primary) dolomites. The "ore-bearing dolomites" developed mainly in Lower and Middle Muschelkalk carbonates (BOGACZ, DŻUŁYŃSKI & HARAŃCZYK 1970). Both sole and top surfaces of the ore-bearing dolomite bodies occur at variable stratigraphic and hypsometric levels, and the thickness of the dolomitized zone varies from nil through a common value of 30-40 m up to 70 m (GÓRECKA 1993b). This is a host rock for majority of the ore mineralization in the Silesian-Cracow region, though both barren "ore-bearing dolomite" (as the lithological variety) and ores hosted by limestones are also known.

ORES

The zinc and lead ore mineralizations are most abundant in the Lower Muschelkalk (mainly in "ore-bearing dolomites", *see* Pls 1-4), in Roet dolomites and, to some extent, in Devonian limestones; also Jurassic limestones bear scarce ores (*see* ŚLIWIŃSKI 1964; GÓRECKA 1993a, b). The number and thickness of ore-bearing zones in vertical extent are variable. The depth of ore mineralization achieves *c.* 500 m below the present-day Earth's surface in the region. Intensive ore mineralization is connected with disjunctive tectonic structures. Karst structures, both in Triassic and Devonian carbonate rocks, are also important ore-forming controls (BOGACZ, DŻUŁYŃSKI & HARAŃCZYK 1970; BOGACZ & *al.* 1973a; SASS-GUSTKIEWICZ 1975; DŻUŁYŃSKI 1976; DŻUŁYŃSKI & SASS-GUSTKIEWICZ 1993).

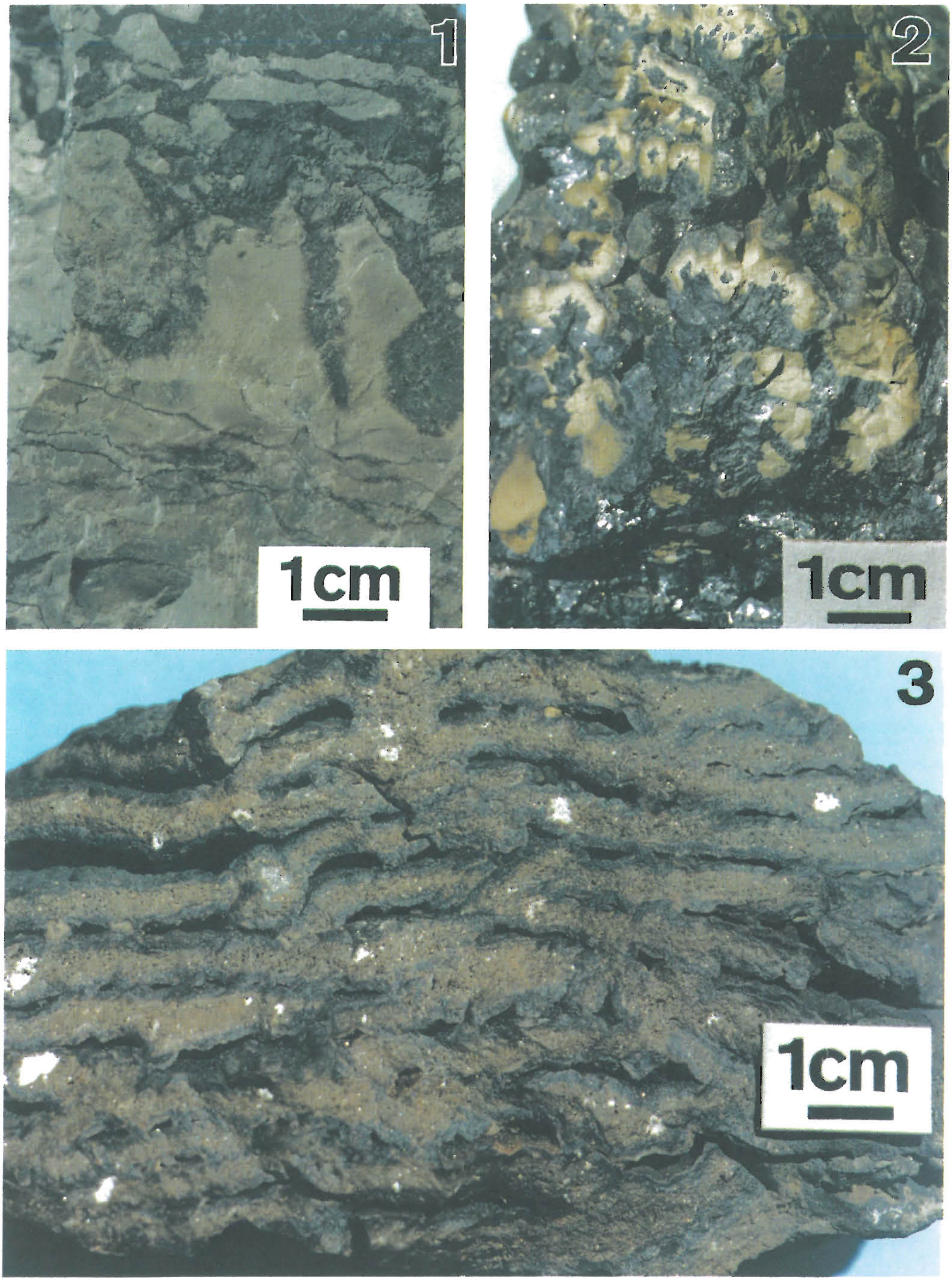
Ore bodies, hosted by Mesozoic sequence, are mainly horizontal lenticular zones or pockets, rarely almost vertical veins (SZUWARZYŃSKI 1991, 1996). The bodies in the Roet sequence exceptionally continue down to those hosted by the Paleozoic beds, but usually they are separated by the Lower Triassic or Permian rocks (GÓRECKA 1993b). In the Upper Devonian limestones the ores are connected with deep dislocation zones, and the steeply dipping lenses and chimneys are the predominant forms there. The four main types of ore occurrence are to be distinguished (GÓRECKA 1993b): (*i*) Ore fillings of fissures and cavities (veins and veinlets, granular assemblages, encrustations, druses, and compact banded or loose masses called "collomorphic", *see* Pl. 1, Fig. 2); (*ii*) Ores replacing the host rocks, mainly "ore-bearing dolomites" (BOGACZ & *al.*1973b), with zebra textures (Pl. 1, Fig. 3), evidencing the replacement origin (*see* WALLACE & *al.* 1994); (*iii*) Ore cement of carbonate breccias (tectonic, and karst collapse ones; Pl. 2, Fig. 1); (*iv*) Brecciated ores (Pl. 2, Fig. 2).

The list of the main primary ore minerals is scarce, to include sphalerite, galena, pyrite and marcasite. The main gangue minerals are: dolomite and its ferrous (GRUSZCZYK & WAŻEWSKA-RIESENKAMPF 1960, BĄK 1993) and zinc varieties (ŻABIŃSKI 1959), calcite (Pl. 2, Fig. 3) and, occassionally, barite and lead aragonite (Pl. 3, Fig. 3), the latter called *tarnovskite* (SEIFERT 1938). The gossan ores (galmei; Pl. 4, Fig. 3) are out of scope of this study.

Phaneritic sphalerite and its cryptocrystalline, chalky variety — *brunckite* (Pl. 3, Fig. 2; *cf. also* HARAŃCZYK 1959b) are associated with minor and not always present wurtzite (HARAŃCZYK 1960, GÓRECKA 1993b); "colloform" does not mean the colloidal origin, as evidenced by ROEDDER (1968b). Sphalerite occurs as two further morphological varieties of granular and fibrous habits; its color changes from dark brown through red-brown, tan-brown, cognac-brown, yellow to colorless. Granular sphalerite occurs as individual disseminated zonal crystals, their clusters or layers, then displaying concentric-banded microtexture, sometimes with microcrystalline or fibrous radial and subparallel aggregates in inner cores or bands. There occur alternating bands of granular and fibrous, or fibrous and colloform varieties, resulting in the so-called *Schalenblende* aggregates (Pl. 3, Fig. 1).

Galena appears as concordant bands, not always continuous, in sphalerite zones, as massive almost monomineral bodies, druses of euhedral crystals (Pl. 4, Figs 1-2), skeletal forms in zinc blende (HARAŃCZYK 1959a), or colloform cryptocrystalline masses called *boleslavite* (HARAŃCZYK 1961).

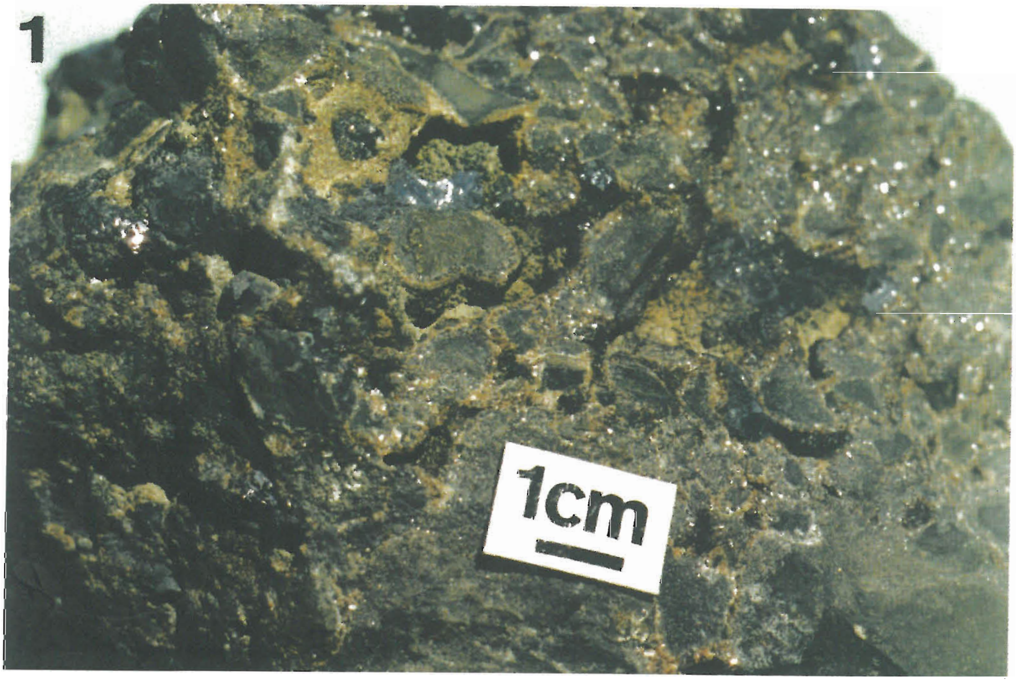
Pyrite and marcasite form separate euhedral grains in zinc blende, continuous fibrous layers up to several centimeters thick on zinc blende, or disseminated grains or encrustations on galena crystals (Pl. 4, Fig. 1). The

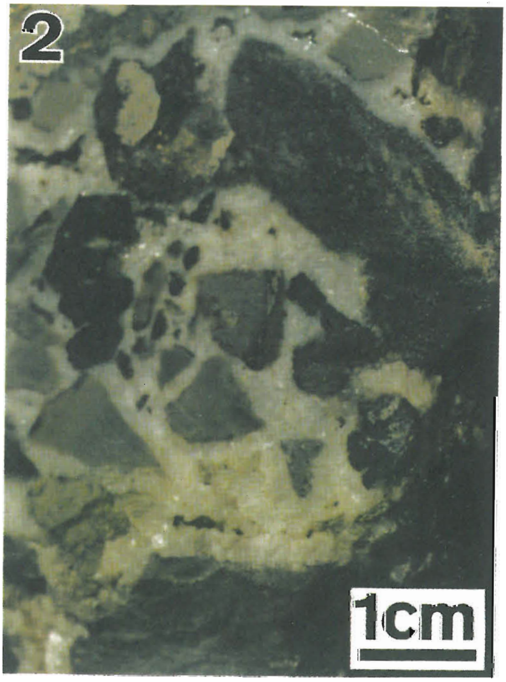


1 – "Ore-bearing dolomite" (*dark gray*) replacing Triassic limestone (*light brownish-gray*); Trzebionka mine

2 – Sphalerite (*beige to grayish-brown*) and massive to dendritic galena (*dark gray*) filling an open fissure in "ore-bearing dolomite"; Trzebionka mine

3 – Zebra textures of metasomatic sphalerite that replaced the host carbonate rock; Trzebionka mine

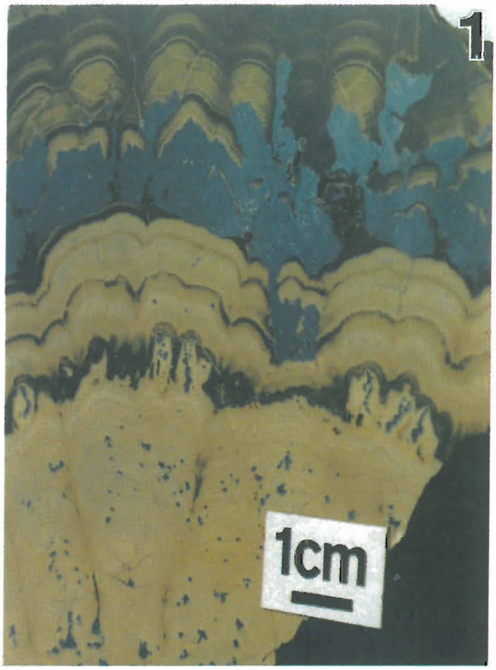


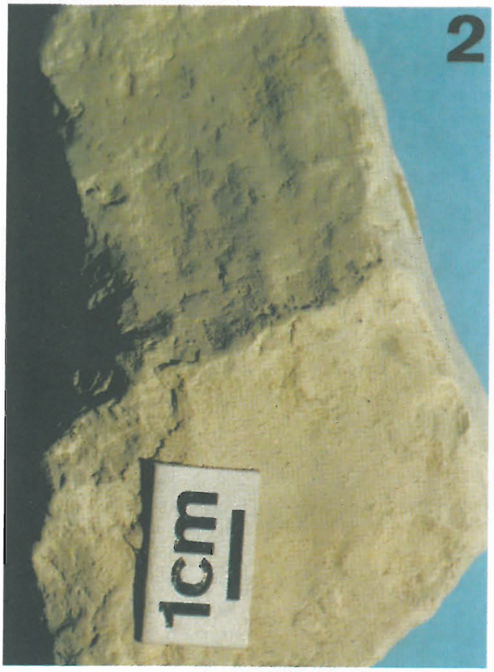


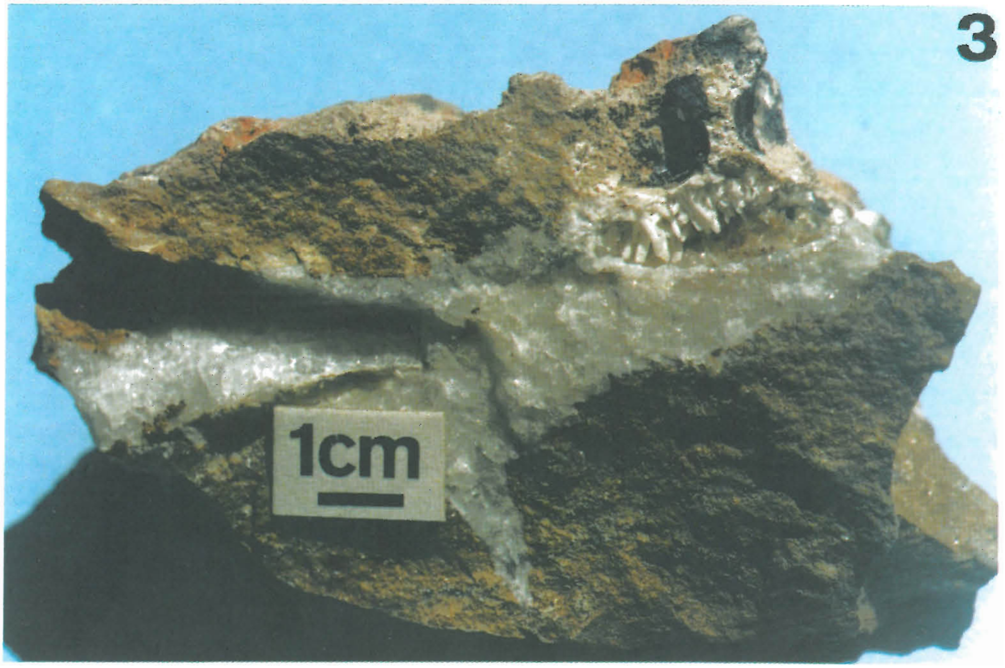
1 – "Ore-bearing dolomite" fragments cemented with sphalerite and galena; Bolesław mine

2 – Limestone, "ore-bearing dolomite" and sulfide ore fragments cemented with dolomite and calcite; environs of Siewierz

3 – A vug in carbonate-sulfide breccia, lined with white-pinkish saddle dolomite and bearing honey calcite crystals; environs of Siewierz



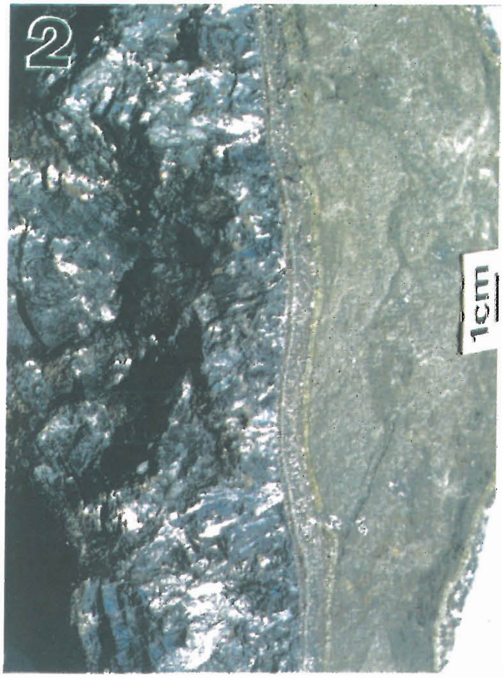




1 – Sequence of bands of consolidated brunckite (*beige*), granular and fibrous sphalerite (*various tints of brown*) and galena (*bluish-black*); upper part of the sequence has the nature of *Schalenblende*; Olkusz mine

2 – A lump of brunckite that can be easily pulverized by rubbing with fingers; Olkusz mine

3 – A veinlet and small druse of tarnovskite in "ore-bearing dolomite", associated is galena (*black*); Trzebionka mine



1 — A druse of octahedral galena covered with colloform iron sulfide; Trzebionka mine
2 — "Ore-bearing dolomite" (*gray*) covered with bands of iron sulfides (*yellow-gray*), fibrous and granular sphalerite (*brown*), and massive galena (*gray-black with luster*) with pyrite; Bolesław mine
3 — Gossan ore: galmei with fragments of weathered dolomite; Olkusz mine

latter are, however, frequently colloform iron sulfide, that is *melnikovite* (*see* Śliwiński 1964).

Few rare and/or minor minerals found in the discussed deposits include thallium jordanite, occurring usually in dark zinc blende (Harańczyk 1958).

The generalized sequence of ore mineral crystallization and accompanying events is similar (with small variations) in the both considered ore districts, *i.e.* Olkusz and Chrzanów ones (Górecka 1993b, and *personal communication* 1995). The crystallization started from sphalerite with minor galena and pyrite, disturbed tectonically by faulting, brecciation and cataclasis. This tectonic event was followed by an increased formation of pyrite and marcasite, and afterwards by major sphalerite precipitation with subordinate galena. When sphalerite formation ceased, ore-forming process continued as crystallization of galena in the Chrzanów district, and pyrite plus marcasite with minor galena in the Olkusz district. This stage of ore formation was completed with intensive karstification, collapse brecciation, broadening of interbed joints, and formation of "sandy" dolomite (*i.e.* its disintegration to loose grains; *cf.* Bogacz & *al.* 1973a). Later, sphalerite plus subordinate galena continued to precipitate, with iron sulfides: pyrite and marcasite in the Chrzanów district, and marcasite in the Olkusz district. The mineral sequence finished with major precipitation of galena.

SAMPLES

Sphalerite was the only investigated ore mineral in this study, as common and transparent component of the ores. Wurtzite, as minor and relatively rare phase, was not appropriate to obtain data from numerous samples of several locations. Both granular and fibrous varieties were studied; brunckite was too fine-grained for fluid inclusion search.

The samples were selected to obtain a collection of sphalerite specimens that would be mainly the representatives of the earliest stage of ores precipitation. Thus the inclusions in these sphalerites should contain solutions, that

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Fig. 2

A — Pyrite covered by two cycles of granular sphalerite → fibrous sphalerite; borehole *BK-288*, Klucze ore field, depth 148.5 m (host rock: Gogolin Limestones of the Middle Triassic), polished preparation etched with HNO_3, polars parallel

B — Sequence starting from fibrous light sphalerite with rare marcasite, covered by tan and dark-brown fibrous sphalerite and next with dark-honey granular sphalerite; sample *T-28*, Trzebionka mine (host rock: Lower Muschelkalk "ore-bearing dolomite"), polished preparation, polars crossed

C — Dark fine-banded fibrous sphalerite on pyrite covered with dark-brown granular sphalerite and next with calcite; borehole *BK-75*, Klucze ore field, depth 136.7 m (host rock: Olkusz Beds "ore-bearing dolomite"), polished preparation, polars crossed entered first or almost first the country rocks at a considered place, being poorly or not affected by the local wall rocks. Such approach should result in obtaining of an internally consistent model of the solutions circulation and of the ores origin. This model would either fit to mineralogical and geological, and structural data of the region studied, or display distinct discrepancies with. As a consequence, the ore products of extensive metasomatic and hydrothermal karst processes (*see e.g.* BOGACZ, DŻUŁYŃSKI & HARAŃCZYK 1970; BOGACZ & *al.* 1973a; SASS-GUSTKIEWICZ 1974, 1975; DŻUŁYŃSKI & SASS-GUSTKIEWICZ 1993) were thus beyond limits of this study.

From several hundreds samples, 91 were selected for detailed fluid inclusion studies. They included 43 samples from Klucze ore field, 14 from Olkusz mine, 11 from Bolesław mine, 12 from Pomorzany mine, and 21 from Trzebionka mine. The samples were taken from Devonian and Triassic host rocks, and they comprised veinlet, vein, cavity fillings, as well as tectonic breccias cemented with ores.

The ore-mineral sequence started frequently in the investigated samples from the earliest pyrite, overgrown by granular sphalerite covered with its fibrous variety; the granular-fibrous sphalerite sequence might have then repeated (Text-fig. 2*A*). The described mineral sequence indicates alkaline solutions initially of low ZnS concentration, thus yielding pyrite and granular sphalerite during slow precipitation. Afterwards, ZnS concentration increased and it caused origin of the fibrous variety on rapid crystallization. After that the parent solution became again dilute, and subsequently its ZnS concentration increased again. Such sequence usually finished with granular sphalerite (not shown in Text-fig. 2*A*), indicating the third dilution event.

However, quite frequently the earliest pyrite was covered with fibrous sphalerite (Text-fig. 2*C*). This indicated the fracture entering by ore-forming solution of high ZnS concentration (*see* Text-fig. 3*A*); the granular sphalerite, that overgrown the fibrous variety could slowly crystallize, when most of ZnS carried by solution precipitated and its concentration was low (Text-fig. 3*B*). Two other reasons of the granular sphalerite precipitation are possible. One mode of slow ZnS supply to solution is related to sphalerite dissolving in the warmer part of a fissure system (Text-fig. 3*C*). In this case, the dissolved substance would migrate to the hypsometrically higher parts of the fissure due to thermic convection. Moreover, sphalerite dissolving and ZnS supply to solution may be caused by tectonic stress (Text-fig. 3*D*); then ZnS would migrate less upwards, but mainly downwards as a solution heavier than its surrounding portions.

Sometimes, the ore precipitation started from marcasite, what indicates acid parent solution (Text-fig. 2*B*). This iron sulfide was overgrown by fibrous and successively by granular sphalerite. The ends of the sphalerite fibers, when oriented favorably to the crystal feeding direction, on the decrease of the ZnS concentration in solution became crystallization nuclei for equant sphalerite crystals. In this case, orientation and number of the latter was determined by the rule of geometric selection (Text-fig. 4; *cf.* LAEMMLEIN 1973a).

INVESTIGATION METHODS

Fluid inclusions were investigated in 352 double-polished sphalerite preparations of thickness of 0.1-0.3 mm, by means of three main methods (ROEDDER 1984): homogenization, freezing, and crushing of individual in-

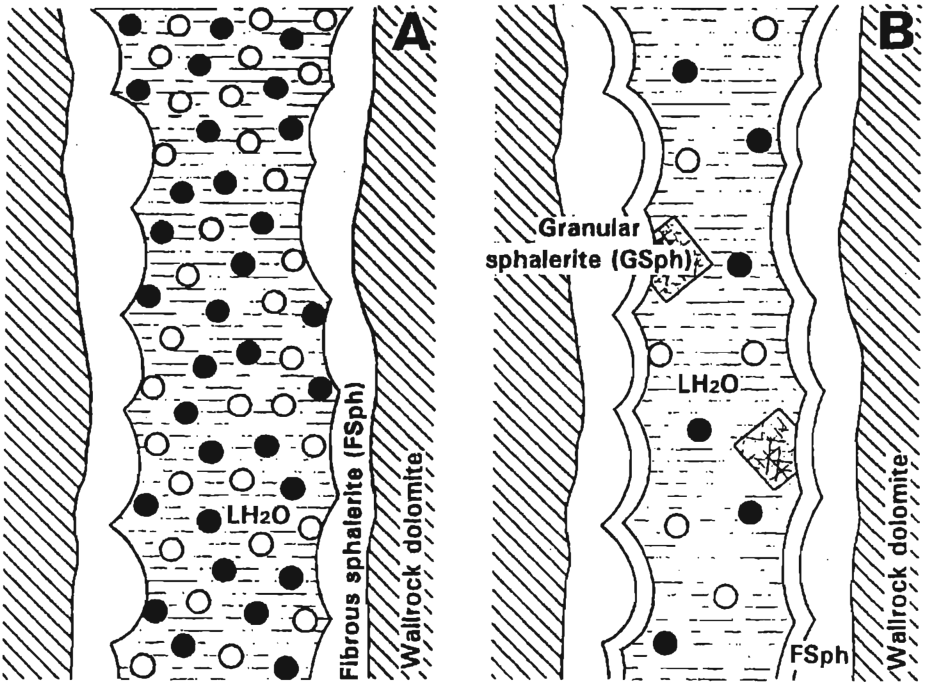


Fig. 3. Precipitation of the early fibrous sphalerite followed by its granular variety originated in a fissure

A — Filling of a fissure with solution oversaturated with respect to ZnS, rapid precipitation of fibrous sphalerite

B — Same solution with decreased ZnS concentration, due to fibrous sphalerite precipitation, that caused slow crystallization of granular sphalerite clusions. For all procedures immersion media were used, because the investigated inclusions were usually very small (<1 to 5 μm), thus due to high refractive index of zinc sulfide the investigated minerals were commonly dark.

Homogenization runs were made by use of an immersion heating stage of the Author's construction, as described by Karwowski, Kozłowski, & Roedder (1979), and immersion objectives 90× or 100×. Silicon oil with ignition point of 314°C was used as the immersion medium, thus the measurements of inclusion homogenization temperature (*Th*) could be run safely up to 280-290°C. At least, three replicate measurements were made for each inclusion, and the obtained values were accepted to calculate the average, if they were in the maximum ranges of 3°C; thus the obtained mean values were in the error ranges of ±1.5°C, but for low values (up to 90°C) usually the error did not exceed ±1°C. The calibration was made on melting points of salts in

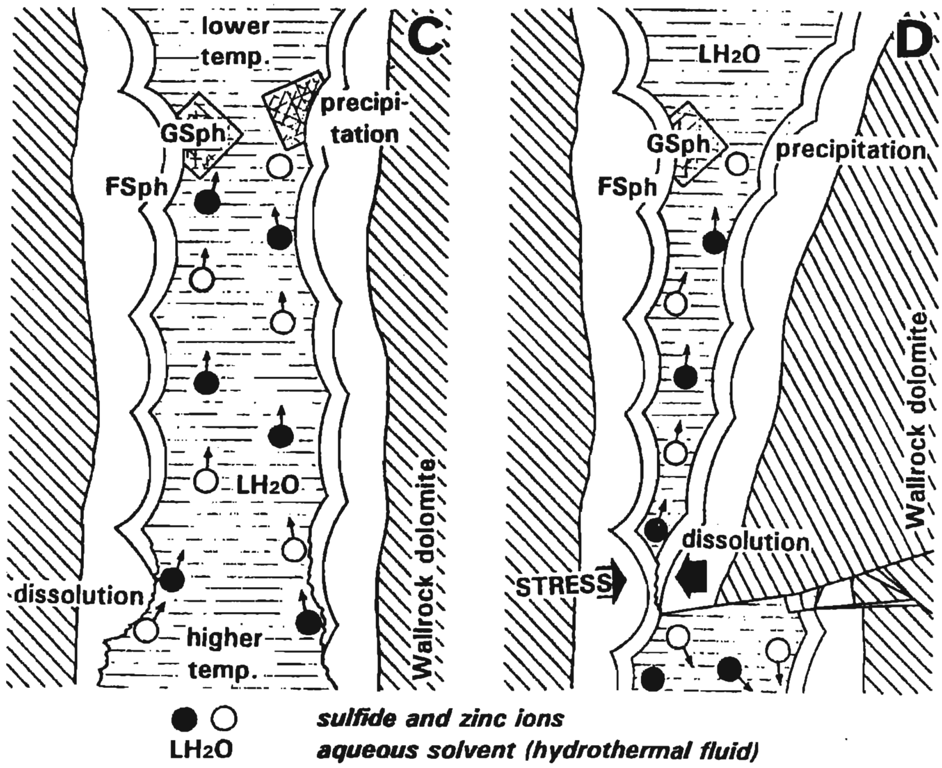


Fig. 3 (*continued*). Precipitation of the early fibrous sphalerite followed by its granular variety originated in a fissure

C — Fibrous sphalerite, dissolved by hot solution, fed slow crystallization of granular sphalerite in a cooler section of the fissure

D — Sphalerite, dissolved under stress conditions, fed crystallization of granular sphalerite in a neighboring part of the fissure

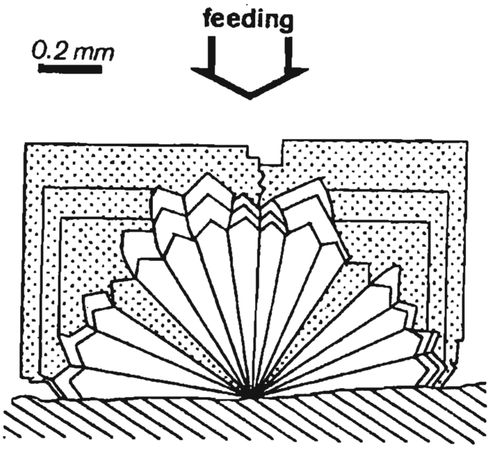


Fig. 4

Geometric selection of sphalerite fibers (*dotted*) as nuclei for crystallization of the granular sphalerite

sealed capillaries 5 mm long, dia. 0.3 mm, with metal weights at the ends to cause them sinking in the immersion medium.

Freezing runs were performed in immersion medium of acetone with organic substances added to increase the acetone refractive index. On cooling to (— 100°C) or (— 140°C) the immersion medium froze as well, but it melted on slow warming, before the preparation achieved temperatures, important for fluid inclusion investigations. Because the applied method requires a very uniform warming, for freezing runs no electric wire heating or heat exchange medium were used. The whole freezing stage warmed from low temperature by maintaining at room temperature without freezing medium (liquid nitrogen) flow; the procedure of inclusion observation on freezing runs was described elsewhere (Kozłowski 1984). The eutectic point temperatures were accepted, if measured within the reproducibility ranges of 1 to 1.5°C for calcium chloride-bearing systems and ±0.2 to 0.3°C for sodium-chloride-dominated solutions; last ice crystal melting point was determined with the latter reproducibility (always minimum three replicate measurements). The data obtained during the freezing runs were plotted on diagrams presented by Yanateva (1946) and Crawford (1981).

Crushing of fluid inclusions was performed in a Chaixmeca microscope crushing stage in organic and aqueous immersion fluids, to distinguish hydrocarbon and aqueous inclusions.

Leaching of salts and hydrocarbons from fluid inclusions was described elsewhere (Karwowski, Kozłowski & Roedder 1979; Kozłowski & *al.* 1980).

PREVIOUS STUDIES ON FLUID INCLUSIONS IN THE SILESIAN -CRACOW ORES

The first data on fluid inclusions in the Silesian-Cracow ores, namely in sphalerite, were published by Gałkiewicz (1965, 1967), who quoted the visual homogenization temperature estimations made by N.P. Ermakov, achieving 120°C. Afterwards, Roedder (1976) made a series of *Th* measurements resulting in values of 100-120°C. The following more extensive studies (Karwowski, Kozłowski & Roedder 1979; Kozłowski & *al.* 1980) of the specimens, taken mainly from the Bytom and Chrzanów districts, yielded *Th* ranging from 92 to 138°C. Hydrocarbon-aqueous type of ore-forming fluids was recognized with the aqueous phase of the total salt concentrations from nil to 22 wt. % NaCl equiv., and chloride, sodium, calcium, potassium plus possibly bicarbonate as the main ions. Organic matter extractions from inclusions and IR absorption studies of the extracted matter were performed for several sphalerite samples (KARWOWSKI, KOZŁOWSKI & ROEDDER 1979; KOZŁOWSKI & *al.* 1980). In a study of over 4,000 samples from 20 stratiform zinc and lead deposits of different regions in Europe and Asia, performed by means of thermovacuum decrepitation method (ALEKSEENKO & *al.* 1978), the samples of the ore-bearing dolomites from the Silesian-Cracow region were included. This study yielded an evidence (*see* ALEKSEENKO & *al.* 1978, Chapter VII, pp. 290-294), that the dolomites were submitted to intensive penetration of hot solutions, what resulted in high decrepitation activity haloes in host rocks of ore bodies. Note, that the decrepitation temperatures given in that study (80-230, 230-290, 310-390°C) cannot be related to temperatures of ores precipitation (*see* KOZŁOWSKI & METZ 1989a, b).

CHARACTERISTICS OF FLUID INCLUSIONS

Fluid inclusions in the studied sphalerite varieties were small, as about 70% of the found inclusions did not exceed 1 μm in their largest dimension, *c.* 25% was in the ranges of 1-3 μm, *c.* 3% in the ranges of 3-5 μm, and less than 2% in the ranges of 5-10 μm. Only thirty-one inclusions were found larger than 10 μm, and the largest one was 42 μm long. Fibrous sphalerite hosted inclusions smaller than *c.* 5 μm; the larger inclusions occurred in granular sphalerite, in addition to the small ones.

Inclusions occurred relatively rarely. One mm^3 contained up to 30 inclusions of the size less than 3 μm, but usually they were not so frequent and large parts of the preparations were without any discernible inclusion. The inclusions of the size < 10 μm are relatively good representatives of the fluids present during origin and existence of sphalerite; the traces of the epigenetic alterations of these inclusions were legible. All large inclusions observed (dimensions > 10 μm) have shown signs of leakage or alterations of the extension difficult to reconstruct, thus their importance was lesser, and they were omitted in the genetic interpretation. The total of the investigated inclusions exceeded 2350, but only 1427 yielded the reliable data during freezing and/or homogenization runs.

The studied sphalerite contained both primary and secondary inclusions. The temperature and salinity data used for genetic interpretation were obtained from 1298 primary inclusions. The data from the balancing 129 secondary inclusions were helpful for explanation of a number of the inclusion alteration processes.

The studied inclusions were frequently very dark inside because of large difference of refractive indices of the host sphalerite and both aqueous and/or organic liquids. Moreover, observations were difficult due to common dark color of the host sphalerite, thus a large number of the observed inclusions contained a filling that could not be determined even tentatively. However, all the inclusions used for genetic considerations had filling recognized unambiguously. The investigated sphalerite contains fluid inclusions bearing at least nine types of fillings, distinguished hereafter as appears at room temperature.

(1) Two-phase inclusions of aqueous solution with shrinkage bubbles

Inclusions of this type comprised 63% of the investigated population of 1427 inclusions, all of which were especially carefully searched for. Their most common habit is tetrahedral, sometimes displaying perfect isometric tetrahedrons (Text-fig. 5*A*). Clusters of the inclusions were observed, sometimes with not completely separated vacuoles. In such cases the communicating vacuoles had usually one joint shrinkage bubble, though separate bubbles in individual tetrahedral parts were also found. The bubble occupied few percent of the inclusion volume. Small inclusions of this type (< 1 µm) were sometimes completely opaque, and thus practically not discernible from crystalline inclusions of *e.g.* galena or iron sulfides.

(2) Three-phase inclusions of aqueous solution with daughter halite and shrinkage bubbles

Two inclusions of this type were only found, despite a careful search, one mentioned by Kozłowski & *al.* (1980). Habit of the inclusions is tetrahedral; they bore small shrinkage bubbles (few percent by volume) and a cubic isotropic crystal occupying *c.* 2% of the vacuole volume (Text-fig. 5*B*), easily dissolving on temperature increase. This soluble crystal was most probably

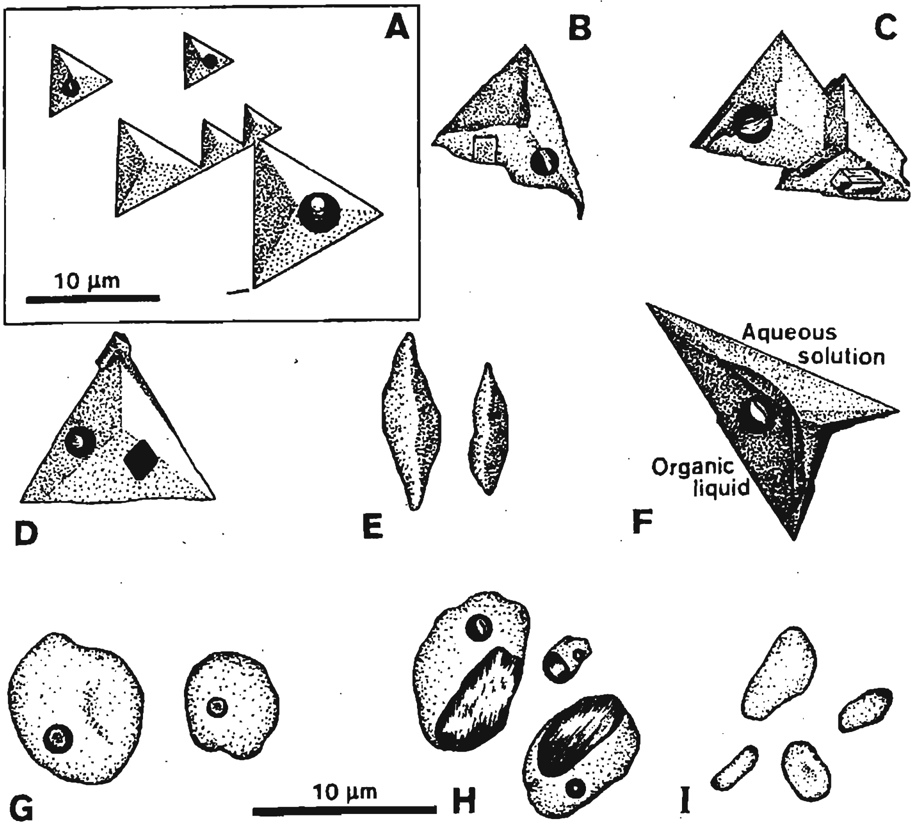


Fig. 5. Fluid inclusion varieties in the studied sphalerite

A — Cluster of tetrahedral aqueous inclusions; **B** — Inclusion with aqueous solution, a gas bubble and halite daughter mineral; **C** — Aqueous inclusion with a gas bubble and the trapped carbonate mineral (dolomite?); **D** — Aqueous inclusion with a gas bubble and the trapped opaque mineral (iron sulfide or galena); **E** — One-phase aqueous liquid inclusions; **F** — Inclusion bearing aqueous and organic liquids, and a gas bubble; **G** — Inclusions with organic liquid and gas bubbles; **H** — Inclusions bearing organic liquid, gas bubbles and organic solid phases, probably daughter minerals; **I** — One-phase inclusions filled with organic liquid daughter halite. The occurrence of such halite-bearing inclusions might have been by far common than observed in the checked population. However, minute isotropic crystals, occupying even tenths percent of the vacuole volume, would have been difficult to recognize in small, partly shaded inclusions.

(3) Three-phase inclusions of aqueous solution with trapped carbonates and shrinkage bubbles

Inclusions of this type comprised *c.* 2% of the investigated population. Their habits were tetrahedral, displaying two or more adhering or even penetrating tetrahedra (Fig. 5*C*). Typically, these inclusions had large size of *c.* 10 μm. They contained euhedral anisotropic crystals of high birefringence, one per vacuole, occupying from fractions to about ten percent of the inclusion volume. No preferred volume percent, occupied by these crystals, has been found. The crystal habits were either rhombohedrons deformed (elongated) to a various degree, or elongated hexagons that should most probably be interpreted as flat rhombohedrons. In three cases such very small crystals dissolved during heating runs two to seven centigrades below homogenization temperatures. Tentatively, this carbonate in inclusions is regarded to be dolomite.

(4) Three-phase inclusions of aqueous solution with trapped opaque minerals and shrinkage bubbles

Such inclusions participated in the studied population in a fraction of *c.* 3%. Inclusion habits were also tetrahedral and the shrinkage bubble occupied few percent of the vacuole volume. These inclusions also contained an opaque mineral of from <1 to *c.* 20 vacuole volume %. The variable volume ratio indicated distinctly a trapped nature of the opaque crystal. Habits of the trapped crystals were rather octahedral than cubic, as possible to recognize inside the vacuoles. In few cases the reflected light shown either bright gray or yellowish color of the trapped crystals faces, thus the crystals were determined as galena or iron sulfides (pyrite or marcasite, because the latter may also form crystals of nearly rhombic outline). On heating runs dissolution of the opaque crystals was not observed.

(5) One-phase inclusions of aqueous solution

This type of fluid inclusions has not been included in the total of the studied population, however, ratio of the frequency of their occurrence to the type 1 inclusions is approximately 1 : 30, that is they are not frequent. One-phase aqueous inclusions have rounded, globular or fusiform habits (Text-fig. 5*E*), and they usually occur in clusters.

(6) Three-phase inclusions of aqueous solution and organic liquid with shrinkage bubbles

These inclusions comprised *c.* 11% of the investigated population. Inclusion habits are tetrahedral or rarely rounded. The shrinkage bubbles occupy constantly few percent of the vacuole volume. Organic liquid appears darker than aqueous solution, and in colorless sphalerite the organic liqiud has a distinct yellowish or brownish tint. The proportion of organic liquid to aqueous solution is very variable, indicating heterogeneous trapping of two immiscible fluids. None of heating runs of such inclusions resulted in homogenization of aqueous solution and organic liquid, and only the bubbles disappeared. However, usually small amounts of organic liquid or small amounts of aqueous solution should be difficult to identification, since they would be hidden in the shaded part of the inclusion. In fact, inclusions bearing few percent of organic or aqueous phase were not found, only some water-rich inclusions displayed in ultraviolet light spots of weak luminescence in the shaded vacuole margins. However, this luminescence could result from carbonate grains as well.

(7) Two-phase inclusions of organic liquid with shrinkage bubbles

The inclusions took over 17% of the investigated population. They had almost exclusively spherical, globular or flat-rounded habits (Text-fig. 5*G*). The shrinkage bubbles occupied few percent of the inclusion volume. Organic liquid was colorless or with gray, yellowish, cognac, tan or brown tint. The inclusions occurred solely, in clusters or in surfaces according to growth layers of sphalerite grains (*see* Fig. 3*C in* Kozłowski & Górecka 1993). Peculiar clusters of these inclusions were found in three samples; they were grape-like and arranged with the cluster elongation parallel to the host sphalerite growth direction (Text-fig. 6*A*). In ultraviolet light, organic liquid displayed white, bluish, bluish-greenish, yellow, weak-orange and weak-pink fluorescence. One should mention, that even more than 10% of aqueous phase in this type of inclusions might have not been detected, because it would be located on the vacuole walls, thus hidden in the dark rim of the inclusion.

(8) Three-phase inclusions of organic liquid with organic solid phases and shrinkage bubbles

Inclusions of this type comprise only *c.* 4% of the studied population. The habits are mostly globular or ellipsoidal. From 5 to 25% of the inclusion volumes are occupied by solid anisotropic substance (Text-fig. 5*H*) with variable birefringence; few percent are taken by shrinkage bubble, and the remaining volume — by organic liquid. Organic liquid has UV-luminescence similar to that displayed by inclusions of the type *7*, but sometimes the luminescence is absent and the liquid is barely discernible from aqueous solution. A solid substance has weak UV-luminescence in whitish, gray, orange, dawn-red, purple and brownish; moreover, very few examples without any luminescence were found. During heating runs the solid substance either dissolved gradually but completely in organic liquid, or it melted first, forming a liquid immiscible with the original organic liquid. The new-formed liquid either homogenized by dissolution in that latter liquid, or rarer slowly splitted in fibers or spindles, floating in the original liquid and finally dissolved in it after an hour-long heating at the temperature of the shrinkage bubble disappearance.

(9) One-phase inclusions of organic liquid

These inclusions have not been included in the total of the investigated inclusions population. They occur in clusters of 3-10 members, and totally only about one hundred of such inclusions was found in the studied preparations. Their habits are irregular rounded, frequently flat (Text-fig. 5*I*). Their filling displays white, bluish or pale orange UV-luminescence.

No preference of any inclusion type was found for either granular or fibrous sphalerite and, on the other hand, for any its color variety. The only exception are the types *5* and *9*, which were found as primary inclusions exclusively in the outermost colorless zone of the granular sphalerite or as secondary ones.

FORMATION OF PRIMARY ORGANIC FLUID INCLUSIONS FROM WATER-DOMINATED MEDIUM

The data on fluid-inclusion fillings yielded the conclusion, that parent media of the zinc and lead ores were aqueous solutions of temperatures close to 100°C, and sometimes significant concentrations of salts, most probably NaCl, were present. These solutions carried organic matter in a form unrecognizable from the simple inclusion observations. The migration of organic matter only in form of water suspension (emulsion) is doubtful, because experimental data indicate a relatively good solubility of petroleum-type hydrocarbons in aqueous solutions (PRICE 1976). Thus, this problem needs further considerations.

The investigated sphalerite preparations contain clusters of organic fluid inclusions similar to grapes, chains or spindles (Text-fig. 6*A*; *cf. also* Pl. 2, Figs 1-4 *in* KOZŁOWSKI & *al.* 1980 and Fig. 3*D in* KOZŁOWSKI & GÓRECKA 1993). Elongation of these clusters is essentially perpendicular to the growth zones of host sphalerite (*i.e.* parallel to the growth direction), and the growth zones accomodated to the outline of inclusions (Text-fig. 6*A*). These features indicate distinctly the primary (syngenetic with the host crystal zone) origin of the inclusions.

One may propose at least two probable modes of these inclusions formation. The first one presents an aqueous heterogeneous medium of sphalerite growth. This solution should be saturated with organic matter and contain floating droplets of organic liquid. These droplets might accumulate on the surface of the growing sphalerite crystal (Text-fig. 6*B*). However, the mechanism of attraction of a large number of floating droplets to one place remains unclear.

A concurrent explanation would require an essentially homogeneous aqueous solution that was saturated, or even oversaturated, with organic matter. The surface of the growing sphalerite crystal could cause nucleation of an organic droplet enlarging its volume due to accretion of organic matter from aqueous solution. The ongoing sphalerite crystallization would tend to separate the growing droplet from the solution. An almost separated droplet was a good nucleus for the next droplet formation (Text-fig. 6*C*). Fast sphalerite crystallization would cease the development of the cluster. Thus, the described inclusion clusters are evidences of the homogeneous, organic-matter-(over)saturated fluid.

Other inclusions, those of the types *6*, *7*, and *8* (Text-fig. 5*F*-*H*), might have formed due to sticking of the floating organic droplets to the growing crystal surface, *i.e.* from heterogeneous medium.

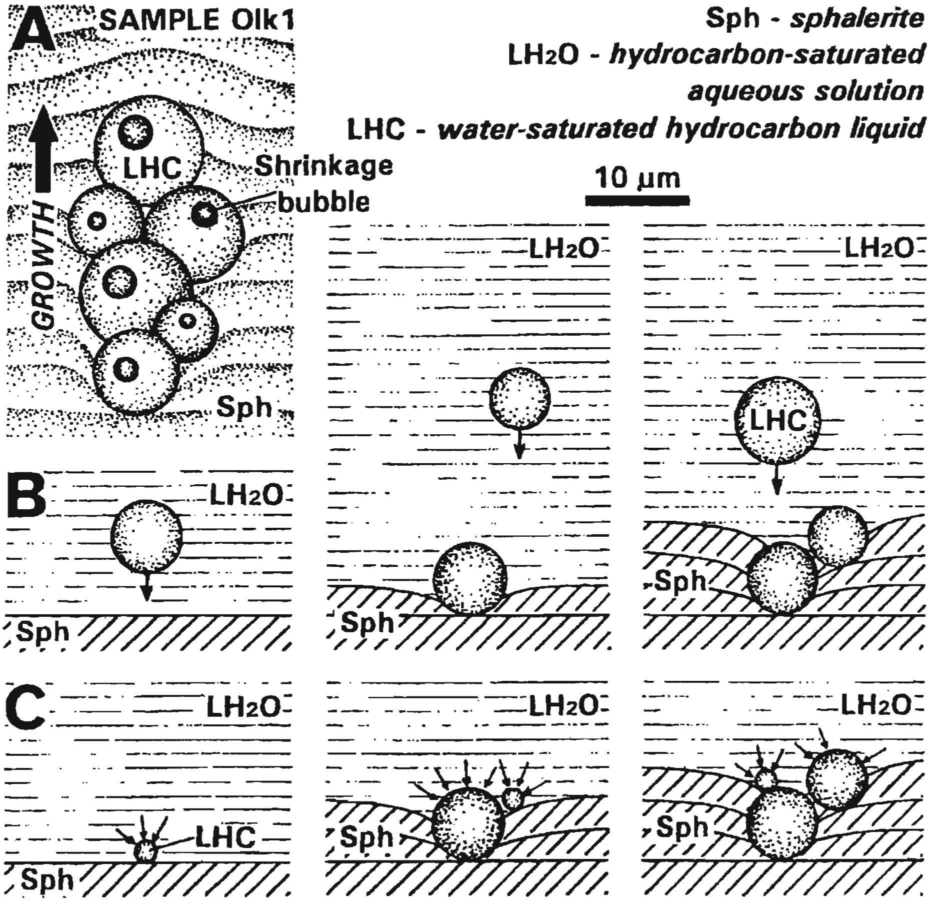
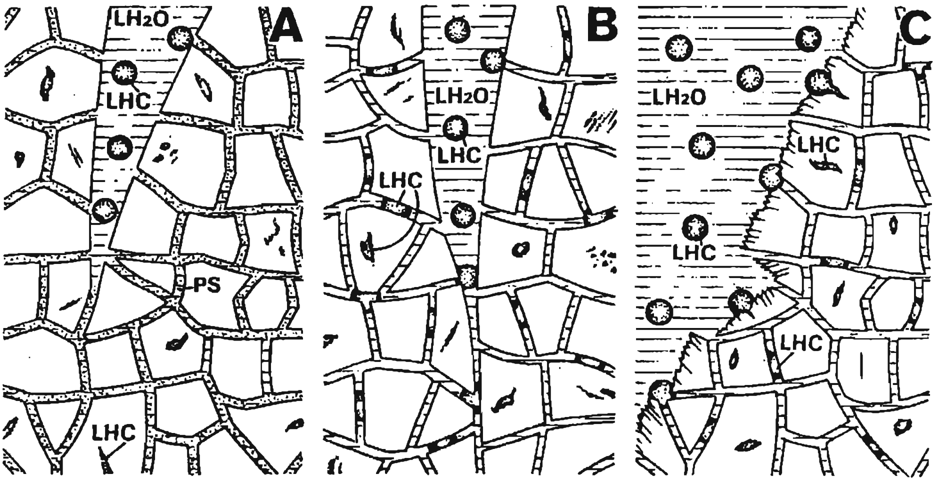


Fig. 6. Cluster of globular inclusions in sphalerite filled with organic liquid (A), and possible modes (B – C) of its formation either by accumulation of organic droplets floating in aqueous solution (*B*), or by accretion of dissolved organic matter by minute organic droplets from supersaturated aqueous solution (*C*), both appeared during ongoing sphalerite crystallization

The extensive variation of the UV-luminescence color of organic matter in inclusions suggests numerous local sources of the organic fluid rather than a single distant one. The carbonate rocks that host ore deposits bear small and variable amounts of organic matter. There were three main modes of the organic matter incorporation to the ore-forming fluids from wall rocks. If organic matter was present in intergranular (pore) fluid as homogeneous solution, opening of a fracture in the rock caused secretion of the fluid to the developing fissure. This fluid in the fissure might remain homogeneous or, due to pressure and temperature decrease, might exsolute droplets of water-saturated organic liquid (Text-fig. 7*A*). These droplets might next dissolve in undersaturated water solution portions coming later to the fissure.

Intergranular fluid might be a two-phase system of aqueous and organic liquids, and in this case the two-phase medium entered the forming fissure (Text-fig. 7*B*). Later dissolution of organic droplets might occur. Moreover, partial or complete dissolution of the wall rock supplied ore-forming solution in significant amount of all kinds of organic matter present in the rock, also those included in mineral grains (Text-fig. 7*C*).

It is also possible, that part of organic fluids could be separated from accumulations of organic matter present in caverns (Sass-Gustkiewicz & Kwiecińska 1994), or these fluids could enter the ore precipitation area, carried by foreign formation waters; in the last case, however, one would expect a rather uniform composition of these organic fluids.



LH_2O - *hydrocarbon-saturated aqueous solution*

LHC - *liquid hydrocarbons of unknown water content when in inclusions in dolomite grains, otherwise water saturated*

PS - *hydrocarbon-rich pore solution*

Fig. 7. Migration of organic fluid from wallrock dolomite to ore-forming solution by including of the pore homogeneous aqueous solution of hydrocarbons with hydrocarbon exsolution due to lower pressure in opening fissure (A), migration of hydrocarbon droplets from pores to opening fissure (B), and dissolution of the wallrock by aqueous solution (C)

FORMATION OF SECONDARY ORGANIC FLUID INCLUSIONS FROM WATER-DOMINATED MEDIUM

The origin of secondary, hydrocarbon-fluid inclusions from a heterogeneous medium of an aqueous solution bearing floating-hydrocarbon-droplets is obvious, if the parent fissure of these inclusions had thickness, distinctly exceeding diameter of the droplets. Otherwise, the floating droplets could not enter the opening fissure easily, to form secondary inclusions according to the scheme: one droplet → one inclusion or a group of several inclusions.

The studied sphalerite crystals contain planes of secondary inclusions with distinctly separated fields of vacuoles, filled with aqueous and hydrocarbon liquids. The hydrocarbon inclusions occupy a zone roughly perpendicular to the edge of the parent fissure and extending from this edge to the crystal face. This zone contacts along both sides with fields of aqueous inclusions (Text-fig. 8*B*). Such distribution can be explained, if one supposes a crystal face

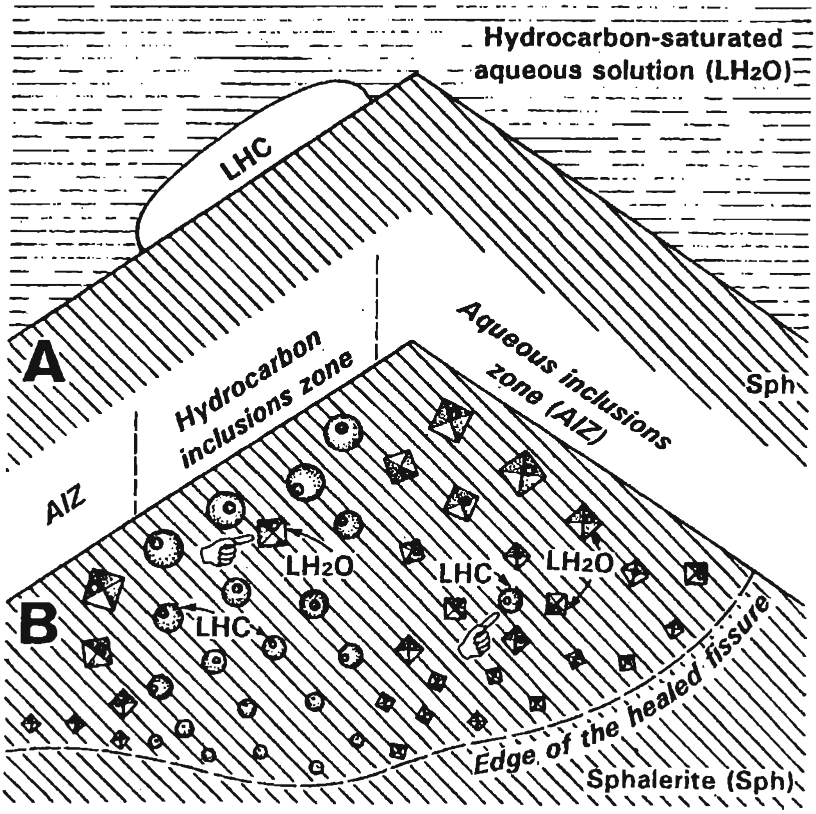


Fig. 8. Formation of the secondary fluid inclusions from a fissure that opened partly under a droplet of liquid hydrocarbon located on the surface of sphalerite crystal (A), and the pattern of these inclusions (B); fingers point to the inclusions formed by exsolution of organic phase from aqueous solution, or aqueous solution from organic liquid

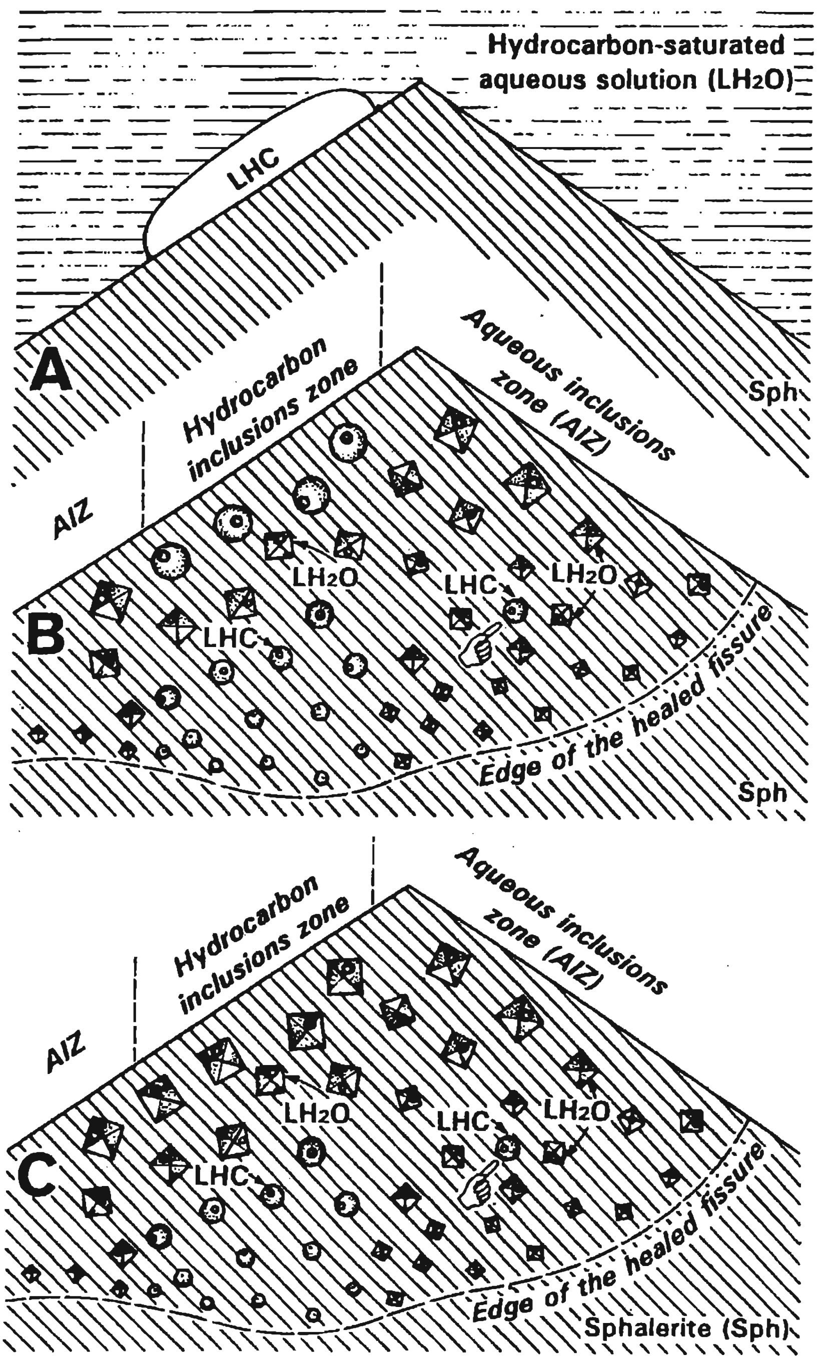


Fig. 9. Inclusion formation mechanism the same as in Fig. 8, but rapid opening of the fissure resulted in discontinuous flow of organic fluid from the droplet (A) to the fissure, and caused origin of aqueous inclusions strip in the hydrocarbon inclusions zone (B), or ceased the inflow of hydrocarbo (C)

with an adhering hydrocarbon drop in aqueous solution (Text-fig. 8*A*). An opening of a fissure in the crystal, partly extending under the hydrocarbon drop, would result in filling of this fissure with both hydrocarbon and aqueous liquids, and yielding the above-described distribution of inclusions.

However, the families of aqueous inclusions in the fissure contain single and rare inclusions of hydrocarbon liquid, and the hydrocarbon inclusion family embeds single aqueous inclusions (*pointed with fingers* in Text-fig. 8*B*). Usually one fissure bears one to three such foreign inclusions in an inclusion family, depending on the fissure size. A reasonable interpretation is, that these inclusions formed due to exsolution of hydrocarbon from aqueous solution or water from organic liquid when pressure decreased in the developing fissure (Text-fig. 10*A*). To maintain the exsolved phase, fast healing of the fissure is necessary; otherwise, it would dissolve again in the solvent.

Sometimes the hydrocarbon inclusions zone contains a strip of aqueous inclusions placed across it. Hydrocarbon inclusions separate the strip both from the fissure edge and from the crystal face (Text-fig. 9*B*). The supposed mode of formation of this inclusion assembly was like the above described (Text-fig. 9*A*), but a very fast opening of the fissure caused entering of aqueous solution through the hydrocarbon drop (Text-fig. 10*B*). Nevertheless, the drop was large enough to seal the break and to supply again the hydrocarbon flow into the fissure. If the hydrocarbon drop was small, it did not seal the break and the aqueous-inclusion strip extended to the crystal face (Text-fig. 9*C*).

The real occurrence of exsolution in fissures is confirmed by single hydrocarbon inclusions (one or two per healed fissure) in planes of secondary inclusions that do not reveal other signs of organic liquid, like hydrocarbon inclusions families (Text-fig. 10*C*).

The distribution of the secondary inclusion types formed from medium composed of two immiscible fluids is thus characterized by special patterns of the fields occupied by two inclusion families and the presence of single, separate representatives of one family within the field of the other family (Text-fig. 11).

A granular sphalerite sample (*Olk 23*) from the Olkusz mine contains a rare abundance of primary and secondary inclusions filled with aqueous and organic liquids (inclusion types 1 and 7, *see* Text-fig. 12*A*). Alternating groups of primary aqueous and hydrocarbon inclusions in one growth zone indicate distinctly the presence of two immiscible liquids. A plane of secondary inclusions starts from the base of this growth zone, heading obliquely to the root part of the sphalerite crystal. It is beaded by both aqueous and hydrocarbon inclusions. Homogenization temperatures of the inclusions in the discussed growth zone form two distinct groups: 111-114°C for aqueous inclusions, and 106-107°C for hydrocarbon inclusions. Temperatures for the secondary inclusions are respectively the same. This coincidence confirms the conclusion,

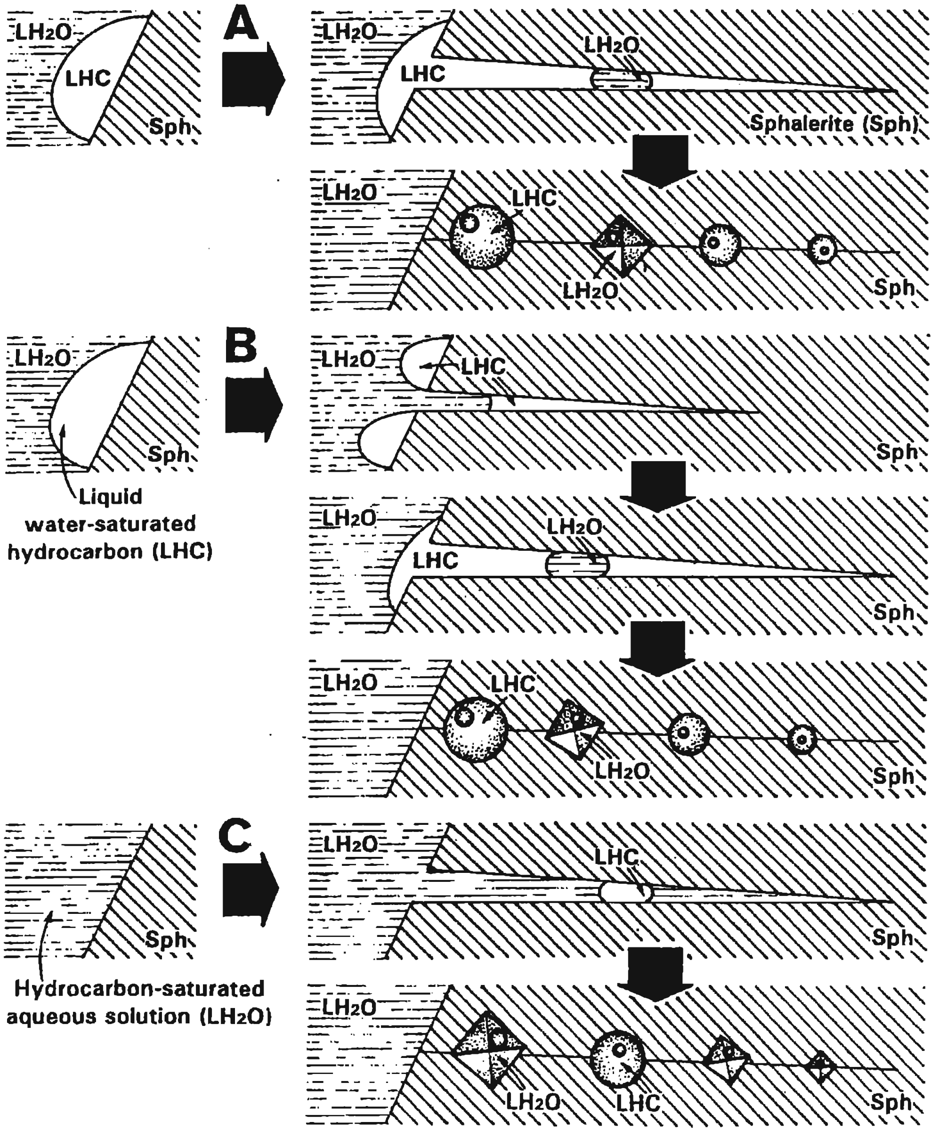


Fig. 10. Exsolution of immiscible liquid phases in homogeneous fluid during filling of an opening fissure and the resulting secondary inclusions

A — Exsolution of hydrocarbon-saturated aqueous phase from water-saturated hydrocarbon liquid migrating from a hydrocarbon droplet adhered to the crystal surface; this process usually results in formation of a single aqueous inclusion in hydrocarbon inclusions family

B — Entering of aqueous solution to the fissure filled essentially with hydrocarbons, caused by quick opening process; this results in trail or stripe of aqueous inclusions in hydrocarbon inclusions family

C — Exsolution of water-saturated hydrocarbon phase from hydrocarbon-saturated aqueous solution; this process usually results in formation of a single hydrocarbon inclusion in aqueous inclusions family that the primary and secondary inclusions are coeval. The difference of 5 to 8°C in homogenization temperatures of aqueous and hydrocarbon inclusions results from different compressibility of these two media, being in fact the difference in values of pressure corrections to be added to homogenization temperatures of both types of inclusions. The correction to *Th* of hydrocarbon inclusions is larger than to aqueous inclusions, if the inclusions were trapped at the same temperature and the same pressure, *i.e.* they are strictly coeval. After exact determination of the hydrocarbon composition, this difference may be the basis of pressure determination for ore-forming process.

The distribution of primary inclusions in growth zone (Text-fig. 12*A*) displays alternation of aqueous and hydrocarbon inclusions. From the sequence of the secondary inclusion types in the healed fissure, it appears, that the fissure opening was rapid (*cf.* Text-fig. 9*C*). To explain the distribution of the primary inclusion types within the growth zone, the following experiment was performed.

A broken glass plate, 6 mm thick, was mounted on a scissors-like device that permitted rapid opening of the break in the glass plate to form *c.* 1 mm thick fissure. At the beginning, the break was tightly closed, and on the broken glass surface a drop of engine oil was placed on both sides of the break, to form a spot *c.* 5 mm in diameter and *c.* 0.7 mm thick. The device with mounted glass was immersed in 10 wt. % NaCl aqueous solution with temperature of *c.* +80°C, the oil drop downwards. The layer of aqueous solution between the droplet surface and the bottom of the vessel with NaCl solution was not thicker than 0.5 mm. After rapid opening of the fissure, a characteristic pattern of tiny oil droplets in parallel rows, perpendicular to the fissure edges, was observed on the glass surface (Text-fig. 12*B*). This experiment delivers an evidence, that the hydrocarbon inclusions in the growth zone (Text-fig. 12*A*) could form from remnant tiny hydrocarbon droplets after the parent fissure of the secondary inclusions opened.

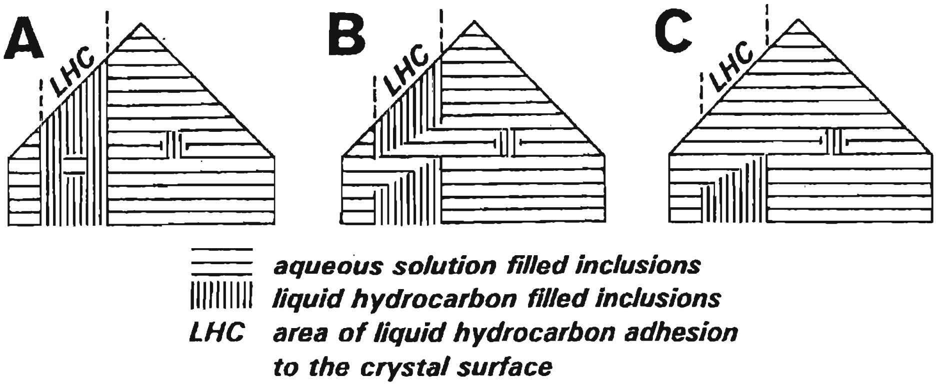


Fig. 11. General distribution of secondary aqueous and hydrocarbon inclusions formed from aqueous solution in part under a hydrocarbon droplet adhering to the host crystal surface

A — Single foreign inclusions of the exsolution origin, B — Strip of the aqueous inclusions caused by discontinuous flow of organic liquid in the fissure, C — Ceased flow of organic liquid in the fissure

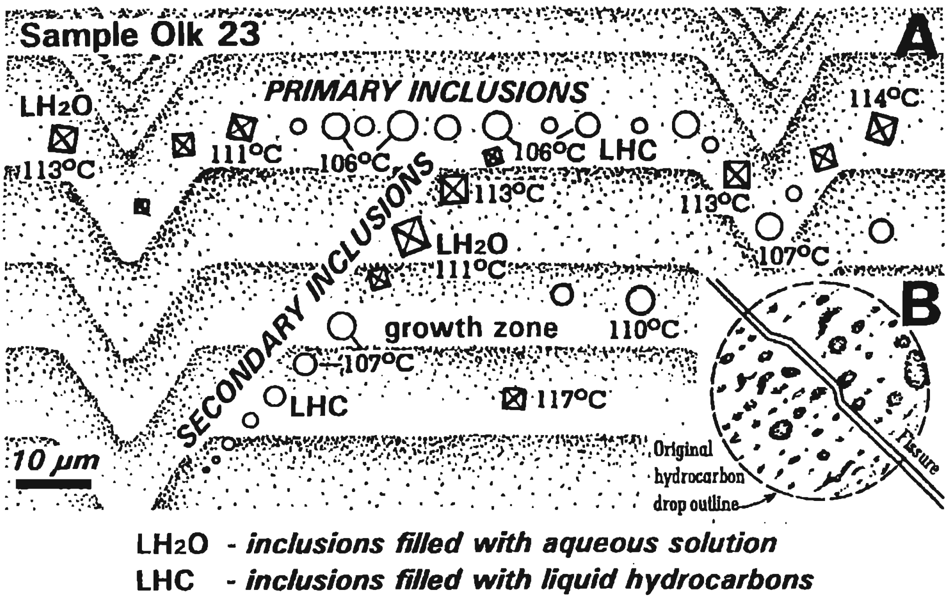


Fig. 12. Cluster of primary and secondary inclusions of aqueous and organic fluids formed probably due to rapid opening of a fissure under large droplet of organic fluid located on the face of the growing sphalerite (A), and an experiment confirming this explanation by obtaining a patchy distribution of oil in NaCl solution environment on glass surface after opening the fissure (B)

LOCATION OF FLUID INCLUSIONS IN CRYSTALS

The studied sphalerite aggregates, both fibrous and granular, are fine-grained. The thickness of the fibers typically is 20 to 100 μm, and the exceptionally large equant grain (*cf.* Text-fig. 20*F*) had dimension of less than 3 mm. The fine grain-size and six systems of the planes of perfect cleavage of sphalerite according to faces of rhombic dodecahedron {110}, caused serious problems in fluid inclusion studies and in interpretation of the obtained data. Before an inclusion was evaluated as suitable to be a source of reliable data, its position in the host crystal was carefully checked, including the distances from grain walls, preparation surface and the nearest fissure, healed or not. This investigation was not only the basis of the reliability estimation for the data obtained, but also the basis to reconstruct the origin and history of odd or special inclusions.

Generally, good data were obtained from inclusions that occurred inside crystals, *i.e.* intracrystalline ones (Text-fig. 13). Contrary, inclusions located between crystals (intercrystalline) did not yield useful data due to frequent leakage either when the mineral was in the deposit, or during cutting and polishing preparations, or on heating/freezing runs. The grain boundaries easily splitted and the vacuole volume dramatically increased or even the vacuole was fully opened. However, a number of the best inclusions was found in the intercrystalline positions, and the careful handling and exact check after heating/freezing runs made possible to rely on the data obtained.

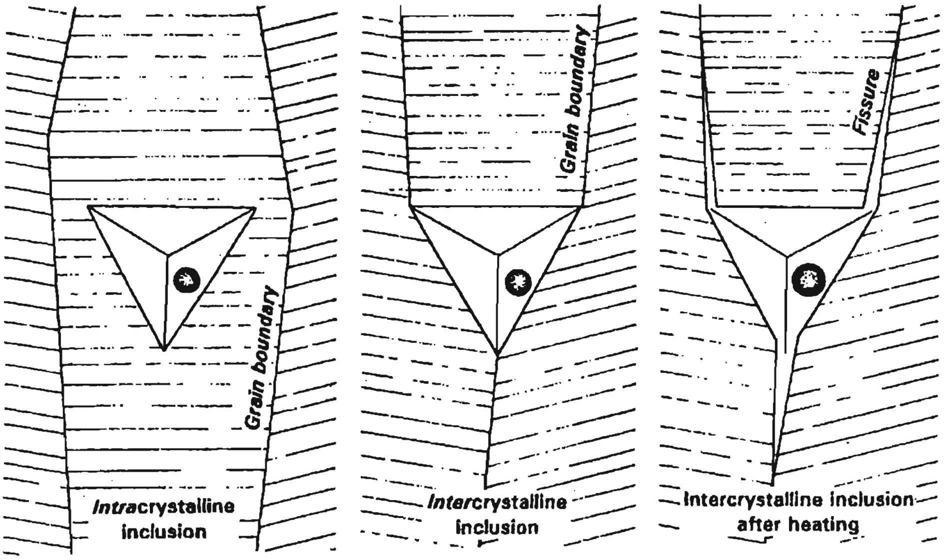


Fig. 13. Inclusions formed *inside* and *between* sphalerite crystals, and leakage of the intercrystalline inclusion during homogenization run

RECOGNITION OF THE SECONDARY INCLUSIONS

The criteria, that permit to distinguish primary and secondary inclusions, were established long ago (LAEMMLEIN 1929, 1973b; ERMAKOV & DOLGOV 1979; KALYUZHNYI 1982; ROEDDER 1984). The essential criterion is the occurrence of inclusions in a plane (surface) or trail, cutting the growth zones of the host crystal, what evidenced the epigenetic origin of the inclusions with respect to the crystal (Text-fig. 14). However, the studied sphalerite specimens yield examples of the secondary inclusion arrangement that made the above simple definition either invalid or difficult to apply.

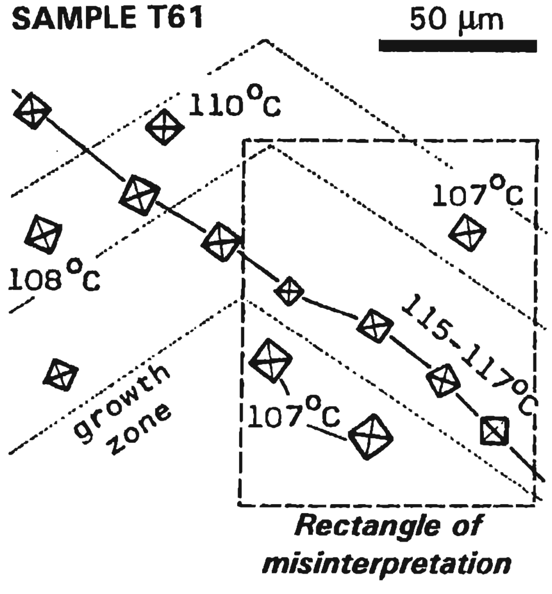


Fig. 14

Primary inclusions and a plane of secondary ones roughly parallel to one of the growth zone orientations; observation of the rectangled part may lead to the determination of the inclusions with *Th* of 115-117°C as primary in growth zone, and thus to estimation of the apparent temperature fluctuation during the crystal growth

First, the problems appeared due to small inclusion size and the necessity of use high power immersion lenses (×90 or ×100). This limited the view field and the depth of observation, and because the planes of secondary inclusions were commonly rarely populated, the tracing of the healed fissure was usually difficult. For instance, four rectangled secondary inclusions of the seven ones (*see* Text-fig. 14) occurred close to the preparation upper surface, but the three ones remaining left of the rectangle were found much deeper in the sphalerite wafer. If the three inclusions were missed, the obvious interpretation of all the rectangled inclusions would lead to the conclusion, that they all are primary. This misinterpretation, joined with the measured homogenization temperatures (*see* Text-fig. 14), would indicate distinct temperature fluctuation during host crystal growth, whereas in fact fluid temperature increased after the host crystallization.

Distribution of secondary inclusions in fibrous and granular aggregates of a mineral that has several planes of perfect cleavage causes further complications in interpretation. The straight linear arrangement in the studied samples was relatively rare (Text-fig. 15; *note*, here and in Text-fig. 16 inclusions are enlarged *c*. 10× with respect to the scale bar). In this case the homogenization temperature differences between primary and secondary inclusions were distinct and indicated cooling after crystallization of the sphalerite assemblage.

Frequently in the same growth zone there occurred inclusions of distinctly different homogenization temperatures (Text-fig. 16, inserts *A*, *B*). However, if considered within the insert fields, the inclusions position strongly suggested their primary origin bound either to growth zones or to grain boundaries. The

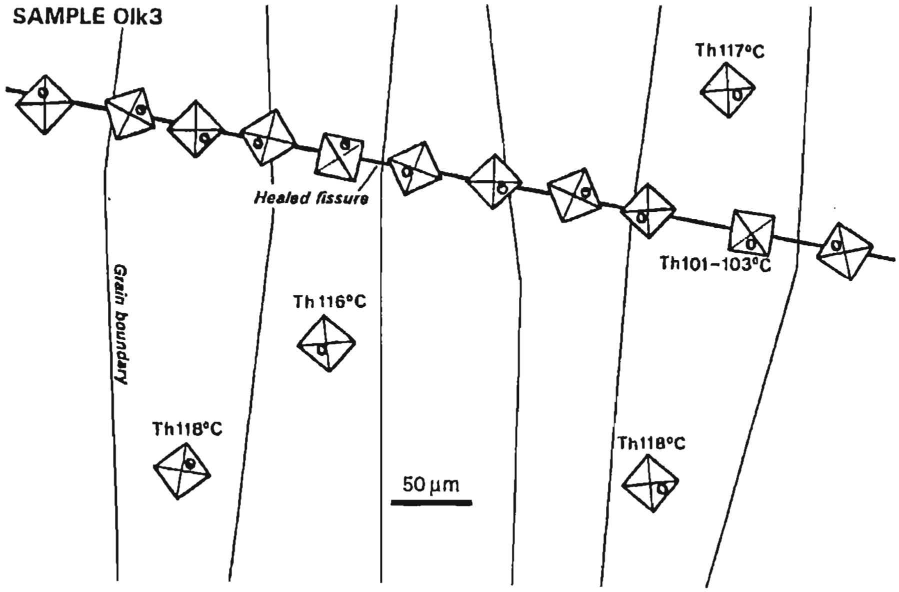


Fig. 15. Classic relation between primary (scattered) and secondary (arranged along a sealed fissure) inclusions, not frequent in the investigated sphalerite samples

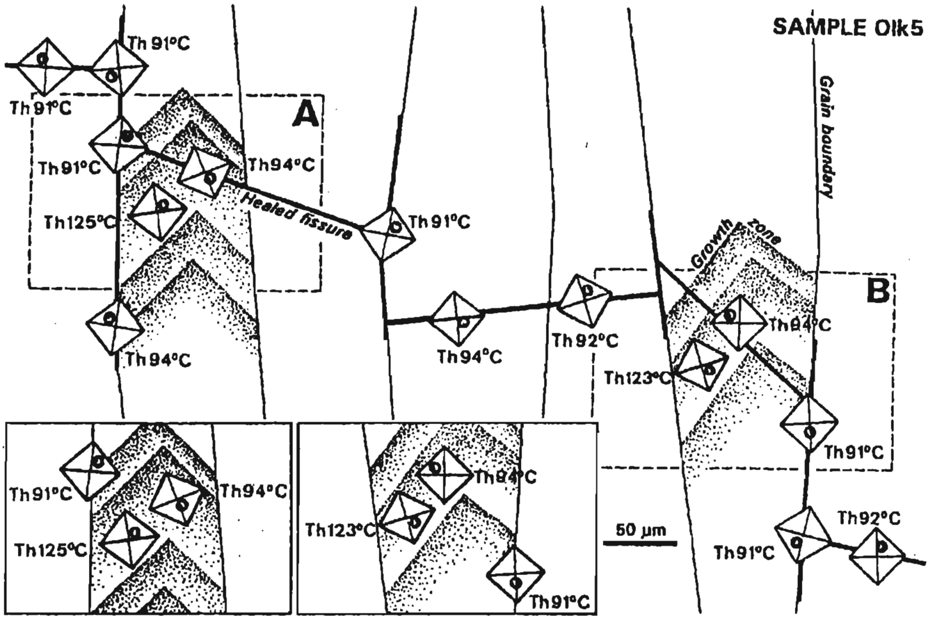


Fig. 16. Fissure path in polycrystalline aggregate of fibrous sphalerite crystals with six planes of perfect cleavage; the healed fissure is usually barely visible and some secondary inclusions may be misinterpreted as primary ones, especially in the rectangled areas A and B (*see* their inserts without the marked healed fissure)

inconsistencies in homogenization temperatures could be explained by possible inclusion leakage or other alterations. This interpretation may be derived from superficial observation, as presented in the lower inserts. An exact analysis of the large cluster of inclusions (shown in Text-fig. 16) resulted in revealing of barely visible trace of a healed fissure with a complicate path, marked in the drawing by heavy line. This path was determined by cleavage of sphalerite fibers and grain boundaries. All homogenization temperatures of the secondary inclusions, developed in this fissure, agree within the ranges of the measurement accuracy. The values for two primary inclusions are very close one to another, differing from those of the secondary inclusions.

REFILLING OF INCLUSIONS

The phenomenon of inclusion refilling was recognized in pegmatitic quartz by Kalyuzhnyi (1971)*, and soonafter characterized in details by thatauthor (Kalyuzhnyi 1982). The mechanism of this phenomenon starts from an opening of an existing inclusion (primary or secondary) by a fissure

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* This inclusion alteration is very useful for establishing the inclusion generation sequence, however, it has been used by subsequent investigators only exceptionally.

(Text-fig. 17). Low pressure at the edge of the expanding fissure causes usually complete removal of the inclusion filling and its mixing and dilution with fluid present in the fissure. Subsequently, the younger fluid fills the older, already existing vacuole of the opened inclusion. At the following stage the fissure is healed and a number of secondary inclusions forms along it. The refilled vacuole is also separated in the process of healing, preservinga portion of the new fluid. Thus, the refilled inclusion is characterized by a vacuole habit typical of the older inclusions, and a filling the same as in younger inclusions.

The sequence of fluids starting from hydrocarbon, and followed by aqueous liquid (Text-fig. 17), is not the only one observed in secondary inclusions in the studied samples. The reverse sequence is quite common (*see* Text-fig. 18*A*). In this case, one observes an increase of homogenization temperatures from the earlier aqueous fluid to the later hydrocarbon one during an unknown time interval. The *Th* difference is 12-17°C, but the real interval of the temperature increase should be even greater of 5-10°C (pressure correction to *Th*), *i.e.* in the ranges of 17-27°C, because hydrocarbon liquid had higher temperature than aqueous one (*see* discussion on the inclusions shown in Text-fig. 12*A*). Primary aqueous inclusions in this part of the sample *T25c* yielded *Th* values of 122-124°C. Hence, from formation of the host crystals till origin of the hydrocarbon inclusions, *i.e.* later secondary ones, the temperature

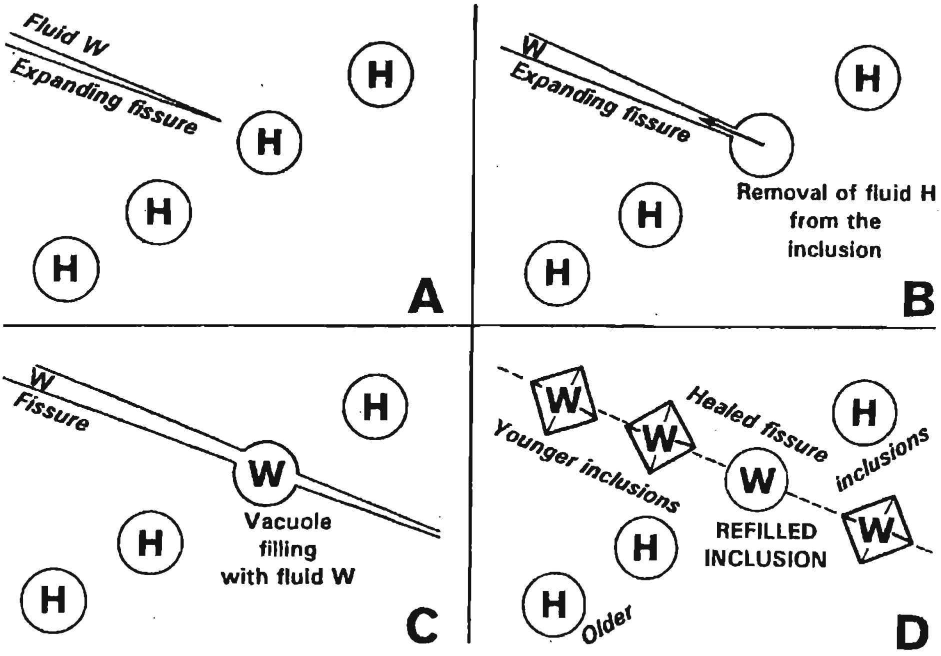


Fig. 17. Inclusion refilling (*after* KALYUZHNYI 1982) as developed (stages A, B, C, D) in the studied sphalerite which existed in the earlier water (fluid *W*) and later hydrocarbon (fluid *H*) medium

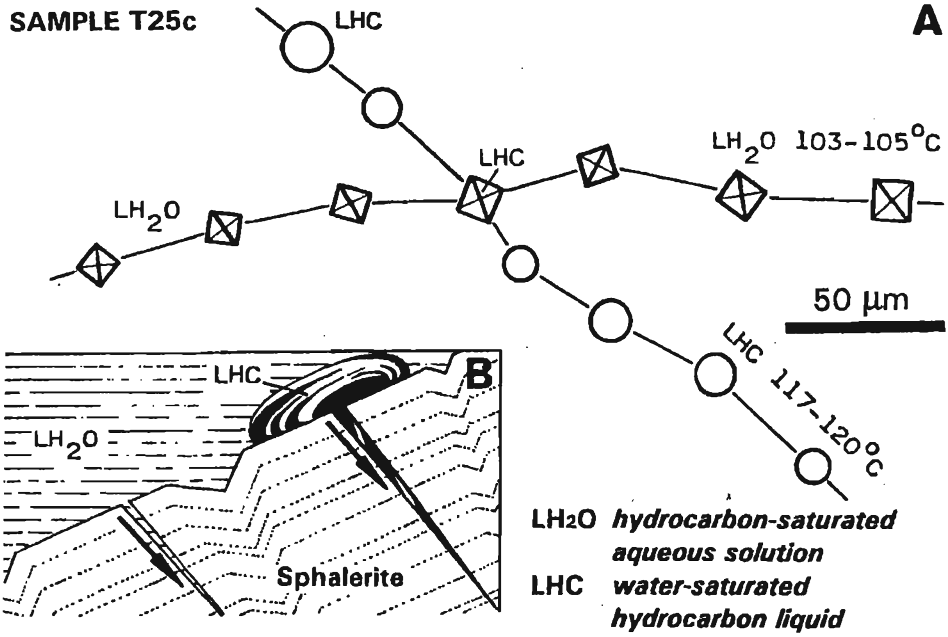


Fig. 18

A — Refilling of an aqueous inclusion vacuole by liquid hydrocarbon; note that the later fluid had higher temperature that the earlier one

B — Explanation of the simultaneous origin of secondary inclusions in one plane filled with aqueous solution, and in another one — with hydrocarbon liquid

of the fluids distinctly decreased and again increased. Note, that in heterogeneous medium the refilling indicates the sequence of fluid types (in this case aqueous or hydrocarbon) in a very limited volume. There is a common possibility of contemporaneous filling of a fissure with organic liquid and another one with aqueous liquid (Text-fig. 18*B*). In this case, the coeval nature of the two fissures may be evidenced by studies of the growth zone, the fissures started from. This is not valid, if fissures started from a crystal face never overgrown with a subsequent layer of the host mineral.

Sometimes, more than one older trail of secondary inclusions was cut by a younger fissure with opening of the old inclusion vacuoles; for instance, two subparallel trails of hydrocarbon-filled inclusions crossed by a trail of aqueous inclusions (Text-fig. 19). The organic inclusions formed at temperatures different for every of the trails (*Th* 115-116 and 118-120°C). The aqueous inclusions yielded lower *Th* values of 111-112°C, thus it is an indication of temperature decrease during the sphalerite existence (the earlier remarks on pressure corrections to *Th* here are valid as well). However, any suggestion on the origin sequence of the two hydrocarbon inclusions trails cannot be derived from the picture quoted (Text-fig. 19).

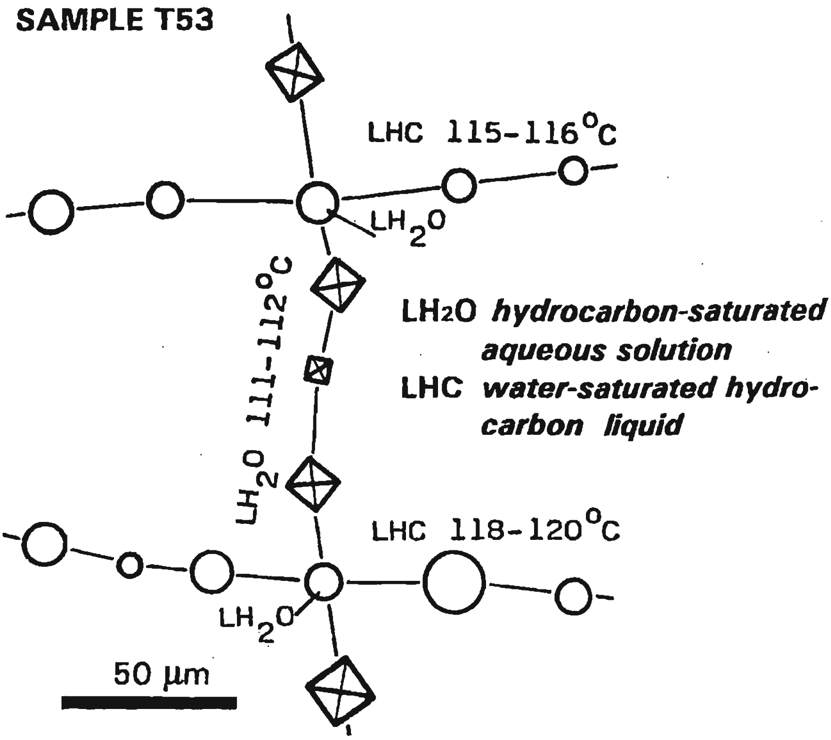


Fig. 19. Aqueous solution refilling secondary hydrocarbon inclusions of two different generations

Exceptional abundance of primary and secondary inclusions in several growth zones and healed fissures was found in a *c.* 3 mm tetrahedral sphalerite crystal from the Trzebionka mine (dominating positive tetrahedron {111} plus negative tetrahedron $\{1\bar{1}1\}$ and cube {100}, *see* Text-fig. 20*F*). Sphalerite displays perfect cleavage in the system of six planes (Text-fig. 20*E*) and this may cause a large number of fissure crossings in any sphalerite crystal.

Primary inclusions formed in the growth zone of the (111) face of tetrahedron of *Th* 129°C were refilled by secondary inclusions (011) of *Th* 103°C (Text-fig. 20*B*). The latter generation refilled older secondary inclusions (101) of *Th* 122°C and was refilled by younger inclusions (110) of *Th* 94°C (Text-fig. 20*C*). This jointly means a recorded sequence from crystallization temperature of 129°C through crystal crushing events at 122, 103 and 94°C. The (101) inclusions, on the other hand, were refilled by $(1\bar{1}0)$ ones of *Th* 88°C (Text-fig. 20*A*), what indirectly locates the inclusions $(1\bar{1}0)$ at the end of the above sequence. The inclusions (011) were also refilled by $(10\bar{1})$ ones of *Th* 97°C (Text-fig. 20*D*). Though the relation between the inclusions $(10\bar{1})$ and (110) is not known, the simplest supposition inferred from the above established changes is a consequent temperature decrease. Thus, the final conclusion may be presented as follows: early part of the sphalerite crystal originated at *c.* 129°C, and subsequently it was broken at 122, 103, 97, 94 and 88°C (*note*: the values are *Th*, not crystallization temperatures). All these crushing episodes occurred before the crystal finished its growth, because all the healed fissures

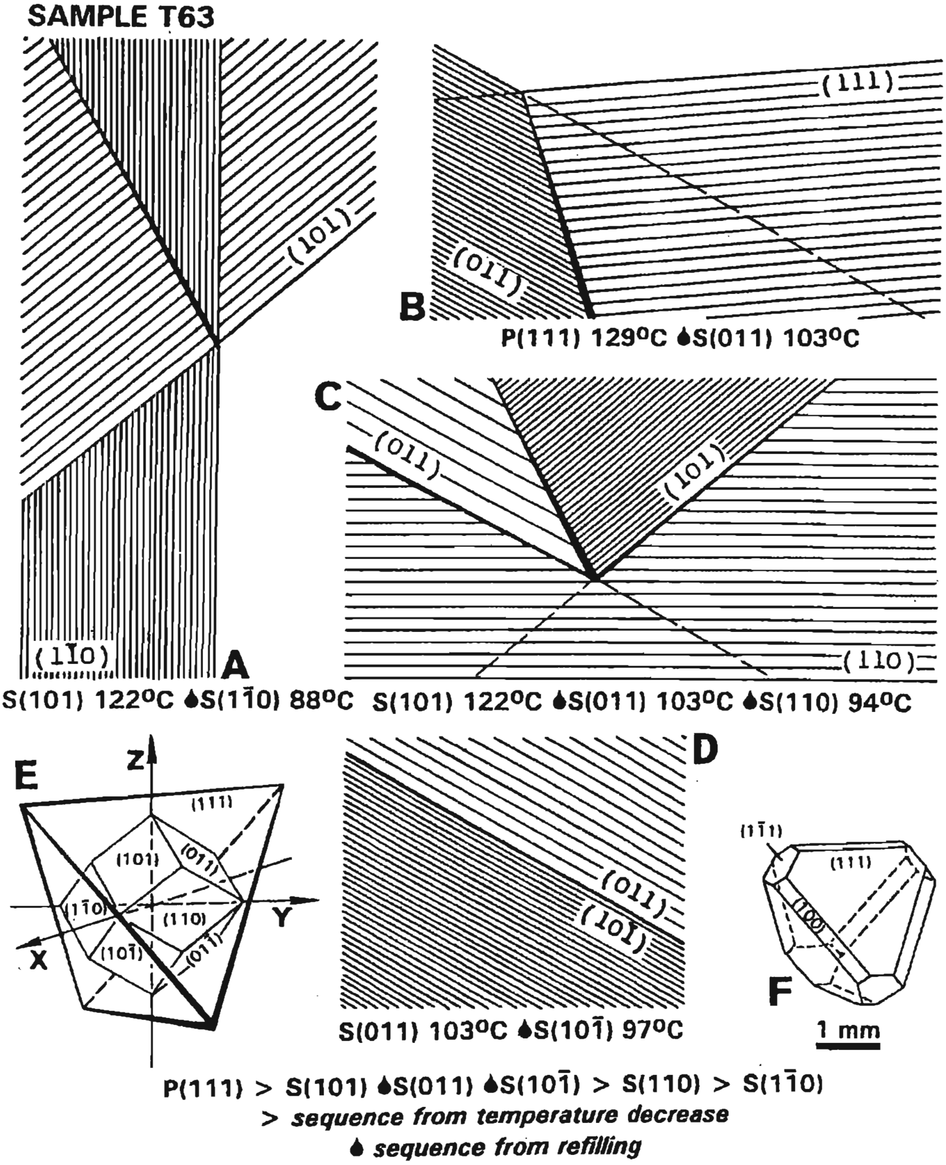
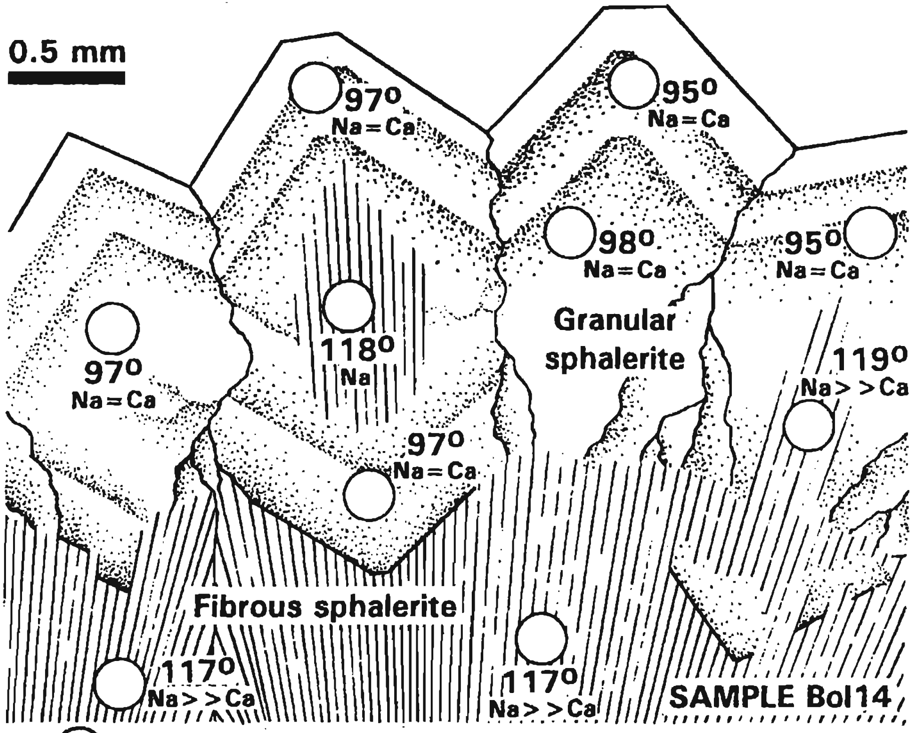


Fig. 20. Primary and secondary inclusions arranged in planes of the indicated symbols, refilled by fluids that yielded the planes of younger secondary inclusions (A, B, C, D); orientation of the cleavage planes of sphalerite shown inside the tetrahedral crystal habit (E), and complete habit of the investigated crystal (F)

listed above did not reach the crystal surface. The *Th* values of the latest primary inclusions found in the crystal were 90-88°C, *i.e.* in fact the same as of inclusions in the youngest healed fissure. An important genetic consequence is, that at the Trzebionka mine (and probably elsewhere), the ores formed on the background of the active tectonic phenomena.

FLUID INCLUSIONS IN RECRYSTALLIZED SPHALERITE

The common opinion attributed both granular and fibrous habit of sphalerite in ore aggregates to their primary, direct crystallization from mineral-forming medium (*cf. e.g.* LEACH & VIETS 1992, GÓRECKA 1993b). This is correct in many observed cases and has been extended to the all existing sphalerite assemblages of the studied region. However, exact search for the relics, that could indicate ores recrystallization, yielded a number of examples

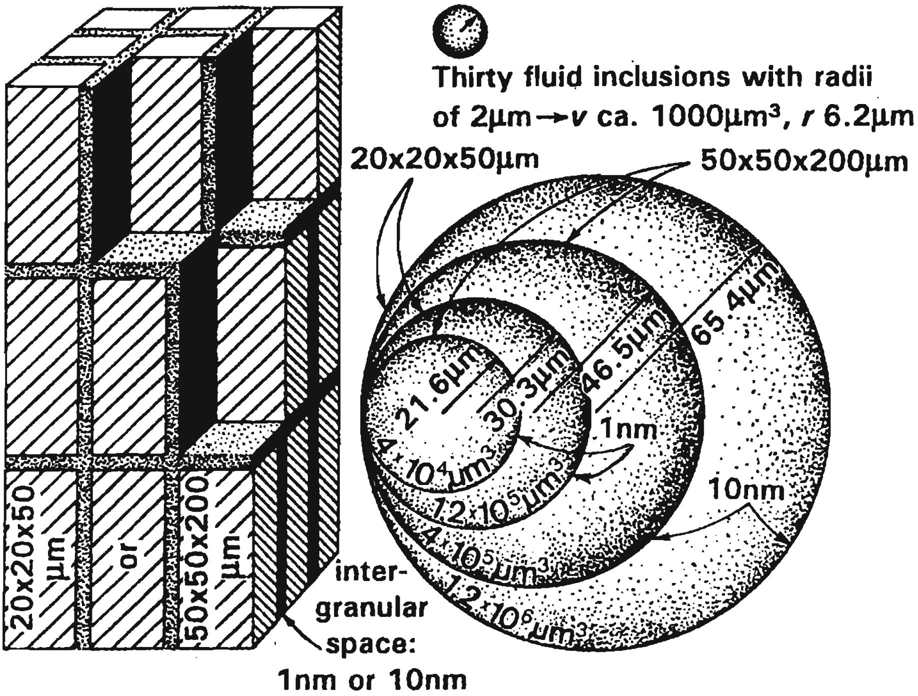


○ ***investigated inclusion in the center of the circle; homogenization temperature in °C and the main cations given***

Fig. 21. Recrystallization of the fibrous sphalerite to the granular habit

of this process.The search was caused by presence of odd assemblages of primary fluid inclusions in one growth zone of many sphalerite crystals. Any explanation of these assemblages origin was not possible except for a process of accretional recrystallization of the host mineral, as given elsewhere (KOZŁOWSKI 1992).

The inconsistency of fluid inclusions in a single growth zone concerned first of all the inclusion fluid composition. The neighboring crystals contained inclusions with either Ca-low or Ca-high solutions, sometimes even with a remarkable amount of potassium. Any possibility of refilling or misinterpretation of secondary inclusions as primary ones was excluded. Thus, the contemporaneous presence of various aqueous fluids remained the only explanation. This implied the recrystallization of fine-grained aggregate to coarse crystals with activity of limited volume of fluid, possibly the intergranular solution only, like described elsewhere for silicate minerals (*see* KOZŁOWSKI 1978, pp. 178-180, Pls 1-2 and 4-6).



Scheme of calculation of the intergranular fluid volume

Volume of intergranular fluid

Fig. 22. Calculation of the total volume of the intergranular fluid in 1 mm³ of the investigated fibrous sphalerite; note the maximum volume of the primary fluid inclusions in the same amount of sphalerite

However, only an independent textural evidence could confirm the above supposition. Such an evidence was found in a laminated sphalerite sample from Bolesław mine, containing in the fibrous aggregate discontinuous bands of clusters of granular sphalerite. The equant grains in polished preparations revealed inner cores of fibrous sphalerite, surrounded by a thick "monocrystalline" rim (Text-fig. 21). Sometimes, in a given section the fragments of equant grains were separated by the fibrous zone, possibly these fragments communicated under or above the polished section plane. At places, also the grain borders had re-entrants of fibers. These features are typical of accretional recrystallization that did not achieve its final equilibrium state.

In inclusions in the two sphalerite habits there occurred distinct differences. Fibrous sphalerite, both in parent matrix and in relics inside equant grains, contained in aqueous inclusions a solution with sodium as the main cation and calcium content very subordinate. The total salt concentrations ranged from 10 to 14 wt. %, *Th* were from 117 to 119°C, *i.e.* the same within the determination error limits. Inclusions in equant grains yielded solution compositions with almost the same contents of calcium and sodium cations (by weight) and lower total salt concentrations, being within the ranges of 5-7 wt. %; *Th* decreased to 95-98°C. One should note that the equant grains in the discussed sample had an unusually uniform fluid composition. Most frequently the differences in cation contents were large.

The acceptation of the accretional crystallization process as causing at places the present-day habits of ore minerals leads to the problem of the genetic interpretation of the fluid inclusion data obtained from recrystallized mineral assemblages. The fibrous aggregates have typical dimensions of fibers from 20 × 20 × 50 to 50 × 50 × 200 µm and these values were used for calculations, which one performed for two supposed numbers of the intergranular space average thickness of 1 and 10 nm. The obtained total volumes of the intergranular space in 1 mm^3 of the fibrous aggregate were *c.* 41 × 04 μm^3 to 1.2×10^5 μm^3 for the thickness of 1 nm and the two above given fibers sizes; for 10 nm the volumes were 4×10^5 μm^3 and 1.2×10^6 μm^3, respectively (Text-fig. 22). The total average volume of aqueous inclusions in 1 mm^3 of the fibrous sphalerite aggregate was *ca.* 10^3 μm^3, thus from 40 to 1200 times less than the total volume of intergranular fluid in the same ore amount. Solution in inclusions was relatively well protected from external influences, however, the intergranular fluid entered the space that was not completely isolated. Thus, the latter fluid could be exchanged in an unknown part and by the solution of unknown composition during the aggregate existence. On the recrystallization process the inclusion fluid was diluted at least 40 times by a fluid of a composition impossible to reconstruct. Hence, the new, mixed fluid in inclusions in recrystallized granular sphalerite had variable composition that could not be bound directly to any peculiar stage of the fluid migration through the ore deposit.

HOMOGENIZATION TEMPERATURES ACROSS A FISSURE FILLING

The problem of temperature variations for fluid fillings of fissures in rocks was discussed elsewhere (Kozłowski 1978, pp. 193-196), and for this peculiar type of mineralization will be presented later (*cf.* Text-fig. 28). Homogenization temperatures of aqueous inclusions in sphalerite depended directly on temperatures of the parent fluid that filled the fissure. When considered in a cross-section perpendicular to the fissure walls, *Th* values changed most frequently according to the same pattern: fibrous sphalerite formed on the wallrock yielded low values, then increasing to a maximum in the last (youngest) band of the fibrous sphalerite. Granular sphalerite following directly the fibrous variety contained aqueous inclusions of lower *Th*, which subsequently decreased also gradually in the growth zones of the granular lamina (Text-fig. 23). This analysis is important for determination of temperature parameters of the general model for ore deposit origin, because it permits to select the *Th* values characterizing the inflowing fluids not cooled by local fluid-rock interaction or inhibition of solution flow. The sequence of color banding (*see* Text-fig. 23) of both fibrous and granular sphalerite is typical, though not always developed completely. The temperature values are not the same for a given color band at any place; rather, the sequence of *Th* changes is similar for most of the banding sets investigated.

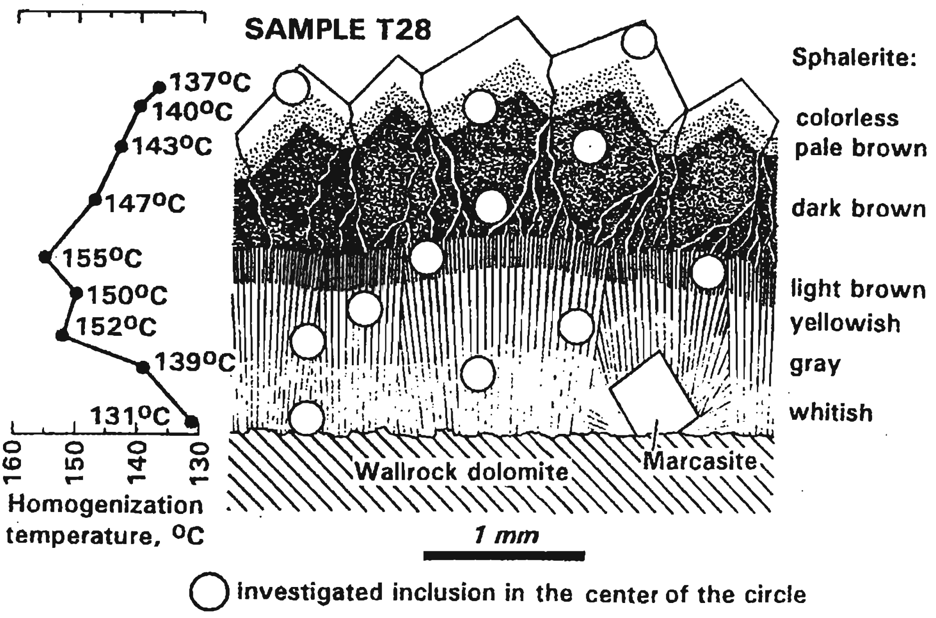


Fig. 23. Sequence of precipitation of the fibrous and granular sphalerite bands and the measured homogenization temperatures of primary fluid inclusions

INCLUSION HOMOGENIZATION TEMPERATURES AT THE STUDIED DEPOSITS

The homogenization temperatures in the current study were measured for 1427 fluid inclusions in sphalerite. This total comprised 1298 primary inclusions and 129 secondary ones. Of course, these data were obtained for two- or three-phase inclusions only, *i.e.* for inclusions of the types *1–4* and *6–8*.

The most abundant and valuable *Th* were obtained for two-phase inclusions of aqueous solution with a shrinkage bubble (*type 1*). They are the best approximation of the sphalerite (and other coeval ore minerals) temperatures of formation. Generally, they ranged from 158 to 80°C, with significant variations in ore parageneses, vertical cross-sections and horizontal distribution.

In one sequence of sphalerite morphological varieties (habit and color banding) with the dimension from wallrock to the outer surface of the last crystals, ranging from fractions of millimeter to >10 cm, there were several patterns of *Th* variation. The obtained values were always lower close to the wallrock than a short distance from it (*see* Text-fig. 23). This indicated that fissures were entered by solutions hotter than wallrocks. Further from the wallrock, the temperature achieved a maximum or several extrema and, finally, *Th* decreased to values either lowest in the sequence or close to the initial ones. The ranges of *Th* variation in the investigated samples did not exceed 30°C, but most frequently they were from 20 to 15°C, if primary inclusions considered. In few samples from the Olkusz region *Th* were almost the same in the cross-section (80-83°C, 81-82°C, 86-90°C, *i.e.* practically, they

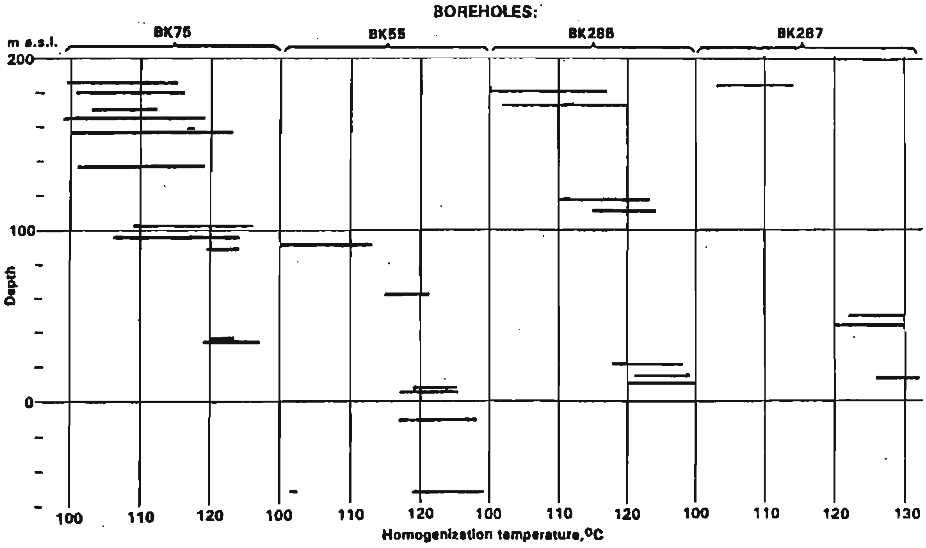


Fig. 24. Homogenization temperatures of primary inclusions in sphalerite *versus* depth of sampling at four boreholes of the Klucze ore field

ranged within the determination error). Such values suggested, that during this sphalerite formation, temperatures of wallrocks and entering solutions were almost the same.

The changes of *Th* along the vertical extent of the ore body were of special interest in this study (*cf.* Kozłowski 1991a,b). Such investigations were performed on samples from four boreholes in the Klucze ore field, namely *BK-55*, *BK-75*, *BK-287* and *BK-288* (for detailed geology and lithology of this area *see* Górecka 1993b, *and* Kozłowski & Górecka 1993, Figs 1 and 7). The joint vertical extent of the ore mineralization, in which *Th* were determined, achieved *c.* 250 m with large sections of overlapping (*cf.* Text-fig. 24). The temperature values, used here for that interpretation, were yielded from primary inclusions. They were selected according to the above described procedures to obtain the characteristics of solutions that were parent of the early unaltered ores and entered the fissures, caverns or breccia zones after the initial stage of solution local cooling. The careful considering of the genetic position of the inclusions used, resulted in revealing of distinct regularities in *Th* variations. The first important feature is the gradual and consistent growth of homogenization temperatures according to the sampling depth increase (Text-fig. 24). This indicates either cooling of ascending solutions or warming of descending ones, and it allows the determination of the thermal gradient of the parent solutions.

The thermal gradient of parent solutions was determined for the upper range of the homogenization temperatures of samples from each depth. When expressed by this mode, it is very distinct and may be evaluated as average value of 6 to 10°C per 100 m of vertical extent (Text-fig. 25). It is to note, that the thermal gradient is pertinent to parent solutions of sphalerite (characterized a paragraph above), not to wall rocks.

The second feature is the clearly legible change of the *Th* ranges according to the sampling depth

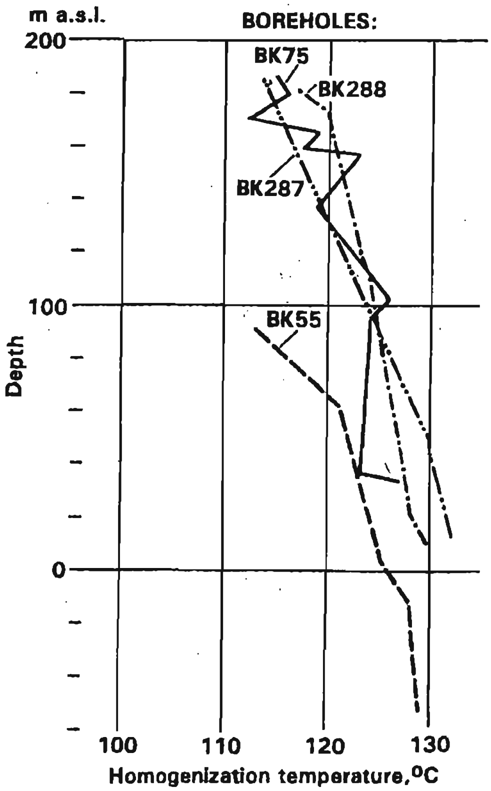


Fig. 25

Vertical thermal gradients of the parent solutions of sphalerite at the Klucze ore field, as inferred from homogenization temperatures of primary fluid inclusions

(Text-fig. 24). The samples from deep parts of the drilling cores yielded homogenization temperatures in narrow ranges of 10 or less centigrades, whereas these from shallow parts achieved the ranges of 20 to 25°C. The change is relatively smooth. This feature is interpreted as a distinct indication of ascending solution type, that cooled on its way to the Earth's surface.

Secondary inclusions with the type *1* fillings yielded homogenization temperatures within almost the same ranges (151-72°C). However, the measurements were not carried systematically but for resolving of special problems, *e.g.* refilling etc.

The type *2*, three-phase inclusions of aqueous solution with daughter halite and a shrinkage bubble were rare and they yielded *Th* 133 and 128°C, *i.e.* within the ranges of the above characterized temperatures. Also the type *3* inclusions filled with aqueous solution, trapped carbonates and shrinkage bubbles had *Th* from 138 to 119°C; carbonate in small part dissolved on very slow and durable heating. The type *4*, three-phase inclusions of aqueous solution with trapped opaque minerals (galena or iron sulfide) and a shrinkage bubble, homogenized at 124-98°C without visible dissolution of the opaque minerals.

Aqueous inclusions, bearing a shrinkage bubble and variable amount of organic liquid (type *6*), homogenized at 133-81°C by disappearance of the bubble; any case of homogenization of organic matter with aqueous solution was not noted. The type *7* two-phase inclusions of organic liquid with shrinkage bubbles yielded homogenization temperatures lower than coeval aqueous inclusions. The obtained *Th* ranges were from 129 to 68°C. The rare type 8 inclusions filled by organic liquid, organic solid phases and shrinkage bubble homogenized at temperatures from 141 to 112°C.

SALINITIES OF THE INCLUSION FLUIDS

Total concentrations of salts dissolved in parent solutions of the sulfide ores from the Olkusz and Chrzanów districts were recognized on the basis of cryometric measurements performed on 1193 primary and 100 secondary inclusions. Most of the obtained data was used to characterize the fluids jointly with homogenization temperatures and the sample positions in the vertical extent of the ore mineralization (*cf.* KOZŁOWSKI 1993).

All primary inclusions studied comprise two groups: (*i*) inclusions in the early, not altered or redeposited sphalerite, and (*ii*) inclusions in other sphalerite generations. The data discussed below came from two-phase aqueous inclusions of the type *1*. Other inclusions, bearing aqueous phase, did not yield values differing from those obtained from "pure" aqueous inclusions except for two halite-bearing ones, indicating extremely high NaCl concentrations in solution.

The relation of salinity *versus* depth of sphalerite precipitation (considered as the present-day hipsometric position in drilling core) showed very characteristic regularities (Text-fig. 26). The borehole *BK-75* from the Klucze ore field was used here as an example, but in the other three studied boreholes, the pattern of salinity variation *versus* depth was the same. All total salt concentrations are given in weight percent of sodium chloride equivalent.

Inclusions in the samples from the bottom parts of the boreholes contained solutions of relatively low salinity, ranging from 5 to 11 %. The solutions achieved maximum concentrations 14.5 to 20.5 % in the middle sections of the core. Unfortunately, there was an interval in the borehole *BK-75* between 40 and 80 m a.s.l., where ore mineralization suitable for fluid inclusion studies was not found, thus direct data from these depths were absent. This gap was in part filled by data from the appropriate depths of the boreholes *BK-55* and *BK-287*. The supporting values suggested a continuous increase of salinity from low to high one. Above the maximum at the depth of 80 to 100 m a.s.l., the salinity gradually and smoothly decreased to 4.5-9 %. One should mention, that this low-high-low salinity sequence occurred on the background of continuous upward-oriented temperature decrease (Text-fig. 26), as described earlier.

The simplest interpretation of the salinity data in this group of fluid inclusions would present the model of occurrence of three types of solutions: (*i*) low salinity, high temperature; (*ii*) high salinity, high and moderate tem-

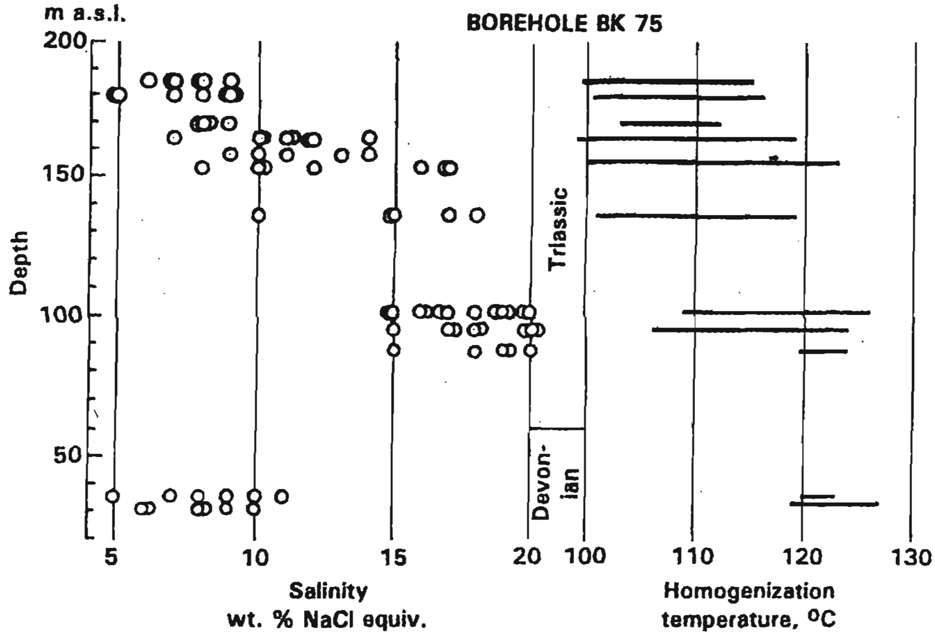


Fig. 26. Solution salinities of primary fluid inclusions in sphalerite *versus* depth of sampling, compared with homogenization temperatures of the same inclusions

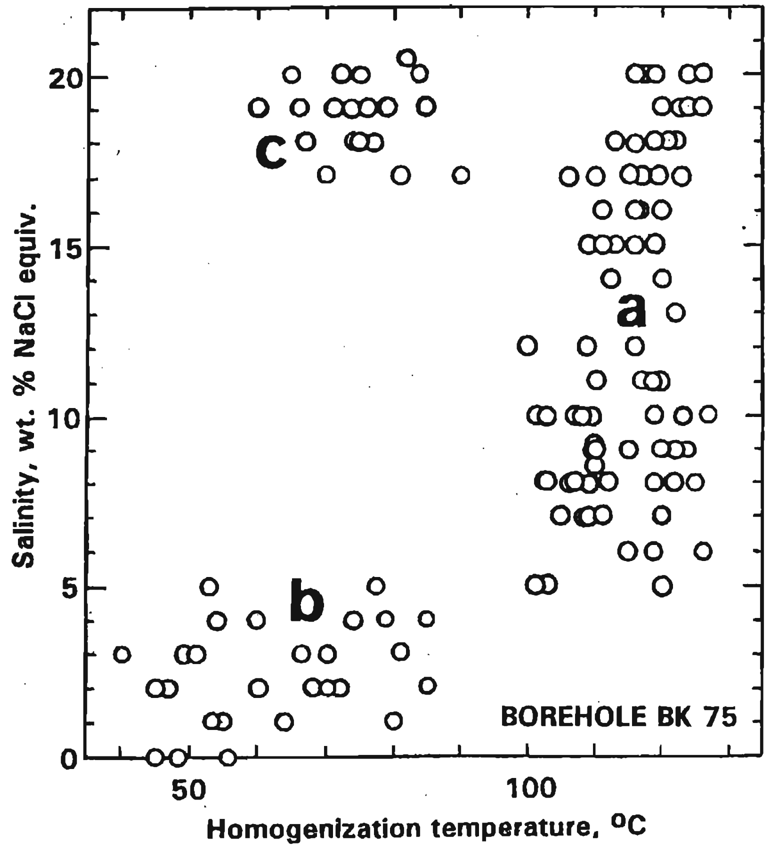


Fig. 27. Salinities of inclusion fluids in sphalerite *versus* homogenization temperatures; the three fields are interpreted as ascending solutions (a), essentially meteoric waters (b), and formation brines (c)

perature; (*iii*) low salinity, moderate to low temperature. A continuous change of total salt concentration and temperature strongly suggest mixing of the three different solutions, that tentatively may be determined as dominated by deep ascending solutions (*i*), saline formation waters or brines, (*ii*) and descending meteoric waters (*iii*). For evidence of the waters ascension *see* the discussion of homogenization temperatures at the boreholes.

If salinity data, obtained from primary inclusions of other sphalerite generations in the same samples studied, were included to the discussed data set, they yielded additional important information (*cf. also* Kozłowski 1994a). At the plot for the borehole *BK-75*: salinity (*S*) *versus* homogenization temperature (*Th*), the data split to three distinct fields: (**a**) *Th* 98-128°C, *S* 4.5-20.5 %, (**b**) *Th* 40-86°C, *S* 0-5 %, and (**c**) *Th* 60-90°C, *S* 17-20.5 % (Text-fig. 27). The field (**a**) of Text-fig. 27 includes all the measurements plotted in Text-fig. 26, *i.e.* inclusions of the solutions that were interpreted as ascending, formation and meteoric waters mixed in various proportion. On the basis of their temperature and salinity, one may conclude that the inclusions in the field (b) are remnants of pure and weakly contaminated meteoric waters, that either might have altered or redeposited in part the earlier precipitated sphalerite. The field (c) denotes these fluid inclusions that formed as relics of the formation brines. Such inclusions are also absent in early sphalerite, but they appear in some later bands, also in those with signs of recrystallization. Presence of the above described inclusion groups confirms the reliability of the mixing of solutions, that came from three separate sources. The three types of parent fluids were found not only in the samples from the borehole *BK-75*, but also in samples from the other investigated drilling cores of the Klucze ore field and from the four mines: Olkusz, Bolesław, and Pomorzany from the Olkusz district and Trzebionka from the Chrzanów district (*see* homogenization temperature *versus* salinity plots: Text-fig. 29). Thus, this mode of parent fluid evolution is typical of the large area, where the zinc-lead ores have formed.

This general feature has, however, exceptions, found till now only in tectonic zones of the Trzebionka mine, *i.e.* in the southern part of the ore region. One of these exceptional samples (Text-fig. 28), a 2-3 mm thick layer of banded, fibrous and granular sphalerite on ore-bearing dolomite in a thin fissure, yielded a typical temperature variation. The salt concentrations were very uniform in all inclusions studied in this sample, and ranged from 6 to 7.5 %, for the whole temperature interval from 131 to 155 and next to 137°C. Such small concentration changes, not exceeding 1.5 %, are not frequent in the investigated ores. Usually, the variation interval of concentrations in a hand specimen or even in one preparation (1.5 × 2 cm) ranged from 5 to 10 %.

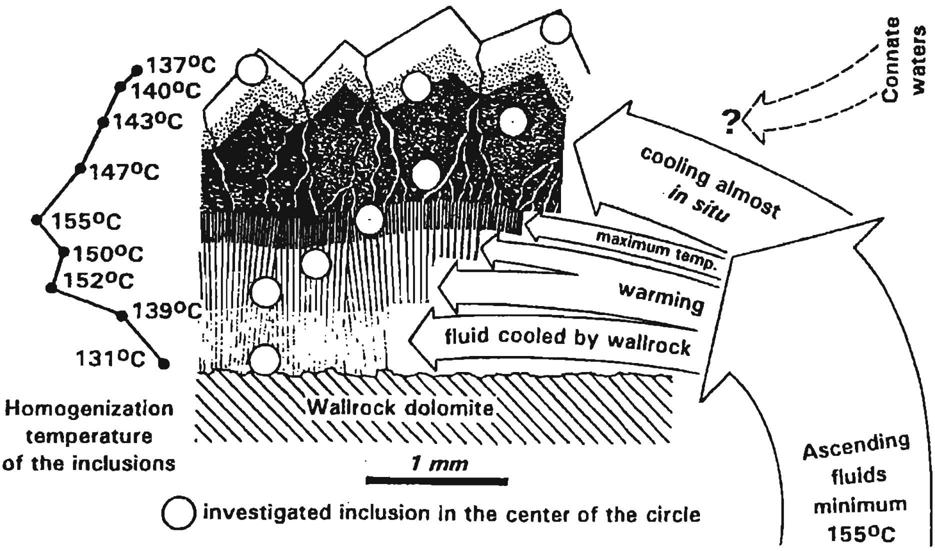


Fig. 28. Evidence of cooling of ore-forming solutions by wall rocks (*cf.* Text-fig. 23) and estimation of the initial temperature of solutions

Inclusion sequence in the sphalerite crystal from the sample *T63* (Trzebionka mine, *cf.* Text-fig. 20) is a good example of such strong salinity changes. Primary inclusions (*Th* 129°C) contained solution of salinity 16.5 %, and subsequent secondary inclusions generations for decreasing homogenization temperatures yielded the following salinities: 122°C and 11 %, 103°C and 18 %, 97°C and 14 %, 94°C and 12.5 %, 88°C and 16 %. The changes evidenced intensive ore-forming solution flow during crystallization of that sphalerite.

The thermic evolution of the parent fluid of the sphalerite layer (Text-fig. 28) can be explained as follows. Hot solution entered the fissure, cooled in contact with the wall rock and this resulted in rapid precipitation of fibrous sphalerite. The maximum temperature of at least 155°C during precipitation of the last band of fibrous sphalerite denoted the last portion of the inflowing solution. Probably this portion had temperature weakly influenced by cooling by wall rocks, because these rocks were already locally warmed by ascending solutions. From this moment the solution inflow to this fissure system was inhibited and granular sphalerite slowly crystallized from the remnant portion of zinc sulfide present in solution. Temperature decrease appeared due to heat outflow, not due to mixing with a cooler solution. This is evidenced by smooth temperature decrease and stable salinity. Thus, one may suppose, that in this case the inclusions are samples of the ascending fluid, and a mixing, if occurred, should take place at a significant distance from the ore precipitation area.

Such narrow variation limits of salinity in inclusions in one sphalerite sequence in a single sample are unknown from the northern part of the ore region, *i.e.* from the Olkusz district. This difference between the northern and southern parts of the region is evaluated as a genetic feature, important for construction of a model of the ores origin, presented hereafter.

CHEMICAL COMPOSITION OF ORE-FORMING FLUIDS

Most of the data on composition of ore-forming fluids have been obtained by cryometric measurements of 1188 primary inclusions in sphalerite. This method yielded only concentrations of the main anions. In the investigated samples there was evidenced the presence of chloride as the main anion, and sodium and calcium as the main cations. Doubtful signs of the presence of potassium were noted; magnesium presence was not possible to verify in these fluids. Thus, the discussion presented below concerns only the main aspects of chemical composition types and evolution of the ore-forming fluids in the Olkusz and Chrzanów districts. Nevertheless, the results led to important genetic conclusions.

Sodium and calcium were found in the inclusion solutions in very variable proportions (Text-fig. 29). However, the ore-forming fluids may be described as calcic-sodic solutions, only rarely achieving pure or almost pure sodic composition. Samples from drilling cores obtained from the Klucze ore field of the Olkusz district contained inclusions, that yielded few pure sodic compositions; most of the 533 investigated inclusions had main salts concentrations from 15 % $CaCl_2$ + 85 % NaCl to 68 % $CaCl_2$ + 22 % NaCl (here and later in weight percent of the salts total). The total salt contents in solutions rarely achieved 20 wt. %.

Samples from three mines of the Olkusz district: Pomorzany, Bolesław, and Olkusz, yielded 409 inclusion solutions compositions, that plotted on one H_2O-$CaCl_2$-NaCl diagram, overlapped almost exactly in the same field (Text-fig. 29). The maximum concentrations of total salts in solutions were lower than those from the Klucze field: Olkusz mine 18 wt. %, Pomorzany

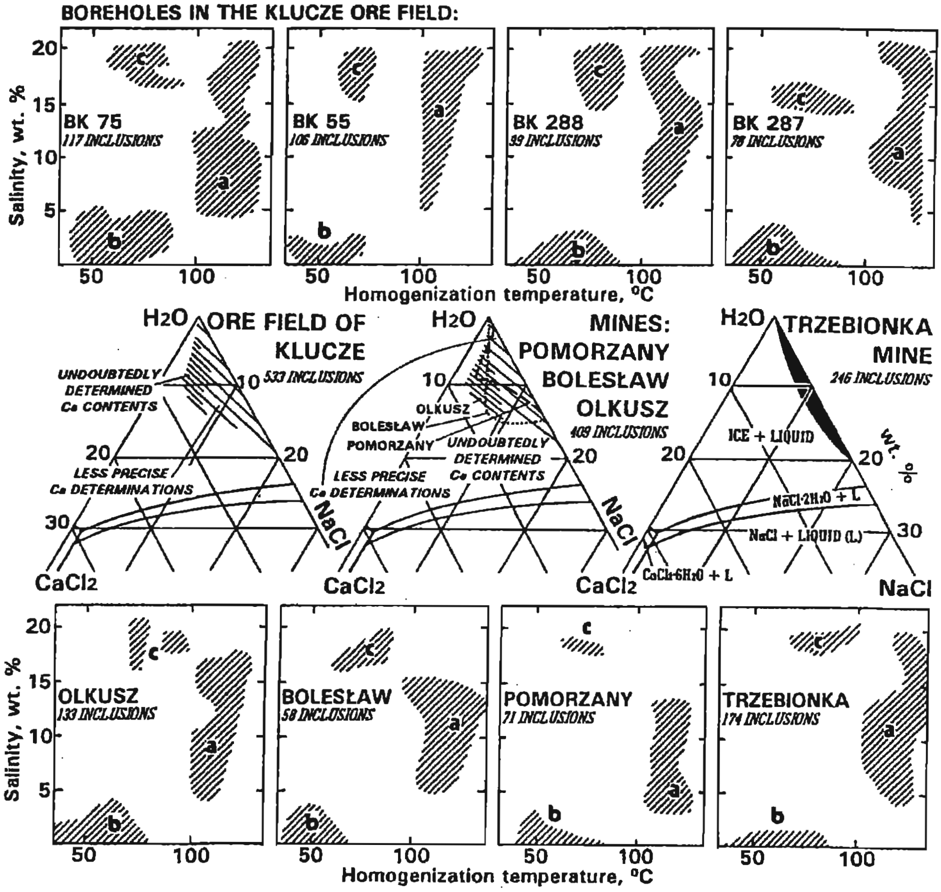


Fig. 29. Characteristics of ore-forming fluids in the investigated ore objects; note the constant splitting of the fields into three parts at the salinity versus homogenization temperature plots (**a** — ascending solutions, **b** — meteoric waters, **c** — formation brines), and the difference in Ca-contents in fluids from the northern and southern ore bodies; the total numbers of the investigated inclusions are given

mine 16.5 wt. %, Bolesław mine 17.5 wt. %. Sodium to calcium proportion varied also strongly: from rare pure sodic inclusion solutions to 80 % $CaCl_2$+20 % NaCl (in samples from Olkusz mine), 70 % $CaCl_2$+30% NaCl (Pomorzany mine) and 50 % $CaCl_2$+50 % NaCl. Thus, the composition fields of ore-forming solutions at various ore objects in the Olkusz district are compatible.

The data for the Trzebionka mine of the Chrzanów district differ distinctly from those of the Olkusz district. Pure or near pure sodic fluids are common here, and $CaCl_2$ fraction of the salt total does not exceed one fifth. The total salt concentrations in parent solutions achieve 20 wt. %, being thus higher than in the Olkusz district (*see* Text-fig. 29). These differences were used to construct the genetic model of the Zn-Pb deposits in the Silesian-Cracow region.

Some additional data on chemical composition of ore-forming fluids were obtained by water leachate method (KARWOWSKI, KOZŁOWSKI & ROEDDER 1979; KOZŁOWSKI & *al.* 1980). This method yielded bulk composition of all inclusions opened in the ground sample, thus it was not possible to consider the variation of chemical composition of fluids in inclusions of different generations. Another problem is caused by great possibility of leachate contamination with foreign mineral inclusions in the sample ground. Nevertheless, it was confirmed, that the solutions are of the Cl-Na-Ca type with minor potassium content. Other common minor or trace components of the parent solutions are as follows: Li, Mg, Ba, Mn, B, and F. Currently, an improved leachate technique combined with ion chromatographic analytical procedure, applied to the Silesian-Cracow ores, yielded information on the presence of nineteen ion species in ore-forming fluids, including ammonia, potassium, rubidium, magnesium, bromide, iodide, phosphate, carbonate, hydrosulfide, thiosulfate, sulfate, nitrate and acetate. This problem, however, exceeds the limits of this report and its consideration is published elsewhere (VIETS, HOFSTRA, EMSBO & KOZŁOWSKI 1996).

The data on organic matter composition from fluid inclusions are very scarce and based on analysis of the infrared absorption spectra of chloroform leachate, extracted from ores in Soxhlet apparatus (KOZŁOWSKI & *al.* 1980). The problems appeared due to very small amount of leachable organic matter. The determinations indicated, that the organic matter consisted of saturated hydrocarbons with minor admixture of hydrocarbon compounds bearing oxygen in their molecules, either in carbonyl, or in ether groups, plus minor content of aromatic compounds. The oxygen-bearing molecules presence might have been connected with oxydation that finally resulted in origin of acetate ions, found in the ore-forming fluids (VIETS, HOFSTRA, EMSBO & KOZŁOWSKI 1996). Experimental studies of GIORDANO & DRUMMOND (1991) indicated the possibility of zinc-acetate complexes existence at temperatures at least up to 295°C. A significant role of the sulfur complexes of intermediate or mixed sulfur valences in formation of the Silesian-Cracow Zn-Pb ores, as suggested by KUCHA & VIAENE (1991), is less probable due to ephemeric existence of such complexes.

The observed UV-luminescence of organic-matter-filled inclusions was in white, bluish, greenish, yellow, orange and red. This scale of luminescence colors suggests a broad variation range of hydrocarbon types. Color of fluorescence may be controlled by multiple variables, thus it may be used as a gross indication only to the petroleum characteristics, *e.g.* in degrees of API gravity. However, if applied, the colors would indicate the values of 10 to 50°API gravity (BODNAR 1991, *fide* Fig. 6.3 *and* p. 77 *in* GOLDSTEIN & REYNOLDS 1994).

Gaseous components of the ore-forming fluids in the Silesian-Cracow region were first determined by LEACH, APODACA, VIETS & *al.* (1993), and LEACH, APODACA, KOZŁOWSKI & *al.* (1996). The authors found, that CO_2 is the main gas component in inclusions both in ore minerals and in sparry dolomite (ore-bearing). Fluid inclusions in sphalerite and galena contain also significant amount of CH_4 plus lesser other hydrocarbon gases, and appreciable H_2S; these admixtures are much lower in inclusions in dolomite.

Thus, the general characteristics of ore-forming fluids, resulting from fluid inclusions studies, may be presented as follows. Ores formed from chloride-carbonate (bicarbonate?) sodium-calcium solutions with variable proportion of these two main cations. Magnesium and potassium were important components, plus minor cations: ammonia, lithium, barium, strontium, and manganese, and minor anions: bromide, nitrate, acetate, boron-bearing (borate?) and occassionally fluoride (partly *from* VIETS, HOFSTRA, EMSBO & KOZŁOWSKI 1996). The fluids contained essentially saturated hydrocarbons with admixture of oxygen-bearing compounds in part dissolved but partly as an independed phase. Carbon dioxide plus minor methane (and other gaseous hydrocarbons) and hydrogen sulfide were the dissolved gases.

ORE ORIGIN MODEL BASED ON FLUID INCLUSIONS

FLUID INCLUSION DATA

Any consideration of the zinc and lead sulfide ores origin in the studied part of the Silesian-Cracow region, *i.e.* Olkusz and Chrzanów districts (Text-fig. 30*A*), must take into account the following features of the ore-forming solutions in this area:

1. The early fluids displayed a vertical thermal gradient of *c.* 6 to 10°C per 100 m, *i.e.* higher than present geothermal gradient in this area, and probably than that coeval with ores origin;

2. Temperature ranges of early ore formation at deep levels were distinctly narrower than closely to the Earth's surface ($\leq$10°C *versus* 20-25°C, respectively);

3. Most frequently temperatures of fluids entering tectonic fissures were higher than wallrock temperature;

4. The maximum temperatures found in the Chrzanów district (158°C) were higher than the maximum values in the Olkusz district (139°C);

5. In tectonic fissures there occurred either single inflows of fluid with its cooling *in situ*, or multiple entering of new portions of fluid;

6. There were three components of ore-forming fluids: ascending solutions, formation brines, and meteoric waters, partly mixed, but probably also occurring as separate fluids;

7. Main cations were sodium and calcium and their concentrations varied from pure sodic solutions to these with prevailing calcium, achieving up to 80 % of total salts; calcium-low fluids are typical of the Chrzanów district and are rare in the Olkusz district; early fluids frequently are poorer in calcium than the late ones, which are commonly calcium-rich or calcium-dominated;

8. Large short-time salinity variations were more common in the Olkusz district than in the Chrzanów district.

DISCUSSION

The above characteristics indicates a set of main features of the ore-forming solutions origin and migration. The presence of vertical thermal gradient evidences a vertical migration of the solutions, whereas an upward increase of temperature ranges points to the ascension of these solutions with their cooling near the Earth's surface. The solutions were not local, at least not all were local formation brines, because of the temperature difference between solutions and wall rocks found commonly in the vertical extent of ore mineralization. On the basis of analysis of the vertical ore zoning at Klucze, HARAŃCZYK (1963) also evidenced the ascending type of ore-forming solutions.

The present-day thermal regime of the area of interest is not known satisfactorily, however, the data published by several authors (KOWALCZUK & PAŁYS 1967, CHMURA 1975, MAJOROWICZ 1977) gave a general outline of temperatures and heat flow. Temperature variation *versus* depth, determined in boreholes, yielded rock (and formation waters) cooling of 2.8 to 5°C per 100 m of vertical extent. The highest temperature was measured in the borehole Goczałkowice *IG-1* at depth of 2950 m for Devonian aquifer as equal 100.5°C (RÓŻKOWSKI & RÓŻKOWSKA 1973). Generally, the western part of the area has higher temperatures than the eastern one. To some extent it is consistent with maximum temperatures of ore formation yielded in this study by fluid inclusions in sphalerite, which were distinctly higher in the south-west area than in the north-east one. However, both rock temperature and geothermal gradient of the rocks are lower than these of ore-forming solutions. If there was no a distinct difference in thermic regime of the country rocks at the time of ores deposition, when compared with the present-day conditions, the quick cooling of ore-forming fluids, as found by inclusion studies, and appearance of ZnS supersaturation in the solutions were reasonable.

The ore-forming solution flow was tectonically controlled at least at the early stages of ore mineralization. It appears from the presence of fissures filled by solution either in a single event with later cooling, or during several events with distinct change of solution type in each event, associated with crushing of the growing sphalerite crystals. The solution type changes resulted in its varying temperature, salinity and sodium/calcium ratio.

The three groups of fluids found, characterized by low salinity/high temperature, high salinity/moderate temperature and very low salinity/low temperature most probably should be attributed to ascending solutions, formation brines and meteoric waters, respectively (Text-fig. 30*B*). Ascending solutions of unknown origin mixed first with saline formation waters. Hypsometrically higher, the second mixing with dilute meteoric waters caused not only a sharp decrease of salinity but also a temperature drop. The mixing mechanism is responsible in part for distinct variations of temperature, salinity and composition of ore-forming solutions. The performed fluid inclusion studies did not submit any indication of possible separate sources of metals and sulfur, and sulfide precipitation on mixing, thus this problem will not be discussed here. Nevertheless, the recent hydrotherms have high Zn transportation capacity, reaching hundreds ppm (WHITE 1967). Surface-temperature waters, *e.g.* outflowing from zinc and lead mines, carry distinctly lower metal amounts, ranging for Zn and Pb from 0.0n to 10 ppm (SERAFIN-RADLICZ 1979). Thus, to cause precipitation of sphalerite (and galena), even with preceding supersaturation, the ore-forming solution cooling alone is a sufficient factor, and any mixing of separate, metal- and sulfide-ion-bearing fluids directly in the ore precipitation zone is not necessary, though possible, to invoke for. The problems, connected with zinc solubility in sulfide solutions on the basis of the laboratory studies were also presented by HAYASHI & *al.* (1990, 1991) and DYRSSEN (1991). An extensive discussion of the possible sulfide ion sources based on the sulfur isotope data is presented by LEACH & *al.* (1996).

HARAŃCZYK (1993), on the basis of isotope studies, presented a two-source solution model, that may mean at least two sources; he also attempted the determination of ores precipitation temperatures by mode of sulfur isotope partition between sphalerite and galena from the ores disseminated in dolomite and in their massive variety, receiving the temperatures of *c.* 300°C. However, RYE (1974) observed a very large variation for sulfur isotope fractionations in natural coeval sphalerite-galena pairs, formed at the temperature range 200 to 110°C. He explained this feature by sulfur isotope disequilibrium, that may occur in the low-temperature hydrothermal deposition. The *Th* values, determined for the Silesian-Cracow sphalerite, are almost exactly in this range, thus an independent check of sulfur isotope equilibria is necessary. Meanwhile, the dendritic, fibrous and colloform sphalerite and galena habits would indicate rather disequilibrium conditions during many mineralization events in the studied ores. The stalactite forms of sphalerite, present in the Silesian-Cracow deposits and interpreted as karstic speleothem, might have resulted from rapid crystal growth under hydrothermal conditions due to mixing of an acidic and an alkaline solution (ANDERSON & *al.* 1995a), *i.e.* disequilibrium crystallization.

Studies of the recent saline waters sampled at various depths in the ranges: from Earth's surface to 3000 m below it, and located in the Silesian-Cracow region, distinctly showed gradual salinity decrease from *c.* 20 wt. % at the largest depth to nearly nil at the surface (*see* RÓŻKOWSKI & *al.* 1979, Fig. 5) . This is an evidence of the transition: brine-meteoric waters, still existing in the area under study, probably due to mixing of the two components. Fossil evidences were found in results of metasomatic dedolomitization processes, that developed in environment of mixed meteoric and hot waters (MOCHNACKA & SASS-GUSTKIEWICZ 1978). The third, ascending component has not been evidenced neither by the latter authors, nor by RÓŻKOWSKI & *al.* (1979), however, the salinity changes, recorded by these authors, fit well to the upper part of the salinity profile found in fluid inclusions. Moreover, RÓŻKOWSKI & *al.* (1979, Fig. 6) gave the main ion characteristics of the brines as rich in sodium in Devonian and Carboniferous rocks, and sodic-calcic to calcic in Devonian and Triassic ones, a distinct two-fold spectrum of compositions like that one found in the studied fluid inclusions in sphalerite.

Changes of the sodium and calcium contents in parent fluids of the ores resulted not only from mixing process, but also from solution-wallrock interaction. Wallrocks were almost inexhaustible source of calcium (and magnesium). During percolation through the wallrocks, solutions should dissolve calcite and dolomite, that resulted in increase of Ca and possibly Mg contents in waters. This differentiation have been found in inclusions in minerals of the investigated ores. The area of the Chrzanów district yielded calcium-poor compositions of fluids, whereas to the north, in the Olkusz district, the calcium-rich fluids are very common (Text-fig. 30*C*). This feature strongly suggests the solution migration from south to north (KOZŁOWSKI 1994b), especially if considered jointly with higher maximum temperatures and smaller short-time salinity variations in the southern area than in the northern one.

The solution/wallrock interaction might have resulted in incorporation of organic matter (hydrocarbons) from limestone or dolomite to ore-forming solutions by any mode presented earlier in this report. Chloroform leachates from Middle Triassic dolomites or limestones without ore mineralization, made by the present author, evidenced the presence of organic matter very similar to that determined in ore minerals. Moreover, thermovacuum decrepitation analysis (ALEKSEENKO & *al.* 1978) yielded gas emission from ore-bearing dolomite samples at temperature above 400—450°C, due to decomposition of disseminated organic matter present in the rocks. The oxygen-bearing hydrocarbon compounds (ether or carbonyl molecules and acetate ion) leached from ore minerals indicated, that the organic matter consumed oxygen, yielding its low fugacity, *i.e.* maintaining reducing conditions. This resulted in the occurrence of sulfide sulfur in ore-forming solutions. Probably ammonia found in ore-forming solutions (*see* VIETS, HOFSTRA, EMSBO & KOZŁOWSKI 1996) was also of organic origin. Note, that the sampling mode excluded the contamination by ammonia from explosives used in mines, as discussed by VIETS, HOFSTRA, EMSBO & KOZŁOWSKI (1996). Thus, this component, whose presence caused alkalization of solution, apparently was introduced to ore-forming fluids from wall rocks.

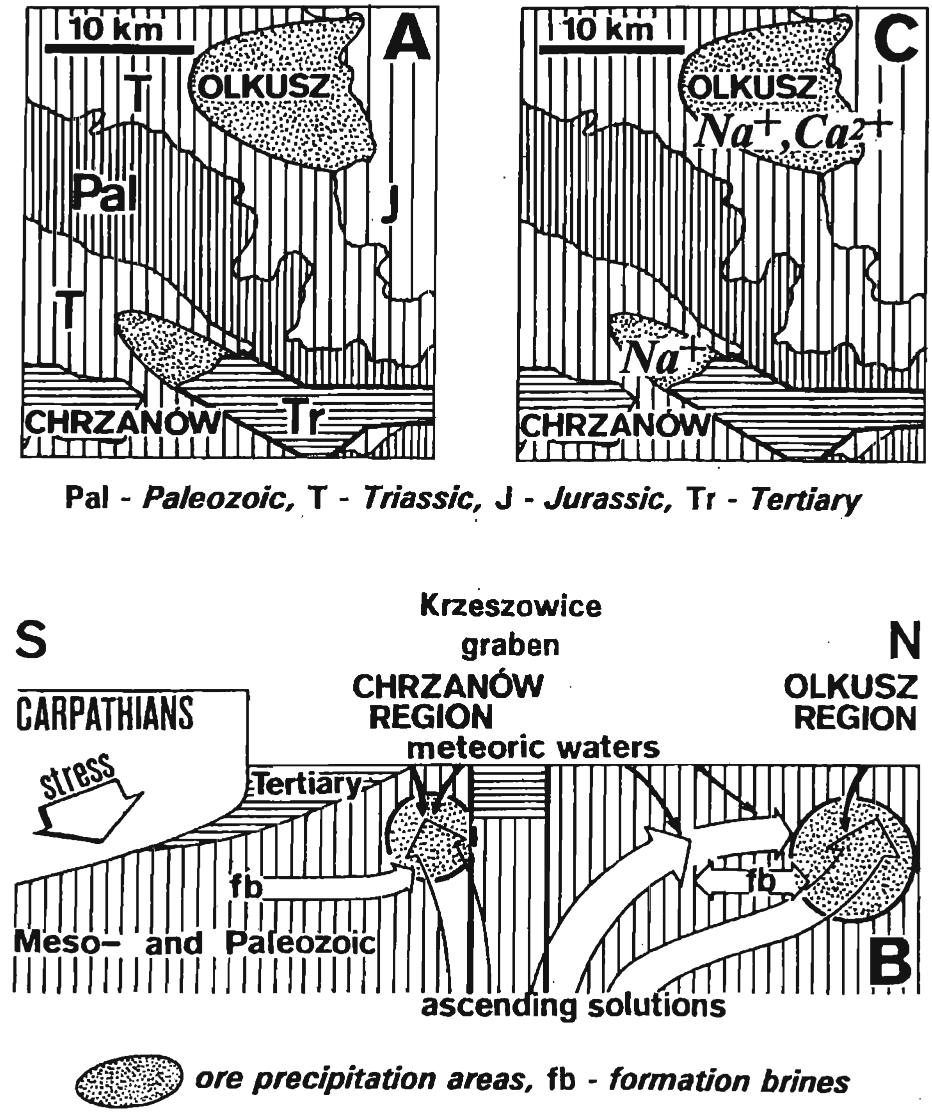


Fig. 30. Simplified map of the Olkusz and Chrzanów ore districts (A), scheme of the ore-forming fluids circulation (B), and distribution of the main cations in parent fluids of the early sphalerite (C)

The age of the ore mineralization has not been determined satisfactorily till now. Zinc and lead ores are hosted by the Devonian to Jurassic strata, and the ore mineralization was also reported from the Tertiary rocks (SZUWARZYŃSKI 1993). If this mineralization developed in one ore-forming cycle, its age should be not older than Tertiary. A time ago, Professor A. TOKARSKI (*fide* ŚLIWIŃSKI 1964) on the basis of post-Jurassic faults age, estimated the age of ore mineralization as Cretaceous or Tertiary, connected with the Alpine orogeny. According to GÓRECKA (1993b), stratiform ore bodies in the Klucze ore field extend undisturbed through Alpine fault zones, that would indicate Alpine/post-Alpine age of the ores. Presently, SYMONS & *al.* (1995, 1996) dated by paleomagnetic methods the ore genesis in the Silesian-Cracow region between the latest Cretaceous and pre-Miocene, preferentially mid-Tertiary, coincident with the latter half of the Alpine orogeny (*cf. also* LEACH, VIETS, KOZŁOWSKI & GÓRECKA 1995). This age (mid-Tertiary) is thus currently the best approximation. However, the isotope age determinations by Sm/Nd, Pb/Pb or Rb/Sr methods, like those performed for North American MVT deposits (*e.g.* BRANNON & *al.* 1992, ALEINIKOFF & *al.* 1993, CHESLEY & *al.* 1994) would be desirable, especially to establish the duration of ore-forming process.

Detailed tectonic studies, performed at the Trzebionka mine by JAROSZEWSKI (1993), KIBITLEWSKI (1993) and KIBITLEWSKI & JAROSZEWSKI (1993), evidenced tectonically-controlled, high-pressure flow of ore-forming fluids that resulted not only in ore precipitation, but also in the wallrock crushing and disintegration. These hydrotectonic phenomena are believed to be of Alpine age. Hence, the suggestion is reasonable, that the rejuvenation of older brittle deformations and their extension to younger rocks plus mobilization of fluids in a regional scale, were due to the Cretaceous/Tertiary (Alpine) orogenic event, that occurred to the south of the present-day ore region. That event was the formation and uplift of the Carpathian mountainous chain with its northward-oriented overthrust of a series of nappes on pre-Tertiary and partly Tertiary basement. Stress of the nappes mass have had to change the hydrostatic equilibria in the aquifers, when the rocks were plunged and new migration paths for waters (tectonic zones) were opened. The present Author avoids the discussion, whether the fluids were formation waters, or waters released from hydrous minerals by increasing pressure and temperature. The pressurized fluids should be pushed to the north of the overthrusting nappes, *i.e.* toward the northern margin of the just-forming Carpathian foredeep and southern slope of the Variscan platform and its post-Variscan cover. The similarity of ages of these phenomena and Zn-Pb mineralization, as well as the characterized features of the mineral-forming fluids, concluded from fluid inclusion studies, make the supposition reliable, that the regional flow of fluids, generated by the folding of the Carpathians, was an important, or maybe, even basic factor, causing the origin of the discussed ore deposits. Similar features were found in North American Mississippi Valley-type (MVT) deposits, confirming a tectonic link between the Appalachian-Ouachita orogeny and the

MVT Zn-Pb ores formation of the Ozarks (CLENDENIN & DUANE 1990, CLENDENIN & *al.* 1994).

The described tectonic activity might yield a water circulation system, in which meteoric waters penetrated downwards either hydrostatically or hydrodynamically, leaching metals from formation rocks and supplying the formation water resources. The persistence time of waters in an underground circulation system may differ in various geological structures. A structure to certain degree similar to the discussed zone, the eastern forefield of the Nevada Mts, USA, the Steamboat Springs area (WILSON & THOMSSEN 1985), has a water circulation system, that retains water during 30,000 to 300,000 years (carbon isotope determinations by CRAIG 1962).

The waters, mobilized by the overthrusting Carpathians, might be the ascending solutions, identified by means of fluid inclusion studies in sphalerite. They could achieve increased temperature from inner Earth's heat inflow, which in the zone between the Carpathians and the Holy Cross Mts is almost highest in Central Europe, between 1.6 and 2.0 μcal per $cm^2 \cdot s$ (HOHL 1977). This narrow high-heat-inflow zone, extending in front of the Carpathians, may indicate a deep discontinuity in the Earth's crust.

The source of sodium chloride in the formation brines, participating in the ore origin, could not be located in Miocene evaporites of the Carpathian foredeep, because the latter are too young. Probably, the marine basin of the future salinary sedimentation was formed as morphologically variable trough (RADWAŃSKI 1968, 1969) at the time of either ores precipitation, or its decline. Proposal of the brine flow from the Upper Silesian parallic coal basin (RÓŻKOWSKI & *al.* 1979), if not supported with evidences, is not necessary, because Triassic sediments in the area of ores formation bear evaporite intercalations.

The source of metals for the deposits of the type similar to the Silesian-Cracow ones, is located commonly in rocks that were the objects of the fluids percolation on their way to the discharge area. The suggestions for the Silesian-Cracow ores made till now were based on lead isotope analyses in insufficient number of the samples (ZARTMAN & *al.* 1979, CHURCH & VAUGHN 1992), thus they may be evaluated only as very preliminary.

SILESIAN-CRACOW *VERSUS* MISSISSIPPI VALLEY-TYPE DEPOSITS: A TENTATIVE COMPARISON

Lately, many publications on the Silesian-Cracow deposits include this object to the Mississippi Valley-type, called further MVT (*e.g.* DŻUŁYŃSKI & SASS-GUSTKIEWICZ 1980, 1989; SZUWARZYŃSKI 1993; SASS-GUSTKIEWICZ & KWIECIŃSKA 1994; LEACH & *al.* 1993, 1996; SYMONS & *al.* 1996a,b). Such approach requires fulfiling of three basic conditions: (*i*) An exact definition of the type

(Zn + Pb ± F) deposit(s), *i.e.* from the Mississippi Valley, *(ii)* Selection of the features that are of genetic importance and are discriminative for this type, and *(iii)* The comparison of the analytical data. Leach & Viets (1992) and Leach & Sangster (1993) attempted to complete the MVT deposit definition and presented it as: "*A varied family of epigenetic ores, precipitated from dense basinal brines at temperatures ranging between 75 and 200°C, typically in platform carbonate sequences*". Chesley & *al.* (1994) proposed a little different definition: "*Deposits formed from hot (50-220°C) saline (10-30 wt. % Na-Ca-Cl) aqueous fluids, very similar in character to present-day oil-field brines (...) expelled from large sedimentary basins.*" The second definition is preferred by the present Author as more restrictive. Features of any MVT deposit must fit to the proposed definition.

Leach & Viets (1992) completed their definition with a list of 14 most important features of the MVT lead-zinc deposits, and this would be the condition *(ii)*. They attempted also to make a comparison of the MVT and the Silesian-Cracow deposits, what would fulfil the condition *(iii)*.

This chapter will not present an exhausting discussion of the definition(s), features and the mentioned comparison; the present Author, however, would like to express his preliminary opinion. The Leach's & Viets' "list of important features" contains items, that are interrelated or result one from another, *e.g.*: *(1)* ores occur principally in dolostone... etc., *(5)* ores occur in platform carbonate sequences... etc., *(11)* there is always evidence of dissolution of carbonate host rocks, expressed as slumping, collapse, brecciation... etc. This example shows, that the list could be condensed and rationalized, and that certain features are typical not only of the MVT deposits. "Dissolution of carbonate host rocks... etc.", *i.e.* hydrothermal karst, occurs also, for example, in contact-metasomatic skarn-carbonate-hosted polymetal-boron deposit Dalnegorsk, formerly Tyetyukhe, in the Russian Far East (Efimova & *al.* 1972, and the present Author's observations 1979), thus not being discriminative of the MVT. A scheme of the seven selected features distribution in 25 ore districts, accepted as the MVT ones (Table 1 *in* Leach & Viets 1992) is very informative about problems, connected with proper definition and a set of discriminative features: no one feature occurs in all the selected deposits, and no one deposit displays all the selected features. This suggests, that the deposits are usually included to the MVT on a very liberal basis and/or that the MVT criteria set should be more intrinsic.

Several features, stemming from the fluid inclusion studies, will be compared below for the Silesian-Cracow and MVT ores.

1. Homogenization temperatures for MVT deposits are given in ranges 75-200 or 50-220°C (*see e.g.* Roedder 1967, 1968a, 1971, 1977; Chesley & *al.* 1994). This agrees well with the *Th* values of the Silesian-Cracow ores, ranging from 80 to 158°C.

2. Vertical thermal gradient of 6 to 10°C, found at the Silesian-Cracow deposits, is "*unusual for MVT deposits and has been documented only in North America at the Nanisivik mine in Canada*" (Leach & Viets 1992).

3. Regional horizontal *Th* change, higher values in the south, lower in the north of the ore-mineralized area in the Silesian-Cracow region. Horizontal thermal gradients were suggested for the Illinois-Kentucky fluorspar district (Taylor & *al.* 1992), next discarded as a small-size local fluctuation near the cryptovolcanic Hicks Dome complex (Spry & Fuhrmann 1994). The figure, presented by Leach (1993, Fig. 3, p. 114), suggests lateral thermal gradient of 0.1°C per km for sphalerite from four principal MVT districts in the Ozark region *versus* the distance from the Ouachita foldbelt. However, the used *Th* values are modes and a mean, thus the values to which any natural importance can barely be bound.

4. Continuous presence of Na and Ca ions in fluid inclusions in MVT ores and variable Na/Ca ratios in inclusions in the Silesian-Cracow ores.

5. Inclusion fluids in the MVT ores yielded total salinity 10-30 wt. %, whereas the Silesian-Cracow ones from nil to *c.* 23 wt. %, what means distinctly lower values for the latter.

6. The MVT deposits have signs of activity of high-salinity connate waters (sometimes of two kinds) and low-salinity meteoric-water dominated fluids, mixed at various stages of minerals precipitation (Spry & Fuhrmann 1994). However, mineral precipitation occurred frequently without parent fluid mixing (Chesley & *al.* 1994). The Silesian-Cracow ores formed from fluid being a mixture of three components, two of them of low salinity and each of the two of different nature.

7. Both types of the ore deposits formed in the presence of liquid organic matter, though their types are different for each of them.

Another difference, not connected with fluid inclusion data, is related to the crystal habits at the Silesian-Cracow and MVT deposits. At the Silesian-Cracow deposits all main ore minerals (sphalerite, galena, pyrite and marcasite) occur commonly in cryptocrystalline, colloform or fibrous habits, indicating quick or even rapid discharge of ore-forming solutions. Only galena forms also large, centimeters-sized crystals. The cryptocrystalline and fibrous habits are distinctly rarer or even absent at the North American MVT deposits, as characterized by Roedder (1968b). Even the deposit of Nanisivik, Canada, that is considered as one of the most similar to the Silesian-Cracow deposits (Leach & Viets 1992), displays different mineral habits. It is the source of superb pyrite crystals up to 7 cm in size, sphalerite crystals achieving 3 cm, smoky quartz specimens up to 15 cm, 10 cm pyrrhotite, 12.5 cm marcasite twins, 4 cm galena crystals, etc. (Gait & *al.* 1990). Note, that the largest sphalerite crystal known from the investigated Silesian-Cracow region had *c.* 3 mm. Clearly more abundant are the ore mineral habits, indicating rapid parent solution discharge at the European deposits of Aachen district in Germany (Krahn & *al.* 1986), Wiesloch in Baden-Württemberg in Germany, and Bleiberg in Austria (Niedermayr 1986), Moresnet in Belgium, but not the deposit of the Belgian Bleiberg mine (Muchez & *al.* 1994). It is also worth noting, that the Irish Zn-Pb deposits hosted by Carboniferous carbonate sediments and displaying striking tectonic, mineralogical and genetic similarities to the Silesian-Cracow deposits (the present Author's observations) in the most recent literature are not compared to the MVT deposits (*see* Anderson & *al.* 1995b).

The above discussion indicates, that despite certain similarities, the including Silesian-Cracow deposits to the MVT is premature, because differences are great and genetically significant; the problem requires further studies, for instance in geochemistry of trace elements in ores and host rocks (*cf.* Qing & Mountjoy 1994).

CONCLUSIONS

Early Zn-Pb ores of the Chrzanów and Olkusz districts crystallized from aqueous liquid solutions at temperatures (*Th*) from 158 to 80°C. Hot solutions of low-to-moderate salinity were mobilized at depths by the folding Carpathians and they migrated from the Carpathian borders to the north and possibly northeast, and percolated to upper rock levels at least partly along fault zones. Thus, the source area of the most mobile, foreign component of the ore-forming solutions was in the south and at relatively significant depth. These ascending waters mixed gradually with saline, local formation waters, cooled, and these phenomena (mixing and cooling), resulted in discharge of the transported metals and precipitation of ores. At small depths there occurred mixing with the third component, *i.e.* descending meteoric waters (cool and of very low salinity). Thus, in the southern part and at deeper levels, the ores formed at higher temperatures, than in the norther part, where the origin temperature distinctly decreased. Vertical thermal gradient of the ore-forming fluids was 6-10°C per 100 m. Temperature of the ore-forming fluids was usually distinctly higher than temperature of wall rocks, thus they were cooled in short time. Cooling and mixing of solutions caused a quick or rapid precipitation of ore minerals. At deep levels ores precipitated in narrow temperature ranges of less than 10°C, whereas at shallow levels the precipitation temperature interval was 2 to 2.5 times larger.

Ore-forming solutions contained liquid organic matter dissolved and locally in form of emulsion of droplet suspension. Organic matter maintained sulfur in sulfide form and at least partly consumed oxygen, entering the discharge zone with meteoric waters.

Ore mineralization in part was syntectonic, and pressure of ore-forming solutions influenced the formation of fissures. Inflows of fluid to fissures could be either single or multiple, determining thus types of ore mineral sequences.

Solutions, mobilized by orogenic event, were essentially of sodic composition, and they were altered during their migration from south to the north to increasingly calcic, even to 80% of calcium chloride in the total salts dissolved, due to the fluid/rock interaction. Early sphalerite crystallized from essentially sodic or sodium-chloride-dominated solutions, late one-from solutions enriched in calcium.

Probably, the migration of fluids and main ore mineralization activity gradually declined shortly after extinction of the tectonic movements, connected with the Carpathians folding.

The proposed model shows some features common with the Mississippi Valley-type deposits, but it has also substantial differences. Thus, the Silesian-Cracow deposits should rather be considered as the carbonate-hosted epithermal type sulfide deposits of complex origin of ore-forming fluids.

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A. KOZŁOWSKI

GENEZA ŚLĄSKO-KRAKOWSKICH ZŁÓŻ CYNKU I OŁOWIU: MODEL OPARTY NA BADANIACH INKLUZJI FLUIDALNYCH

(Streszczenie)

Praca przedstawia wyniki badań inkluzji fluidalnych w najwcześniejszym sfalerycie z kruszców złóż cynku i ołowiu obszaru śląsko-krakowskiego (fig. 1-4 oraz pl. 1-4). Kruszce krystalizowały z ciekłych roztworów wodnych zawierających ciekłą substancję organiczną w postaci rozpuszczonej lub w postaci emulsji albo zawiesiny (fig. 5-7). Rozpoznano oraz rozważono cechy szczególne inkluzji pierwotnych i wtórnych, powstających z roztworów wodnych, zawierających substancję organiczną (fig. 8-12), wpływ położenia inkluzji w kryształach na ich cechy oraz przydatność badawczą (fig. 13), cechy inkluzji wtórnych w agregatach polikrystalicznych (fig. 14-16), zjawisko wtórnego napełnienia inkluzji (fig. 17-20) oraz przemian inkluzji w czasie rekrystalizacji skupień kruszców (fig. 21-22). Przedyskutowano zmiany temperatur homogenizacji inkluzji (*Th*) w obrębie wypełnienia szczelin przez kruszce (fig. 23).

Temperatury homogenizacji inkluzji zawarte są między 158 a 80°C, przy czym najwyższe wartości występują w południowej części obszaru, niższe o około 20°C — w części północnej. Pionowy gradient termalny roztworów macierzystych kruszców wynosił 6 do 10°C; na głębokościach około 200 m zakres temperatury krystalizacji jest wąski (do 10°), natomiast w pobliżu powierzchni Ziemi zwiększa się do 25°C (fig. 24-25).

Skład soli w roztworach macierzystych kruszców wahał się od sodowego, występującego głównie na południu omawianego obszaru, do wapniowo-sodowego, niekiedy z przewagą wapnia, częstszego na północy. Wydzielono trzy grupy roztworów w inkluzjach, charakteryzujących się następującymi cechami: (*1*) zasolenie niskie do umiarkowanego przy wysokich *Th*, (*2*) zasolenie wysokie przy umiarkowanych *Th*, (*3*) zasolenie niskie przy niskich do umiarkowanych *Th*. Wyrażono przypuszczenie, że grupy te odpowiadają roztworom ascensyjnym, solankom formacyjnym, oraz descensyjnym wodom meteorycznym, które ulegały mieszaniu w czasie tworzenia się kruszców (fig. 26-29). Omawianą zmienność składu roztworów zinterpretowano, łącznie z poziomym regionalnym zróżnicowaniem temperatur, jako dowód migracji roztworów z południa ku północy (fig. 30). Czynnikiem powodującym tę migrację mogło być fałdowanie i wypiętrzanie Karpat na południe od obszaru występowania złóż.

Złoża śląsko-krakowskie reprezentują zatem epitermalny typ siarczkowy, występujący w skałach węglanowych, o niejednorodnym źródle roztworów macierzystych kruszców. Porównanie tych złóż ze złożami typu Mississippi Valley na podstawie danych wynikających z badań inkluzji fluidalnych wskazuje, iż włączanie badanych złóż śląsko-krakowskich do wymienionego typu nie jest oparte na wystarczających przesłankach.