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Parent fluids of the zinc and lead ores from the Silesia-Cracow region

ABSTRACT: Fluid inclusions in sulfide minerals (sphalerite, wurtzite) of the zinc and lead ores from the Silesia-Cracow region, Southern Poland, bear water solution (brine) and liquid and gaseous hydrocarbons, probably extracted from wall rocks of ores. These ores have formed at temperature close to homogenization temperature of inclusions, ranging from 92 to 138°C.

INTRODUCTION

Ores of zinc and lead in the Silesia-Cracow region, Southern Poland*, essentially occur in weakly inclined or almost horizontal layers of Triassic dolostones cut by a series of faults. The ore-bearing dolostones sometimes are supposed to be of primary or synsedimentary metasomatic origin, but their secondary metasomatic formation is recently well documented (Bogacz, Dżułyński & Harańczyk 1970; Przeniosło 1976; Dżułyński & Sass-Gustkiewicz 1977, 1978; Pawłowska, Chidester & Wedow 1979).

The ores have very simple composition: they consist of galena, sphalerite plus wurtzite, pyrite and marcasite. Locally such sulfosalts are to be found, as jordanite, gratonite, rathite etc. Calcite, dolomite and rarely barite are the gangue minerals. The sequence of precipitation of ore minerals is very variable. The minerals most interesting for the inclusion studies, namely sphalerite and wurtzite, are fine-grained or colloform, with prismatic crystals some tenths of a millimeter in length. The

* The problem was discussed at the meeting of The Mineralogical Society of Poland, Cracow 1979, and at XIV Pacific Science Congress, Khabarovsk 1979.

sphalerite aggregates form encrustations, reniform masses, or they cement the fragments of wall dolostone.

Investigations of fluid inclusions in sphalerite, intending to obtain new data of genetic value, are very important for the recognition of origin both of the ores and of the wall dolostones. The essential problem appeared during searching of inclusions due to the extreme rarity of good inclusions in the studied sphalerite. Dark color of sphalerite, its high refractive index, small crystals of the host mineral, and minute size of fluid inclusions caused severe difficulties and needed some improvements of the homogenization technique. The authors used the immersion heating stage based mainly on the Sorby's (1858) construction and permitting for use of objectives 100× up to temperatures 300°C in silicon oil immersion (Karwowski, Kozłowski & Roedder 1979).

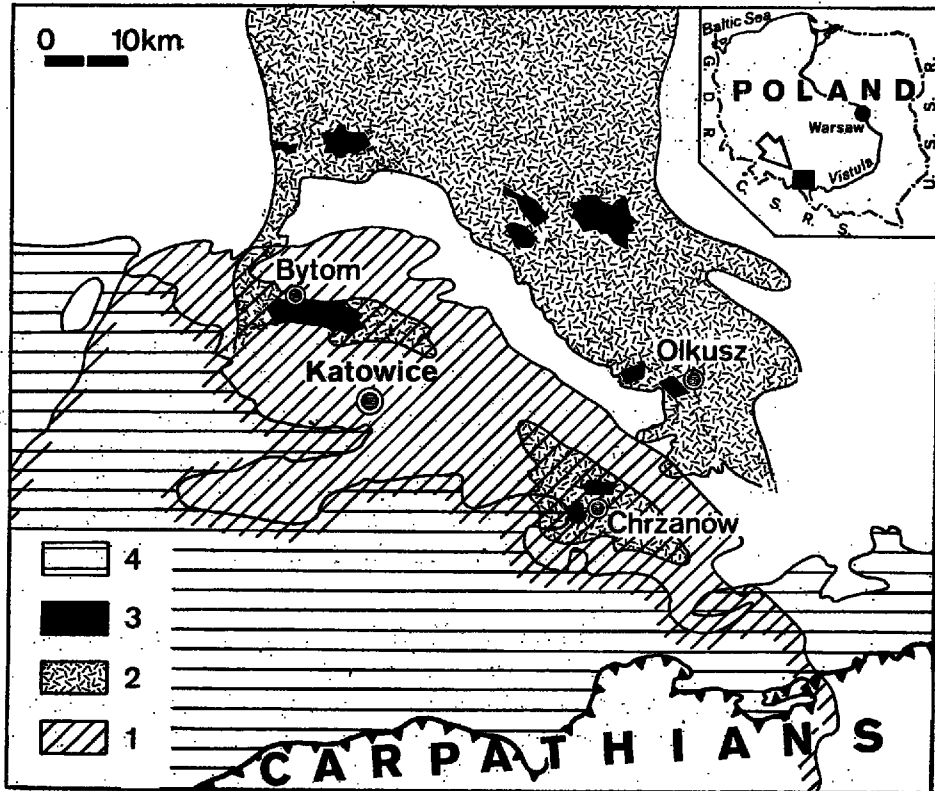
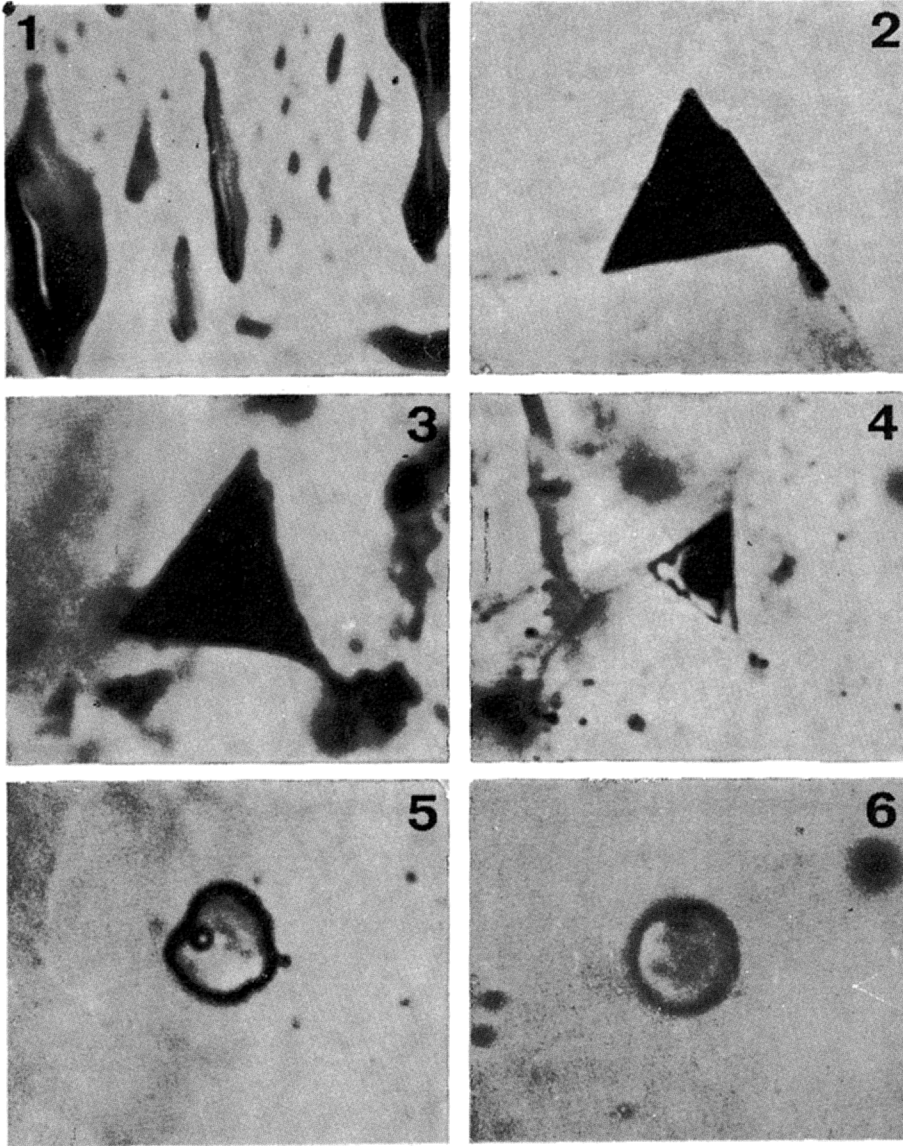


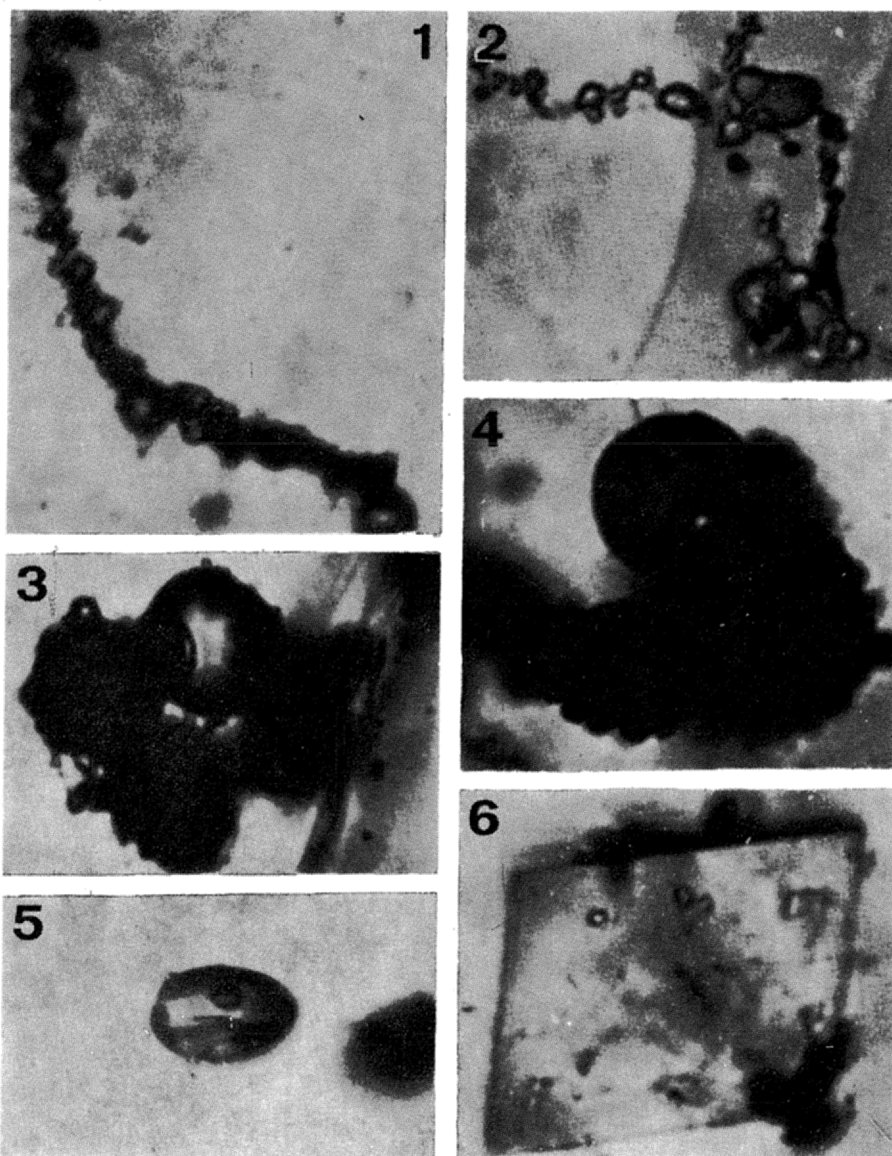
Fig. 1. Location of the Zn-Pb deposits in the Silesia-Cracow region (adopted from: Pawłowska & *al.* 1979)

1 — Variscan Upper Silesian Depression (coal basin), 2 — ore-bearing dolostones in Triassic carbonate beds, 3 — Zn-Pb deposits, 4 — Miocene sediments in the Fore-Carpathian Depression



- 1 — One-phase, most probably liquid aqueous inclusions
- 2 — Interstitial two-phase aqueous inclusion, almost completely opaque
- 3 — Tetrahedral, very dark two-phase aqueous inclusion
- 4 — Tetrahedral aqueous-organic inclusion
- 5 and 6 — Single two-phase inclusions of organic liquid and gas

All samples from Orzeł Biały mine, Bytom region, Upper Silesia; the micrographs are approximately 15 μm along their longer side



- 1 and 2 — Chains of inclusions of organic fluid; their arrangement is determined by crystal growth
- 3 and 4 — Inclusions of solid, liquid and gaseous organic matter: black — solid, dark translucent — liquid, black with light dot — gas
- 5 — Three-phase organic fluid inclusion, filled with liquid (light), organic solids (dark gray) and round gas bubble
- 6 — Carbonate crystal in sphalerite with adhering black inclusions of organic matter

All samples from Orzeł Biały mine, Bytom region, Upper Silesia; the micrographs are approximately 15 μm along their longer side, except. Fig. 6 which is about 50 μm

FLUID INCLUSIONS

The fluid inclusion studies were performed using specimens of zinc sulfides collected in three mining regions (Text-fig. 1): Bytom ("Orzel Biały", "Marchlewski" and "Waryński" mines), Chrzanów ("Trzebionka" mine) and Olkusz ("Olkusz" and "Bolesław" mines).

Seven varieties of fluid inclusions were distinguished in sphalerite. The varieties belong to two groups. Inclusions of water solutions are the first group of varieties, consisting of:

(i) One-phase inclusions found in sphalerite but most common in calcite; they are filled with almost fresh water, as indicated by freezing temperature very close to 0.0°C (Pl. 1, Fig. 1).

(ii) Two-phase primary gas-liquid inclusions, almost exclusively of tetrahedral habit, dark and almost opaque (Pl. 1, Figs 2—3); sometimes they are interstitial between sphalerite and/or wurtzite crystals.

(iii) Polyphase primary inclusions bearing gas, water, solution and daughter minerals still not determined but probably being halite.

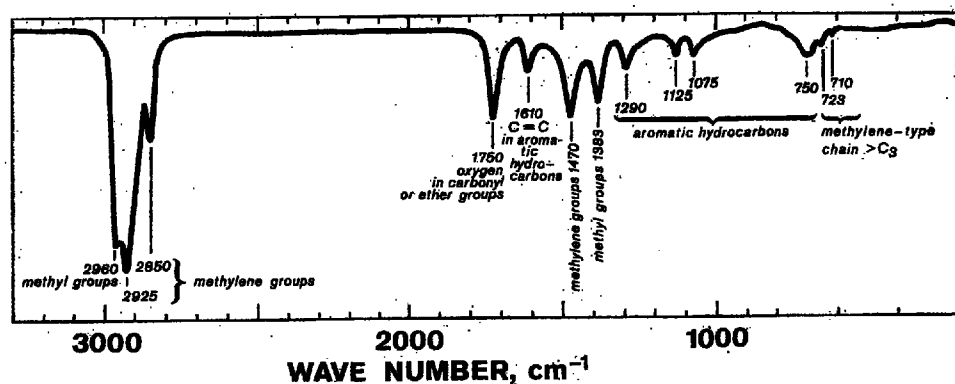


Fig. 2. IR absorption spectrum of organic matter extracted with chloroform from sphalerite: Orzel Biały mine, Bytom region, Upper Silesia.

The second group consists of varieties of inclusions filled by organic matter, sometimes with water phase present in:

(i) Two-phase primary inclusions of globular, oval or flat-round habit, bearing organic liquid and most probably hydrocarbon gas (Pl. 1, Figs 5—6 and Pl. 2, Figs 1—2).

(ii) Polyphase primary inclusions of the same shape and of the filling that contains liquid, gas and one or two probably organic daughter minerals; the latter occupy usually less than 10 volume percent of a vacuole (Pl. 2, Fig. 5).

(iii) Primary inclusions of reniform aggregates of acicular, seemingly organic crystals plus liquid and/or gas hydrocarbons. Crystals occupy big but undeterminable volume of the inclusion vacuole (Pl. 2, Figs 3—4). The organic substance inclusions are sometimes trapped together with carbonate crystals (Pl. 2, Fig. 6).

(iiii) Primary inclusions bearing water solution, organic liquid and/or organic solids, not homogenizing up to 300°C and being probably of heterogenic origin (Pl. 1, Fig. 4).

Organic substance was extracted with chloroform in the *Soxhlet* apparatus and analysed by means of IR absorption method (Text-fig. 2). The analysis yielded that organic substance consists of saturated hydrocarbons C_nH_{2n+2} with some admixture of hydrocarbon compounds bearing oxygen in their molecules, either in carbonyl or in ether group, plus minor content of aromatic compounds.

Homogenization temperatures have been obtained only for two-phase inclusions, both water and hydrocarbon variety (Karwowski, Kozłowski & Roedder 1979). They range from 92 to 138°C, and T_H of hydrocarbon inclusions rather are adjacent to the lower limit, whereas T_H of water ones are close to the upper limit. It is easy to understand for syngenetic pairs of inclusions, since pressure derived from the possible former thickness of overlying rocks, ranges seemingly from 60 to 120 bars. This pressure would require an addition of the pressure correction of 8–15°C to the homogenization temperature, assuming pure water inclusions, and about half of that value for inclusions of saline brines, as indicated by T of freezing of one of the water inclusions in sphalerite (the first melting point below -28.6°C, last ice crystal disappeared at -17.6°C hence salt concentration equals 22 wt.% of NaCl equivalent). As the compressibility of hydrocarbons is generally much greater than that of even pure water, the pressure corrections for hydrocarbon inclusions would be even greater than for water inclusions. Thus, the temperatures of trapping the couple of both kinds of inclusions may be the same. The above T_H data are in good agreement with the former estimations by Ermakov (up to 120°C, as quoted in Gałkiewicz 1965, 1967) and by Roedder (1976) as 100–120°C.

Water leachate method yielded that inclusions are filled with solutions of Cl-Na-K-Ca type (Karwowski, Kozłowski & Roedder 1979), sometimes with high content of HCO_3^- . Ions of fluorine, lithium, magnesium, barium, manganese and boron are common components. The composition of leachates suggests that parent solutions were saline brines strongly influenced by carbonate wall-rocks and assumingly mixed with magmatic hydrotherms.

FINAL REMARKS

The presence of organic matter in the parent fluids of the investigated ores is a special problem. The simplest and most probable explanation is that it was extracted by hot solution from wall limestones and dolostones. The data on phase composition of the inclusions like those presented above are usually interpreted as the evidence of migration of two-phase fluid. However, migration of two-phase fluid through pores

of rock or even along thin fractures is difficult for explanation, especially if to take into account the differences of adhesion, viscosity etc. of water solution and hydrocarbons. On the other hand, experiments performed by Price (1976) have shown that the solubility of hydrocarbons in hot brines is surprisingly high. It is of course possible, that the droplets of oil that are trapped in fluid inclusions represent precipitation of a new liquid hydrocarbon phase on slight cooling and/or pressure drop. Oil might precipitate from a one-phase solution that formerly became saturated with respect to hydrocarbons on its filtrating through rocks.

The possible chambers of heterogenisation of this one-phase water-hydrocarbon-salt solution were in fractures or zones of collapse breccias found commonly in the deposits (cf. Sass-Gustkiewicz 1974). At the same time they were also chambers of precipitation of a part of ores from brine of hydrothermal type. It is noteworthy, that the presence of hydrocarbons has another aspect in the mineral-forming process of the sulfide Zn-Pb ores. They displayed probably an important role to maintain the reducing conditions when ores have precipitated, supporting the sulfur activity in the S^{2-} ionic form.

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ROZTWORY MACIERZYSTE ŚLĄSKO-KRAKOWSKICH KRUSZCÓW CYNKU I OŁOWIU

(Streszczenie)

W minerałach siarczkowych cynku ze śląsko-krakowskich złóż Zn-Pb (fig. 1 stwierdzono występowanie inkluzji gazowo-ciekłych, będących relikdami roztworów mineralotwórczych. Obok inkluzji roztworów wodnych rozpowszechnione są inkluzje zawierające substancje węglowodorowe, tworzące jedną lub kilka faz organicznych (pl. 1—2). Analiza widma absorpcji w podczerwieni ekstraktów chloroformowych ze sfalerytu (fig. 2) dowodzi, że substancja organiczna zawarta w inkluzjach ma głównie skład węglowodorów nasyconych z domieszką węglowodorów aromatycznych i związków z tlenem w postaci grup eterowych lub karbonylowych. Na podstawie temperatur homogenizacji inkluzji można przyjąć, że krystalizacja kruszców przebiegała w temperaturach 90—140°C, natomiast skład roztworów macierzystych kruszców, oznaczony metodą ekstrakcji zawartości inkluzji wodą, można określić jako chlorkowo-wodorowęglanowo-sodowo-potasowo-wapniowy, przy obecności także jonów F, Li, Mg, Ba, Mn, oraz B. W konsekwencji uznać należy, iż gorące roztwory pochodzenia magmowego oddziaływały na skały ościenne, ługując z nich związki organiczne, które były dalej transportowane prawdopodobnie w postaci roztworu właściwego, ulegającego heterogenizacji, tj. wydzieleniu subtelných kropli węglowodorów przy spadku temperatury lub ciśnienia.