Sulfur isotope models of genesis of the Silesian–Cracow Zn–Pb ore deposits

A new classification of genetic models of the Zn–Pb ore bodies of the Silesian–Cracow deposits have been introduced, using sulfur isotope composition as the criterion. Following models were distinguished: 1) mesothermal model, one solution with reduced sulfur; it explains formations of ore lodes; 2) cascade model, one solution, sulfate reduction with organic matter; it explains formation of the hydrothermal karst crustification ores; 3) infiltration model, percolation mixing of two solutions; it explains speleothems formation; 4) conflux model, two solutions mixing upon the confluent flowing; it explains brunckite formation.

INTRODUCTION

Stable isotope studies of sulfur in correlation with geologic informations have provided substantial evidence for different genetic processes controlling formation of particular sulfide generations during intermittently developed hydrothermal activity in Mesozoic and Tertiary times. Previous papers described isotope composition of the crustification ores (K. von Gehlen, H. Nielsen, 1969), brunckite (C. Harańczyk, 1972), crustification ores hosted in the hydrothermal karst caves (C. Harańczyk, J. Lis, 1973b), sphalerite associated with dolomitization (C. Harańczyk, 1973). Correlation of the sulfur isotope ratio and ontogenetic features of the ores were described by C. Harańczyk and J. Lis (1973a). First summaries were presented by C. Harańczyk (1974, 1989). In this summary paper, some new results concerning root veins and stalactite ores are added (the same methods were applied as in former investigations) and J. Lis was also the analyst but the primary purpose of this paper is a first attempt to model...
the isotopic fractionation processes influence on formation of the main ores in the Silesian-Cracow Zn-Pb ore deposits.

GEOLOGICAL SETTING

The Silesian-Cracow Zn-Pb ore deposits are the largest stratabound ores of the Mississippi Valley-type. The proved economic Zn-Pb ores are confined to the Middle Triassic Muschelkalk Formation as well as Younger Paleozoic Givetian and Dinantian carbonate beds. The Upper Silesian ore deposits were exploited by the mines located in the Bytom Trough. Also the Trzebionka mine actually exploits ores in another trough of the marginal part of the Upper Silesian Coal Basin. The Cracow ore deposits are localized further eastward, in the zone between Silesian Block and the Zawiercie-Rzeszoty suture dislocation, bordering the uplifted blocks of the Caledonian transpressive origin i.e. Boleslaw, Pomorzany and Olkusz mines. Along this dislocation, adjoining from east side, there are several middle size Zn-Pb ore deposits with proved reserves, however, they have not been put into operation localized in Zawiercie, Rakotino Szlachecie, Rodak, Chechlo and Klucze (C. Haranczyk, 1988a). Save Zawiercie, the Zn-Pb ores are mainly hosted there in Devonian carbonates. Within the Upper Silesian Block, the ore bodies in the Mesozoic beds are underlain by a few thousand meters thick Carboniferous formation with coal measures. Outside this block, the Mesozoic strata are underlain by a few hundreds meters thick series of the Lower Permian conglomerates and 2000-3000 m thick Givetian to Namurian A carbonate sequence (C. Haranczyk, 1979). Beneath it, the Emsian sandstones are underlain by a Caledonian molassa which rests unconformably upon the folded Cambrian to Silurian metasediments, up to 15 000 m thick. The ore deposits hosted in Mesozoic carbonate beds, lying above the discordance were protected from oxidation during their formation by a screen of impermeable clayey Keuper beds.

ISOTOPE MODELLING

In the investigated ore deposits, several different morphological types can be distinguished, each bearing distinct spatial relationship to a supposed dislocation which served as a feeding way, and usually one morphological type include ores of one dominant generation.

On the other hand, the ore minerals of the Silesian-Cracow Zn-Pb ore deposits may be divided into two groups; one enriched in heavy sulfur and another enriched in light sulfur. This contrasting tendency is correlated with regional Silesian-Cracow Zn-Pb zoning which seems to elucidate many regularities of distribution of the ore generations; and may be used as a base for isotope modelling. General outline of such models is presented beneath.
Table 1

Crustification and stalactite ores (Pomorzany mine)

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sulfur form</th>
<th>$\delta^{34}S$ %o</th>
</tr>
</thead>
<tbody>
<tr>
<td>79-103</td>
<td>crustification</td>
<td>-15.70</td>
</tr>
<tr>
<td>79-104</td>
<td>stalactite</td>
<td>-37.47</td>
</tr>
<tr>
<td>79-106</td>
<td>crustification</td>
<td>-6.45</td>
</tr>
<tr>
<td>79-107</td>
<td>stalactite</td>
<td>-25.60</td>
</tr>
<tr>
<td>79-108</td>
<td>crustification</td>
<td>-4.56</td>
</tr>
<tr>
<td>79-109</td>
<td>stalactite</td>
<td>-32.83</td>
</tr>
<tr>
<td>79-110</td>
<td>crustification</td>
<td>-10.95</td>
</tr>
<tr>
<td>79-111</td>
<td>stalactite</td>
<td>-17.67</td>
</tr>
<tr>
<td>79-112</td>
<td>stalactite</td>
<td>-6.00</td>
</tr>
<tr>
<td>79-113</td>
<td>stalactite</td>
<td>-28.39</td>
</tr>
</tbody>
</table>

Mesothermal Model

Mesothermal ore deposits include ores which bear some features indicating higher temperature of origin and show more aggressive morphological forms than the remaining ores. The sphalerite ores, disseminated in the ore-bearing dolomite and closely associated with dolomitization, occur in many ore bodies (C. Harańczyk, 1973). They have one model sulfur isotope composition similar to troilite sulfur.

The same isotope composition has almost pure sphalerite ore I ZnS contributing to massive ore bodies more than 20 m thick. This ore was directly sent without dressing to a smelter (F. Wernicke, 1931). These massive zinc-sulfide ore bodies were localized on the axis of the Bytom Trough and was exploited by Cecylia mine. The museum samples indicate standard troilite sulfur isotope composition. Also pure galena are forming lodes, more than 1 m thick, is spreading at the bottom of the ore-bearing dolomite in the Bytom Trough under the Bytom City. This galena ore was exploited in the last century. A similar lode of pure galena, more than 1 m thick, was exploited in the eastern part of the Trzebionka mine. Galena was rich in silver and did not show cubic cleavage.

Sulfur in the hydrothermal system may origin from two sources, namely magmatic (mantle) and marine basins (H. Ohmoto, R. O. Rye, 1979), that means, it is extracted from magmatic rocks or is reduced from sea water sulfates. In low temperatures (less than 80°C) reduction of sulfate may proceed by the help of bacteria. Such an environment is characteristic for hydrothermal karst caves in phreatic conditions, where temperature oscillates about 100°C (L. Karwowski et al., 1979). However, in the above mentioned massive ore bodies the metasomatic processes proceeded in higher temperature, probably in the mesothermal conditions. In temperature above 250°C, in thermodynamic equilibrium, $SO_4^{2-}$ is enriched in $\delta^{34}S$ in relation $H_2S$ 70%o.

Measurement of equilibrium pairs from Trzebionka mine gave $\Delta ZnS- PbS = 3%o$, indicating temperature ca. 300°C. We may assume after H. Ohmoto (1986) that ZnS and PbS are precipitated by simple reaction:
where: \( n \) — divalent metals.  

Sulfates (barite) have their \( \delta^{34}S \) values very close to those of aqueous sulfate.

**CASCADE MODEL**

The Mesozoic ores, including sulfur considerably enriched in heavy isotopes, are forming crustifications lining dolomite fragments of the collapse breccia, filling hydrothermal karst caves in the Bytom Trough and especially in its western part (Nowy Dwór mine). Most heavy sulfur occur in pyrite forming later bands of crustification, namely \( \delta^{34}S = +67\% \) (K. von Gehlen, H. Nielsen, 1969) and +49\% (C. Haranęcz, J. Lis, 1973a), and Schalenblende, respectively \( \delta^{34}S = +54\% \) (K. von Gehlen, H. Nielsen, 1969). The crustification ores formed in well isolated hydrothermal caves in the central and eastern part of the Bytom Trough (J. Marchlewski and Orzel Biały mines), show progressive enrichment in \( \delta^{34}S \) values successive bands, however, the extremal values were not reached (C. Haranęcz, J. Lis, 1973b). Such progressive enrichment in the successive bands was observed by K. von Gehlen and H. Nielsen (1969) in crustification ores in Wiesloch and Aachen ore deposits. The enrichment in heavy sulfur isotopes is a well investigated thermodynamic effect in a closed system (J. W. S. Rayleigh, 1896). It is applied to enrichment in heavy sulfur isotopes, proceeding during reduction of sulfates (J. Hoefs, 1987). Below 80°C the reduction of the sulfates may proceed due to presence of an organic matter. The precipitated sulfide is richer ca. 20\% in lighter sulfur, however, the remaining solutions are gradually depleted of light sulfur isotopes and in a closed system it becomes enriched in heavy isotopes (Fig. 1). The cascade enrichment requires a strictly closed system, what is also a condition *sine qua non* of virtually hydrothermal karst system. Therefore, it is not observed in the crustification ores of the Paleozoic karst caves (normal karst) Rokitno Szlacheč-
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Table 2

Stalactite ores (Trzebionka mine)

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Structure</th>
<th>δ²⁹S %o</th>
</tr>
</thead>
<tbody>
<tr>
<td>75-12</td>
<td>ZnS stalactite</td>
<td>+3.40</td>
</tr>
<tr>
<td>75-13</td>
<td>PbS lining on the stalactite</td>
<td>-2.90</td>
</tr>
<tr>
<td>80-123</td>
<td>ZnS stalactite</td>
<td>+2.03</td>
</tr>
</tbody>
</table>

kie, Rodaki, Chechlo and Klucze ore deposits. These karst caves were formed in the uplifted and outcropping blocks of Devonian carbonate rocks, and then these blocks were dropped down and visited by hydrothermal mineralizing solutions. The lower part of the caves are filled with clastic sediments of surficial origin and then covered by floor of sulfides, and finally, walls and collapse breccia in the upper part of the caves are lined with crustification ores.

Some slight enrichment in heavy sulfur isotopes was observed in the ores, even in the ore stalactites (Table 2) from the Trzebionka and Matylda mines, located within the block of the Upper Silesian Coal Basin where the screen of the Keuper impermeable clayey beds is thick enough (a few ten meters) and well preserved.

Comparing the occurrences of the ores with heavy sulfur and features and differences of the karst open spaces one may draw a conclusion that an enrichment in heavy sulfur isotopes is a good indicator of not disturbed hydrothermal karst environment.

INFILTRATION MODEL

The ore deposits, hosted in carbonate platform cover above an unconformity, are always subjected to infiltration of downward percolating meteoric waters, if they are not protected by a screen of the impermeable clayey rocks. The Keuper siltstones form such a screen in the Silesian-Cracow ore deposits. The main difference between the ores of Upper Silesian and Cracow Zone and genesis of the ores hosted in the caves of the hydrothermal karst in the ore-bearing dolomite is based on the fact that in the first zone the ore deposits have been protected during their origin and until now by such a screen (save Dąbrówka mine in the eastern part of the Bytom Trough and eastern part of Trzebionka mine). On the contrary, in the Cracow Zone all ore deposits are partly weathered or even during formation of younger ore generations were formed in a system not completely closed. They were formed by interaction of hydrotherms and some percolating down meteoritic water. Presence of the stalactite ores is the best prove of downward infiltration. The stalactite ores are well known from upper levels in all existing mines.

The differences of sulfur isotope composition of the crustification ores formed in phreatic environment and stalactite ores formed in vadie conditions, in the same
hydrothermal karst caves, provide good evidence of isotope fractionation upon infiltration by percolation down of solutions which mix with the true hydrotherms.

The intergeneration break of the hydrothermal activity induced not only increased share of the infiltration waters in the ore bodies, but the outlets of main feeding ways on the palcosurface were opened for the integrated pouring in of the meteoric water. An intensive weathering of the previously formed crustification ores were described by present author (C. Haranczyk, J. Lis, 1973b). This weathering is anticipating formation of the brunckite masses in the Olkusz mine.

Due to post-Jurassic tectonic events and especially Laramide tectonic phase, this screen was partly destroyed in much of the discussed area. The intergeneration oxidation of ore bodies went along the feeding ways, down to the hydrothermal karst caves, lined with dolomitic crustification in the Devonian carbonate beds, introducing cementation sulfides (borehole Boleslaw I, depth 740-760 m). Presence of bottom caves of the hydrothermal karst system, lined only with hydrothermal dolomite crustifications, suggests that most sulfur stemmed from infiltration solutions (C. Haranczyk, 1989).

The infiltration model was again put into operation when the conflux generation of ores was completed. The infiltration has induced transformation of the colloform masses. This is brilliantly seen in the large vertical ore body intersecting whole Triassic sequence in the former Ulisses mine, also called ore body near the 71 shaft of the Bolesław mine, described by C. Kuźniar (1928) and F. Ekiert (fide M. Nieć, 1980). Some results of the sulfur isotope composition of the internal segregation stalactites, including galena and brunckite, are presented in Table 3. They display the same trend of enrichment in light sulfur.

### Table 3

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Structure</th>
<th>$\delta^{34}S$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>80-118</td>
<td>ZnS, brunckite stalactite</td>
<td>-15.92</td>
</tr>
<tr>
<td>80-119</td>
<td>ZnS, brunckite stalactite</td>
<td>-18.75</td>
</tr>
<tr>
<td>80-120</td>
<td>PbS stalactite, outer lining</td>
<td>-17.80</td>
</tr>
<tr>
<td>80-121</td>
<td>ZnS stalactite, outer lining (Carol shaft)</td>
<td>-15.16</td>
</tr>
<tr>
<td>80-124</td>
<td>ZnS calcites (Carol shaft)</td>
<td>-18.11</td>
</tr>
<tr>
<td>80-122</td>
<td>FeS$_2$ stalactite</td>
<td>-23.75</td>
</tr>
<tr>
<td>80-125</td>
<td>FeS$_2$ karst flowers</td>
<td>-20.13</td>
</tr>
</tbody>
</table>

**CONFLUX MODEL**

White, pulverulent, cryptocrystalline variety of zinc sulfide (brunckite), showing sedimentary features indicating colloidal transport phenomena (C. Haranczyk, 1972),
Sulfur isotope models of the genesis of the Silesian-Cracow

Table 4
Brunckite ores (Olkusz mine, Level 278)

<table>
<thead>
<tr>
<th>Structure</th>
<th>( \delta^{34}S ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical vein, white pure brunckite</td>
<td>-29.4</td>
</tr>
<tr>
<td>Vertical vein, white pure brunckite</td>
<td>-28.0</td>
</tr>
<tr>
<td>Vertical vein, white pure brunckite</td>
<td>-29.4</td>
</tr>
<tr>
<td>Vertical vein, white pure brunckite</td>
<td>-27.3</td>
</tr>
<tr>
<td>Vertical vein, white pure brunckite</td>
<td>-28.5</td>
</tr>
<tr>
<td>Brunckite nest</td>
<td>-28.6</td>
</tr>
<tr>
<td>Brunckite nest</td>
<td>-28.4</td>
</tr>
<tr>
<td>Fault fissure, white brunckite</td>
<td>-29.0</td>
</tr>
</tbody>
</table>

Brunckite is best fitting the conflux model. It fills the upper part of the hydrothermal karst caves and is usually overlain by partly weathered crustification ores (C. Harančzyk, 1988c). Scanning microscope investigations revealed structure of loose 1-15 \( \mu \)m euhedral crystals of spalerite. The brunckite ores occur in youngest ore bodies, distributed in a zone extending from the Bolesław mine to the Olkusz mine. The most frequent morphological types are caves in ore-bearing dolomite, vertical pocket veins in Gogolin Limestones (C. Harančzyk, 1972) as well as empty spaces in fault fractures (C. Harančzyk, 1988c), completely or partly filled with pulverulent brunckite. In the caves surrounding the central cave, filled by brunckite, the contemporaneous zinc sulfides form betroidal, frambooidal, oolithic and ooidic ores while the crustification ores occur in the further located caves (C. Harančzyk, 1979, Plate III, Fig. 2). More details concerning the genesis of brunckite are in the paper of C. Harančzyk (1988b).

The previously carried out investigations showed a monomodal sulfur isotope composition \( \delta^{34}S = -30% \) (C. Harančzyk, 1972). The investigations using scanning microscope precluded clastic origin of the brunckite grains, suggesting two mineralization solutions model of genesis (C. Harančzyk, 1988c, 1989). The brunckite precipitated along the confluent way of migration of the descending solutions, transporting sulfur of composition \( \delta^{34}S = -5% \) from the oxidation zone of earlier generation of sulfides and of the solutions which ascended bringing new portions of heavy metals (C. Harančzyk, 1988b).

The unique, transformed colloform ores, occurring in the vertical karst cave near the 71 shaft of the Bolesław mine, were described in the chapter on infiltration model of genesis, as they were formed in a complex history with conflux and infiltration stages. Sulfur isotope composition may be compared with pure brunckite presented in Table 4.

ROOT VEINS

In the discussed area, the large ore deposits with proved reserves are confined, probably due to paleohydrogeological situation, to carbonate beds lying above an
unconformity, that means to the Middle Triassic sequence of the Muschelkalk formation in the Upper Silesian zone and Triassic and Devonian carbonate beds in the Cracow zone, where the Young Paleozoic rocks contribute to the epi-Caledonian cover. However, as a root vein we regard all veins beneath the main ore horizon. Therefore, in the Silesian zone, all the veins intersected by coal mine stopes were regarded by K. Kossmann (1884) as root veins. In the Cracow zone Cambrian to Silurian sequences belong to the real basement, and Devonian and Carboniferous carbonate sequences to the epi-Caledonian cover. We must remind that the zoning in the root veins described by C. Haraniezyk (1963) proved that rapid evolution of mineralizing solutions in Triassic horizon caused mass precipitation of ores showing colloform features.

Fig. 2. Sulfur isotopes in ores from Silesian-Cracow ore deposits; first level — Paleozoic mineralization—pyrite from skarn and porphyry Cu-Mo deposits; second level — Zn-Pb ores

Another strange root vein, intersecting outcropping Ordovician metasediments, were presented by present author in the Proceedings of the Tbilisi IAGOD Symposium, Fig. 3 (C. Haraniezyk, 1984). It is so far the first photo of the outlet of a vent of the paleo-smokers introducing mineralizing solutions to the Triassic sea in the Zawierec area. However, the crustification on the sea bottom surface, deposited by this smokers, is consisting of a clayely sediments. The vent continuation of the smoker as a root vein is filled with marcasite and pyrite.
Numerous typical root veins, recently intersected by boreholes drilled down to the depth of 1500 m, are characterized as follows. They are mostly vertically (80–90°) dipping. The vein fissures are opened by strike-slip dislocations what is evidenced by horizontal tectoglyphs. Two photos of such veins with Mesozoic Zn-Pb mineralization are also presented (Figs. 5, 6) in the same paper of the Tbilisi IAGOD Symposium. Frequently, our root veins intersect older veins of the Paleozoic ore formations (C. Harańczyk, 1983). The following main vein formations of the Mesozoic and Tertiary mineralization may be distinguished:

- ankerite-sphalerite-galena;
- crustification ores Schalenblende and melnikovite-pyrite shell;
- barite-sphalerite-galena;
- blue anhydrite-marcasite.

It is interesting that the root veins have the same thickness when intersecting Ordovician clastic metasediments and marbles what indicates that not lithologic control but paleohydrogeologic control is the main factor of deposition (Pl. I, Fig. 3, Pl. II, Fig. 4). Moreover, the formation of the crustification ores (especially of melnikovite-pyrite — depends on composition of solution, what is also evidenced by the sulfur isotope composition; Table 5) admitedly colloform interpretations were expressed (F. Wernicke, 1931). The melnikovite-pyrite of the Silesian-Cracow and similar ore deposits should be regarded, as suggested P. Ramdohr (1975), as mineralogical species.

**CONCLUSIONS**

The analysis of the inhomogenous and widely distributed population of determination of sulfur isotope results, determination composition, suggests heterogenic origin and different model explanation of the particular generation of ores.
Crustification ores in the hydrothermal karst caves show heavy sulfur, suggesting westward migration of mineralizing solution in the Bytom Trough. Massive sphalerite and galena ores display troilitic type of sulfur isotope composition, and isotope geotemnometry suggests mesothermal conditions of their genesis (single mineralizing solutions) while other ores were formed by two solutions model.

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**REFERENCES**


Sulfur isotope models of genesis of the Silesian-Cracow...


Czesław HARANČZYK

IZOTOPOWE MODELE GENEZY ŚLĄSKO-KRAKOWSKICH ZŁÓŻ RUD Zn-Pb (IZOTOPY SIARKI)

Streszczenie

Przedłożono nową klasyfikację modeli genetycznych ciał rudnych śląsko-krakowskich złóż Zn-Pb, stosując jako kryterium skład izotopowy siarki. Wyróżniono: 1) model mezotermalny, jednoroztwórowy; 2) model kaskadowy, jednoroztwórowy, kruś hydroteermalnego; 3) model infiltracyjny, dwurozdrowowy, rozwoju utworów speleothemowych; 4) model przepływu zespółonego i mieszanina dwóch roztworów: hydroteermalnego i powierzchniowego.
PLATE I

Fig. 3. Polished section of a fragment of the vein from the root zone of Zn–Pb deposits. The vein is ca. 2.2 m wide. It was formed in a reopened strike-slip fault in Silurian strata, and infilled with crustifications of rouge barite, white calcite (Cc), marcasite (Ms) with traces of chalcopyrite, galena (Ga), Schalenblende (Sph) and anomalous pyrite (Py) — melnikovite-pyrite according to P. Ramdohr (1975) terminology. Zawiercie, borehole RK 1, depth 1086.0 m, the core is 85 mm wide.
Fig. 3

Czesław HARAŃCZYK — Sulfur isotope models of genesis of the Silesian–Cracow Zn–Pb ore deposits
PLATE II

Fig. 4. Polished section of the vein from the root zone of the Zn-Pb deposits. The vertically dipping multicrustification vein intersecting Ordovician marbles. The crustification include bands of barite (Ba), dolomite (D), galena (Ga), marcasite (Ms), calcite with druses (Cc) and empty spaces. Zawiercie, borehole RK 1, depth 1190.8 m, magn. x 2, diameter of the core 65 mm.

Powierzchnia polkrowna żyły ze strefy korzeniowej złóż Zn-Pb. Pionowo zapadająca wielokrustykacyjna żyła przecina marmury ordowiku. Krystykacje zawierają baryt (Ba), dolomit (D), galenę (Ga), markasyt (Ms), kafel druzowy (Cc) powłoka puszek żyły. Zawiercie, otwór wiercenia RK 1, głęb. 1190,8 m, pow. 2 x, średnica rdzenia około 65 mm.
Fig. 4

Czeslaw HARAŃCZYK — Sulfur isotope models of genesis of the Silesian-Cracow Zn-Pb ore deposits