

## ORIGIN OF THE CRACOVIAN-SILESIA Zn-Pb DEPOSITS

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**Abstract:** Previous work has shown that most of the mineralization occurs as metasomatic replacement of hydrothermal dolomite, and as cavity-filling in hydrothermal karst breccias. It was emplaced along a paleoaquifer within the Muschelkalk mainly during Early Cimmerian movements. Available geological and geochemical data suggest that the hydrothermal fluids were episodically expelled from the Upper Silesian coal basin as a result of fluid overpressure generated during burial and diagenesis. Initially the fluids were buffered by quartz-illite-K feldspar, and aqueous carbonate-methane equilibria. During hydrothermal karst formation and ore deposition they became more oxidizing and acid, probably as a result of mixing with near surface waters and the generation of hydrogen ions by oxidation of methane. The zinc and lead could not have been transported as chloride or bisulphide complexes, but may have been transported as organometallic complexes.

**Key words:** Zn-Pb ores, Mississippi Valley-type, Cracovian-Silesian area, fluid emplacement, fluid provenance, metal transport, metal deposition.

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### INTRODUCTION

The Cracovian-Silesian zinc-lead ore deposits lie to the northwest of Cracow, near the northeastern boundary of the Upper Silesian basin (Fig. 1). They are largely stratabound ores of the Mississippi Valley-type (Harańczyk, 1979; Sass-Gustkiewicz *et al.*, 1982; Dżułyński & Sass-Gustkiewicz, 1985) which are mainly confined to the Middle Triassic Muschelkalk Formation. Opinion regarding the origin of these deposits is divided. One group of workers including Keil (1956), Gruszczyk (1967, 1978), Smolarska (1968), Zartman *et al.* (1979) and Pawłowska & Wedow (1980) favour a synsedimentary origin with varying degrees of diagenetic modification. The other more numerous group represented by Duwensee (1943), Seidl (1960, 1961, 1962), Harańczyk (1963), Śliwiński (1964), Bogacz *et al.* (1970, 1975), Gałkiewicz (1978), Harańczyk (1979), Rózkowski *et al.* (1979), Karwowski *et al.* (1979), Mochnacka & Sass-Gustkiewicz (1981), Sass-Gustkiewicz *et al.* (1982), Harańczyk (1983, 1984) and Dżułyński & Sass-Gustkiewicz (1985) favour an epi-

genetic origin whereby hydrothermal fluids originated at depth. In recent years detailed field observations of Bogacz *et al.* (1970, 1972, 1973, 1975), Sass-Gustkiewicz (1975), Mochnacka & Sass-Gustkiewicz (1981), Sass-Gustkiewicz *et al.* (1982)

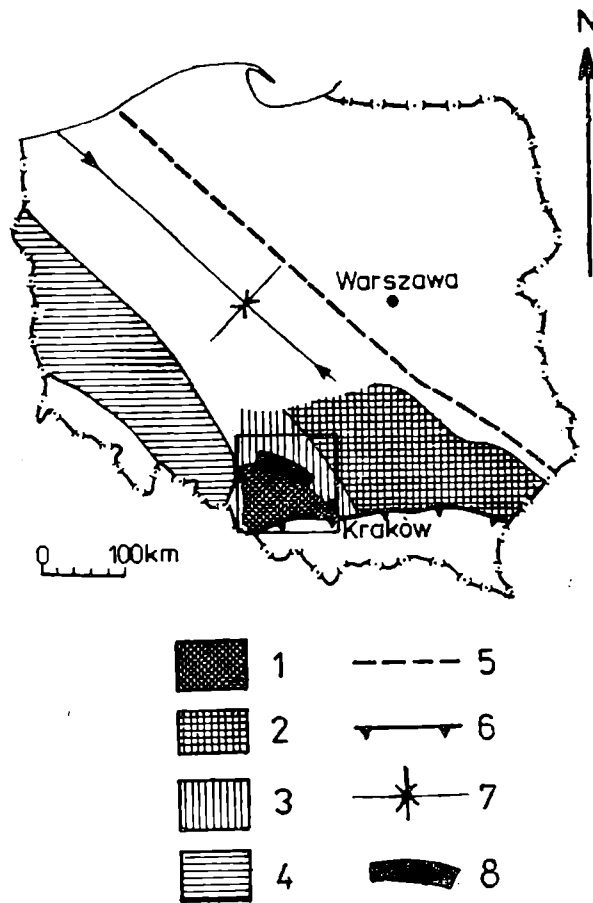


Fig. 1. Tectonic sketch map of southern Poland (modified after Harańczyk, 1979). 1 – Upper Silesian massif; 2 – Małopolska massif; 3 – Caledonian Cracovian orogen; 4 – Variscan orogen; 5 – Tornquist-Teisseyre line; 6 – Carpathian front; 7 – axis of Polish trough; 8 – Cracovian-Silesian Zn–Pb district; the area in rectangle enlarged in Figs 2 and 3

and Dżułyński & Sass-Gustkiewicz (1982, 1985) have demonstrated that the dominant ore-forming processes were metasomatic replacement of carbonate rocks and filling of open spaces generated during hydrothermal karst formation. Furthermore, fluid inclusion studies of Karwowski *et al.* (1979) have demonstrated that the fluids responsible for ore deposition were hot saline brines. Thus, the evidence for a hydrothermal origin of most of the ores is overwhelming, and in this paper it is accepted that the bulk of the known Cracovian-Silesian deposits are epigenetic, and that they were emplaced by hydrothermal processes.

In the following discussion available stratigraphic, tectonic mineralogical, geochemical and hydrogeological data concerning the Cracovian-Silesian area are summarized and interpreted. On this basis an attempt is made to answer the

following questions: What was the source of the hydrothermal fluids? What caused their emplacement into the ore-bearing strata? What were the physical and chemical conditions during metal transport and deposition? Answers to these questions are important because they will lead to a more complete understanding of ore genesis, and allow predictions to be made regarding location of favourable environments for ore deposition.

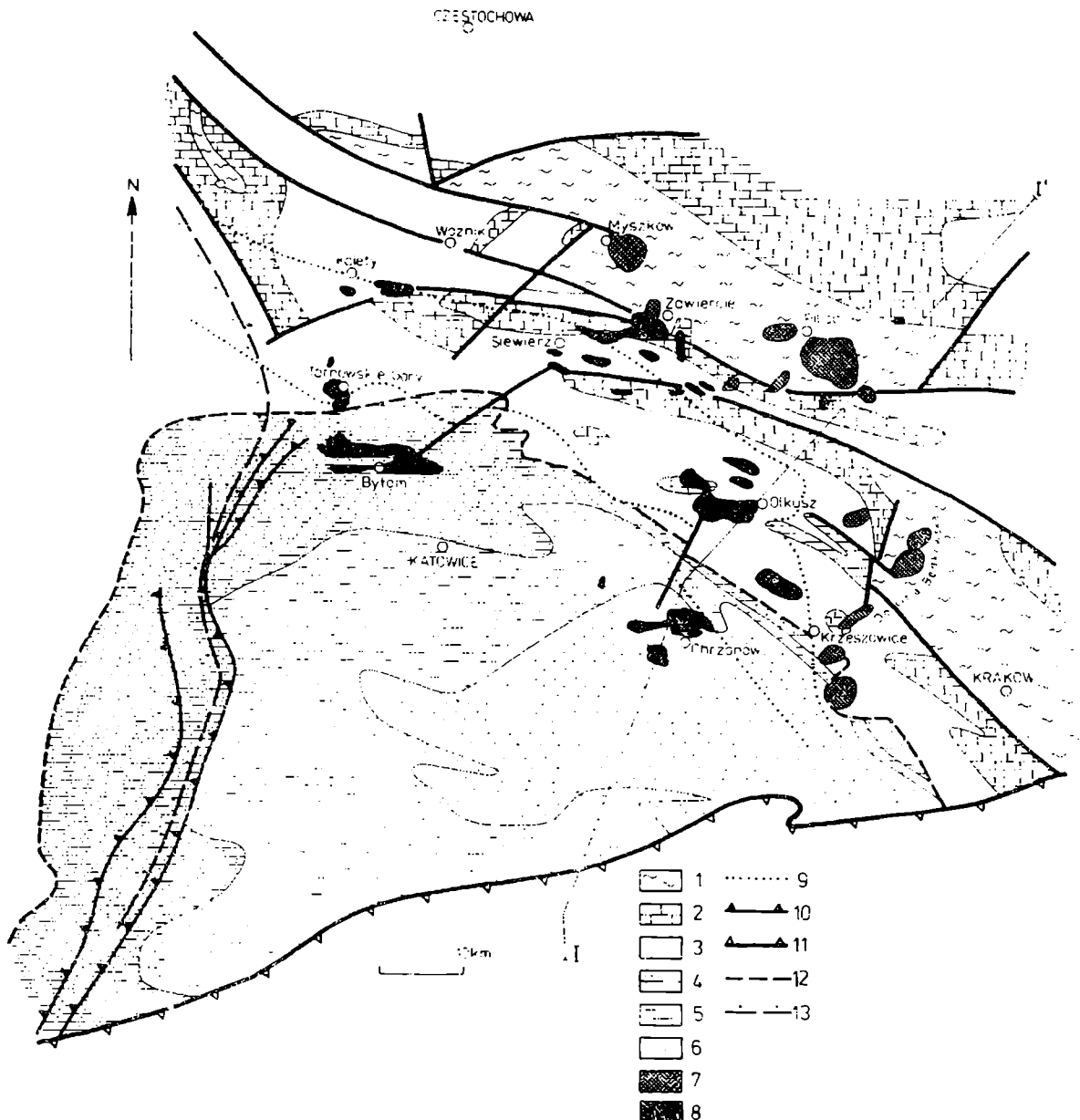


Fig. 2. Pre-Permian geology map of Cracovian-Silesian region (modified after Pożaryski & Dembowski, 1984). 1 - Proterozoic and Lower Paleozoic rocks metamorphosed during Caledonian orogeny; 2 - Devonian, mainly carbonates; 3 - Lower Carboniferous carbonates, shales, sandstones; 4 - Namurian sandstones and mudstones; 5 - Westphalian, mainly mudstones; 6 - Westphalian mainly sandstones; 7 - Caledonian and Variscan intrusives; 8 - Zn-Pb mineralization of Cracovian-Silesian ore district; 9 - boundary of Permian tectonic graben (after Harańczyk, 1979); 10 - Variscan thrust faults; 11 - Carpathian front; 12 - boundary of Upper Silesian basin; 13 - limit of strong Variscan deformation

## GEOLOGICAL SETTING

The Cracovian-Silesian ore deposits are located near the boundary between the Upper Silesian basin and the Caledonide Cracow-Myszków zone (Fig. 1). The Caledonides lie between the Upper Silesian massif of Precambrian consolidation, and the Małopolska massif of Early Caledonian consolidation (Harańczyk, 1979; Pożaryski, 1984). These massifs may represent microcontinents (Harańczyk, 1982) that accreted onto the East European plate during the Caledonian. The pre-Mesozoic geology and the pre-Cretaceous geology of the Upper Silesian basin and the

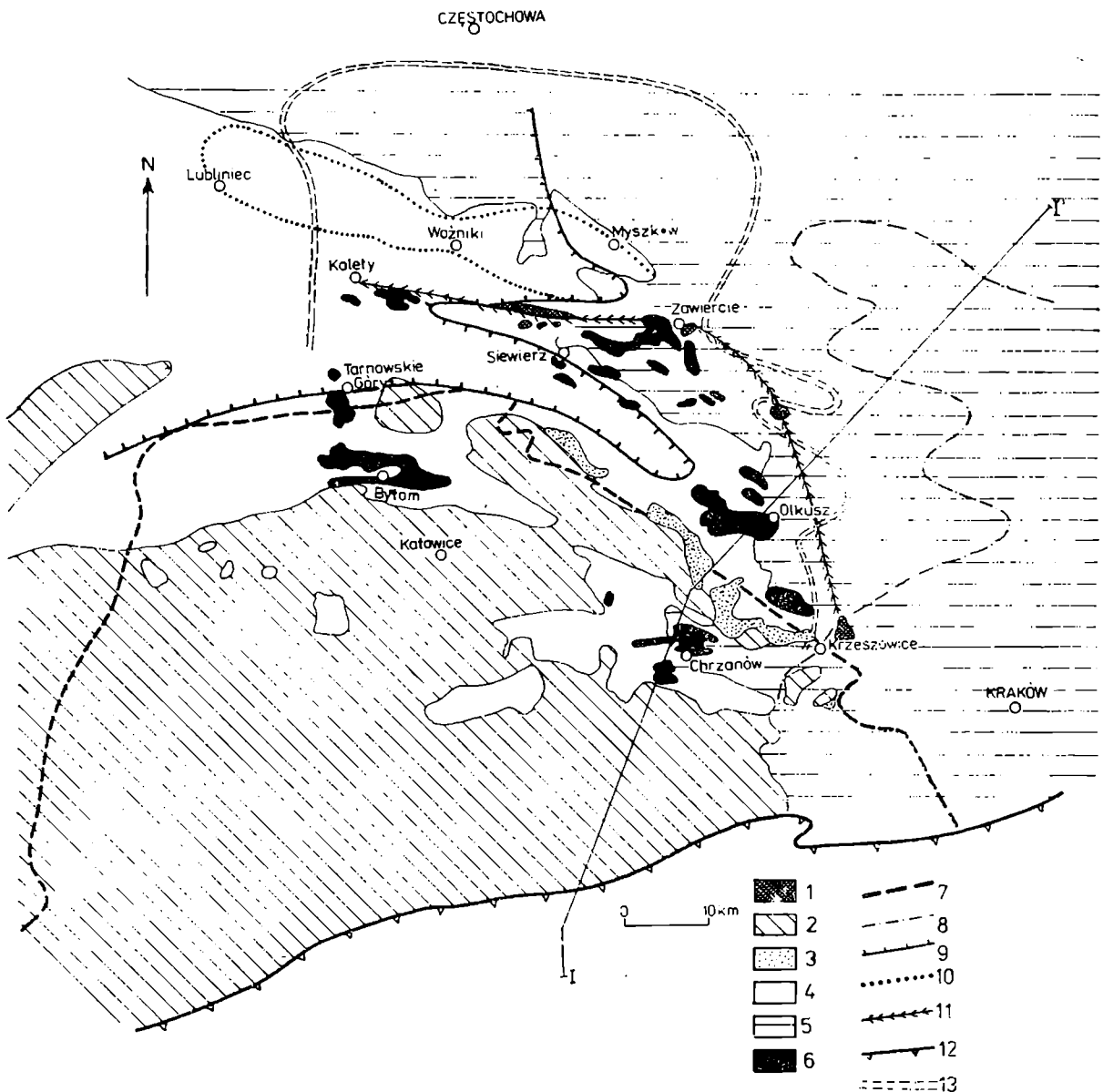


Fig. 3. Pre-Cretaceous geology map of the Cracovian-Silesian region (modified after Celińska, 1978). 1 – Devonian; 2 – Carboniferous; 3 – Permian; 4 – Triassic; 5 – Jurassic; 6 – Zn–Pb mineralization of the Cracovian-Silesian ore district; 7 – boundary of Upper Silesia basin; 8 – limit of Muschelkalk sedimentation (after Czerwiński & Pajchłowa, 1975); 9 – limit of gypsiferous sediments within the Buntsandstein (after Śliwiński, 1969); 10 – limit of Woźniki Limestone (after Gąsiorowski & Piekarska, 1977); 11 – axis of Devonian elevation in Triassic sea (after Ekiert, 1971b); 12 – Carpathian front; 13 – limit of ore-bearing dolomite (after Przeniosło, 1978)

Cracow-Myszków zone are shown in Figures 2 and 3, respectively. Stratigraphic columns of the central Silesian basin and of the Cracow-Myszków zone are shown in Figures 4 and 5, and a geological cross-section across their boundary in Figure 6. The geologic history of the two areas is quite distinct during the Early Paleozoic and Late Carboniferous, however, during the Devonian, Early Carboniferous and Mesozoic there was no strong discontinuity between the two regions.

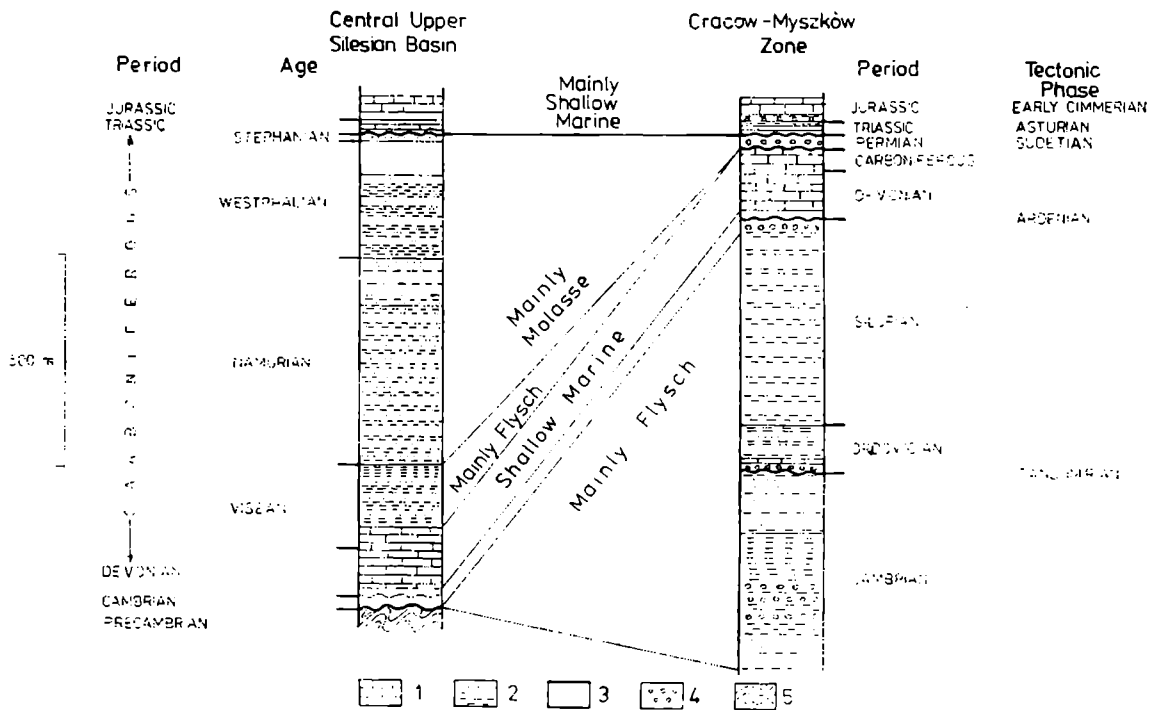


Fig. 4. Stratigraphic column of the central part of the Upper Silesian basin (after Kotas, 1984) and the Cracow-Myszków zone (after Harańczyk & Oliver, in prep.). 1 – carbonates; 2 – mudstone; 3 – sandstone; 4 – conglomerate; 5 – crystalline basement

The pre-Mesozoic geology of Upper Silesia has been summarized by Bukowy (1974), Znosko (1983) and Kotas (1984). Precambrian crystalline basement is unconformably overlain by up to 400 m of Cambrian and Lower Devonian sandstones, up to 1500 m of Middle Devonian to middle Viséan limestones and dolomites, up to 1500 m of upper Viséan flysch-like mudstones and fine-grained sandstones, and up to 8000 m of Namurian and Westphalian locally coal-bearing molasse. During the Sudetic and Asturian phases of the Variscan, the western part of the basin was intensely deformed and cut by NNW-striking thrust faults (Fig. 2), whereas in the east, generally WNW-striking normal faults were active. Clay-bearing sediments in the basin have undergone diagenetic dehydration accompanying recrystallization of smectite to interlayered illite/smectite (Środoń, 1979), so that near the base they contain only 10% interlayered smectite. Tuffaceous horizons occur within the Viséan sediments (Pożaryski & Dembowski, 1984).

The pre-Mesozoic geology of the Cracow-Myszków zone has been described by Ekiert (1971a, 1978), Harańczyk (1979, 1982), Znosko (1983) and Harańczyk & Oliver (in preparation). The Lower Paleozoic sequence consists mainly of flysch and includes at least 5 km of Cambrian, 1.2 km of Ordovician and 5 km of Silurian sediments. The Caledonian basement is unconformably overlain by Lower Devonian sandstones and Middle Devonian to middle Viséan carbonates, which extend from Upper Silesia onto the eroded Caledonides (Figs 4 and 6). Permian terrestrial rocks lie along a WNW-striking tectonic depression which is connected to the main Permian basin in central Poland (Pokorski, 1981), and according to Siedlecka (1970), consist of 200 to 400 m of conglomerates, sandstones, tuffs, porphyres and melanophyres. The sediments have a clay-carbonate matrix and are highly impermeable. They have a characteristic hematite-red colour reflecting an oxi-

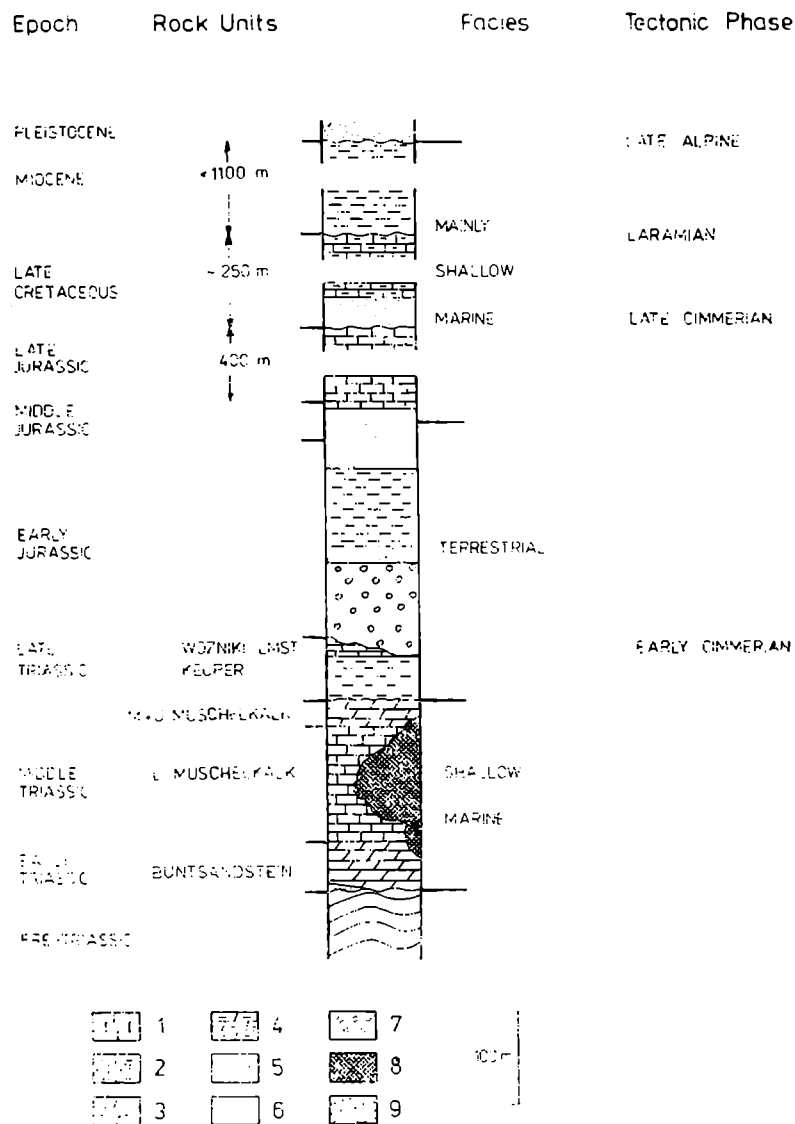


Fig. 5. Schematic stratigraphic column of post-Palaeozoic deposits (mainly after Senkowiczowa, 1976; Dadlez, 1976; Małkowska *et al.*, 1976; Cieśliński, 1976). 1 — limestone; 2 — marl; 3 — dolomite; 4 — clayey dolomite; 5 — mudstone; 6 — sandstone; 7 — conglomerate; 8 — ore-bearing dolomite; 9 — Paleozoic basement

dizing environment of deposition. During the Sandomirian and Ardenian phases of the Caledonian, the Lower Paleozoic rocks were intensely folded about NNW axes (Ekiert, 1971a) and were metamorphosed to the greenschist facies (Ryka, 1978). Northeast and WNW-striking faults were active during both the Caledonian and Variscan orogenies. According to Harańczyk (1984) the northeast-striking faults have a right-lateral strike slip displacement and have acted as loci for later igneous and hydrothermal activity. According to Harańczyk (1979, 1984) Caledonian intrusives include gabbro, granodiorite, quartz monzonite and microgranite that are generally unaltered, whereas Variscan intrusives consist of porphyritic rhyolite, rhyodacite and andesite that locally have been intensely altered. Both intrusive series lie along a well-defined zone (Fig. 2) that trends north through Krzeszowice and then northwest through Zawiercie and Myszków.

The Cracow-Myszków zone has been the focus of extensive pre-Mesozoic mineralization described by Górecka (1978), Górecka & Nowakowski (1979) and Harańczyk (1978a, 1979) and summarized recently by Harańczyk (1984). Mineralization of probable Caledonian age includes massive stratiform pyrite-siderite deposits in Ordovician rocks near Zawiercie, Cu-Zn andradite skarns in Ordovician limestones near Zawiercie, tourmaline-bearing breccia near a Caledonian intrusive at Pilica and Bi-Ag-Te±Au±W quartz veins in various Lower Paleozoic

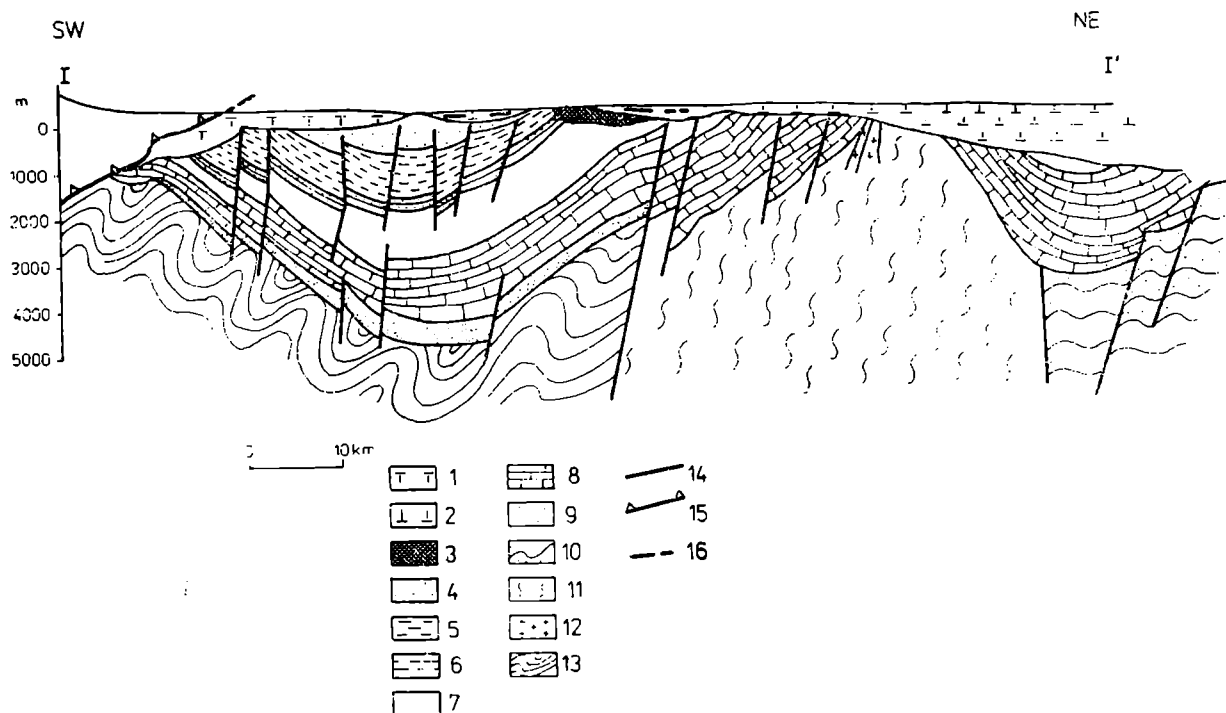


Fig. 6. Geological cross-section of the Upper Silesian basin and the Kraków-Myszków zone (after Pożaryski & Dembowski, 1984). 1 – Tertiary; 2 – Mesozoic; mainly carbonates; 3 – Permian, mainly conglomerates; 4 – Westphalian, mainly sandstones; 5 – Westphalian, mainly mudstones; 6 – Namurian, mudstones and sandstones; 7 – Viséan, mudstones, sandstones and carbonates; 8 – Devonian: carbonates and sandstones; 9 – Cambrian sandstones; 10 – Lower and Middle Cambrian, folded; 11 – Cambro-Ordovician, folded and metamorphosed to greenschist facies; 12 – Caledonian and Variscan granitic intrusives; 13 – Precambrian crystalline basement; 14 – faults; 15 – Carpathian nappes; 16 – Zn-Pb ore deposits

rocks near Pilica, Zawiercie and Dolina Będkowska. Mineralization of probable Variscan age includes a Cu-Mo skarn deposit at Zawiercie and Cu-Mo disseminated and vein deposits of porphyry copper association near Myszków, Pilica, Zawiercie and Dolina Będkowska.

At the close of the Paleozoic era considerable relief was present in the Variscan basement (Ekiert, 1971a), and during the Triassic marine transgression a chain of islands was present along a north to NNW trend between Krzeszowice and Zawiercie, and along a WNW trend from Zawiercie to Kalety (Fig. 3). The stratigraphy of the Triassic has been described amongst others by Śliwiński (1969) and Senkowiczowa (1976) and is summarized in Figure 5. The Buntsandstein consists of a locally developed basal red sandstone, and up to 50 m of clayey dolomite, dolomite and grypsiferous beds (Fig. 3). The Muschelkalk varies in thickness from 75 to 160 m and consists of Gogolin, Górażdże, *Terebratula* and Karchowice limestones, *Diplopora* and Tarnowice dolomites, and locally Boruszowice claystones, dolomites and sandstones. According to Bogacz *et al.* (1972) the Muschelkalk contains very little terrigenous material and it was deposited in shallow-marine, well-aerated waters. It is overlain by up to 50 m of non-marine claystones of the Keuper. Between Lubliniec and Myszków (Fig. 3), the Keuper is overlain by up to 40 m of Woźniki Limestone of probable Rhaetian age. According to Gašiorowski and Piekarska (1977), the limestone consists of basal muddy sediments overlain by almost pure micrite which they interpret as a playa lake deposit. Bogacz *et al.* (1970) consider that the calcium carbonate was supplied by hot springs related to, and coeval with, hydrothermal dolomitization of the underlying Muschelkalk. This theory is supported by recent oxygen isotope studies of the Woźniki Limestone (Szulc, pers. comm.), which suggest that the temperatures during calcite precipitation were elevated. During Early to Middle Jurassic the region remained above sea level and in the northeast up to 230 m of gravels (the Polomia Gravels), sands and claystones were deposited (Dadlez, 1976). These terrestrial deposits were overlain by up to 400 m of late Middle Jurassic and Late Jurassic limestones (Malinowska *et al.*, 1976). In the east, up to 300 m of Late Cretaceous sandstones and marls are present (Cieśliński, 1976). The Cracovian-Silesian area was affected by uplift and mild tectonism during the Early Cimmerian, Late Cimmerian and Laramian tectonic phases of the Alpine Cycle. Evidence for magmatism at this time is restricted to the presence of thin tuffaceous layers in the Upper Cretaceous.

#### HYDROLOGY

The chemistry of groundwaters in the Upper Silesian region has been intensely studied by Pałys (1966, 1971), Rózkowski *et al.* (1979), Rózkowski & Rudzińska-Zapaśnik (1983) and Rózkowski (1985). These studies are important because present day groundwaters may provide important clues regarding the chemistry of the hydrothermal fluids responsible for the formation of the Cracovian-Silesian Zn-Pb deposits. The range in composition and chemical parameters of deep-seated brines within Carboniferous sediments are shown in Tables 1 and 2. The waters



Table 1

Concentration ranges in natural brines [log M]

	Upper Silesia	Mississippi Valley	
	deep groundwaters <sup>a</sup>	oil field brines <sup>b</sup>	fluid inclusions <sup>b</sup>
Ca	-1.0 to -0.8	-1.4 to 0.1	-0.9 to -0.2
Mg	-1.1 to -0.9	-1.7 to -0.7	-1.3 to -0.5
K	-1.8 to -1.4	-2.5 to -0.7	-1.2 to -0.8
Ba	to -2.3	-6.0 to -2.6	—
S	-4.1 to -1.7	-3.0 to -1.0	-4.2 to -1.7
C	-3.2 to -2.5	—	-4.5 to -2.2

<sup>a</sup>Rózkowski *et al.* (1979). <sup>b</sup>Giordano & Barnes (1981).

Table 2

Chemical indices of groundwaters from Carboniferous sediments of the Upper Silesian basin and from fluid inclusions in the Cracovian-Silesian Zn-Pb deposits

Source of fluid	Depth [m]	pH	Salinity [g/l]	Na+K	Na+K	Cl	References
				Ca+Mg	Cl	SO <sub>4</sub>	
Deep-seated reduced groundwaters							
Carboniferous sediments	288	7.0	35.2	4.16	0.48	1239	a
„ „	566	6.4	78.0	4.16	0.49	4128	a
„ „	705	6.9	110.5	3.64	0.47	8243	a
„ „	415	7.0	23.3	5.86	0.54	352	a
„ „	580	—	124.0	—	0.51	27608	b
„ „	500	—	101.0	—	0.51	797	b
„ „	746	—	171.0	—	0.50	23583	b
„ „	820	—	181.0	—	0.51	60000 <sup>+</sup>	b
„ „	400	—	—	—	0.54	3641	b
„ „	—	—	—	—	0.48	9666	b
	Mean	6.8	103	4.46	0.50	8806	
Fluid inclusions in sulphides							
Galena	Orzeł Biały mine			0.89	0.48		c
Sphalerite				0.29	0.19		c
Galena	Ludwik Waryński mine			—	0.44		c
Sphalerite				0.16	0.21		c
Galena				0.44	—		c
Galena	Trzebionka mine			1.97	2.00 <sup>+</sup>		c
Sphalerite				5.88	0.79		c
Sphalerite				0.71	0.54		c
Galena	Bolesław mine			0.42	0.33		c
Galena				1.72	0.54		c
			Mean	1.40	0.44		

<sup>+</sup> analyses excluded from mean.References: a — Rózkowski *et al.*, 1979; b — Pałys, 1966; c — Karwowski *et al.*, 1979.

are saline (20–180 g/l), Cl-Na±Ca brines whose salinity generally increases with depth. The Cl/SO<sub>4</sub> ratio is much higher than 100 indicating reducing conditions, and the Na+K/Ca+Mg and Na+K/Cl indices are constant and low (4.5 and 0.5, respectively) indicating that the waters have undergone intense diagenesis. The waters are methane-bearing and the methane content is highest in areas of high-rank coal metamorphism (Rózkowski & Rudzińska-Zapaśnik, 1983). The maximum temperature recorded within the Upper Silesian basin is 100.5°C at a depth of 2950 m (Rózkowski & Rózkowska, 1973), representing a geothermal gradient of about 34°C/km.

Oxygen and hydrogen isotopic composition of groundwaters in Upper Silesia are reported by Rózkowski *et al.* (1979) and the results are summarized in Figure 7.

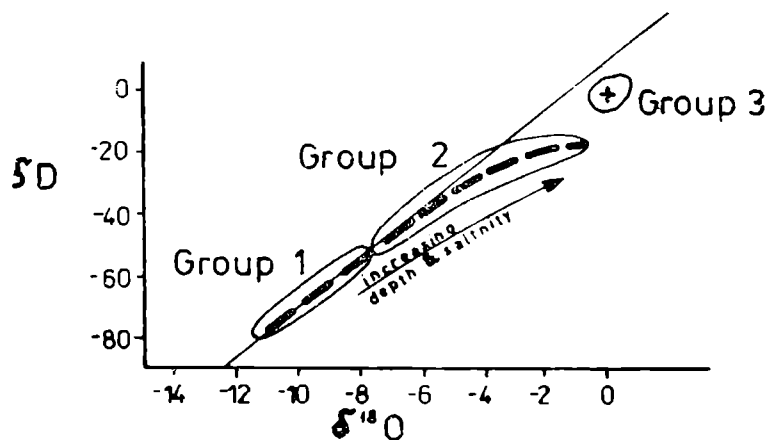


Fig. 7. Isotopic composition of Upper Silesian basin groundwaters (after Rózkowski *et al.*, 1979). Fields of main composition groups are modified after Rózkowski *et al.* (1979). Meteoric water line (*solid*), composition trend of groundwaters in pre-Tertiary sediments (*dashed*) and SMOW (*cross*) are indicated (see text for discussion)

The analyses fall into three compositional groups: *Group 1* lies along the meteoric water line and includes waters from strata exposed to surface infiltration. *Group 3* brines are similar in isotopic composition to sea water and are from Tertiary sediments that locally overlie the Paleozoic rocks. *Group 2* brines lie between groups 1 and 3, and with increasing depth deviate from the meteoric water line and become isotopically heavier.

The derivation of *Group 2* waters from Miocene sea water or from overlying Miocene sediments can be excluded on the basis of the isotopic evidence. Pre-Miocene infiltration is supported by most workers. Pałys (1966, 1971) considers that the infiltration took place during the Early Permian, a time of maximum relief, but additional less intense infiltration may also have occurred during Liassic, Early Cretaceous and Early Tertiary continental periods (Rózkowski *et al.*, 1979). Contribution from original connate water and from diagenetic water released during burial, may also have taken place. In any case present day deep-seated groundwaters from the Upper Silesian area have been in contact with Paleozoic sediments

for a long time and are likely to have reached chemical equilibrium with them. Their chemical composition may therefore reflect the composition of formation waters present in the Upper Silesian basin in the past.

### THE Zn-Pb MINERALIZATION

The Zn-Pb deposits are mainly located in the Kalety, Tarnowskie Góry, Bytom, Siewierz, Zawiercie, Olkusz and Chrzanów mining districts (Figs 2 and 3) where they are largely confined to the Lower Muschelkalk, but locally penetrate the Middle Muschelkalk, Buntsandstein and adjacent Devonian paleoelevations (Gałkiewicz & Śliwiński, 1983). In the following sections they are briefly described in terms of their relation to regional geology, form, paragenesis, geochemistry, ore fluid composition and age, because these data may place constraints on possible ore genesis models.

### RELATIONSHIP TO REGIONAL GEOLOGY

The spatial relationship between the mineral deposits and regional geologic features are shown in Figures 1 to 6 and are summarized below. The Cracovian-Silesian Zn-Pb deposits lie near the boundary between the Małopolska and Upper Silesian massifs (Fig. 1); near the southwestern margin of the Caledonian geosynclinal sequence (Figs 2 and 5); near the northeastern margin of the Late Carboniferous Upper Silesian basin (Figs 2 and 5); above and on either side of the Permian tectonic trough (Figs 2 and 5); to the west and southwest of the Caledonian and Variscan granitoid intrusives (Fig. 2); above and to the southwest of intense Caledonian and Variscan tectonism (Fig. 2); to the south and west of the axis of Devonian paleoelevations in the Triassic sea (Fig. 3); near the periphery of gypsum-bearing beds within the Buntsandstein (Fig. 3); to the south of the Woźniki Limestone (Fig. 3); mainly along a hypsometric surface which lies below Late Triassic to Middle Jurassic unconformities and terrestrial sediments (Fig. 6); and to the northeast of present-day hot saline brines located in the deeper parts of the Upper Silesian basin. The interplay between ore genesis and geological history may have been very complex.

### FORM OF DEPOSITS

The Zn-Pb deposits are largely stratabound and tabular in form. They consist of metasomatic and cavity-filling ores that are enclosed in a hydrothermally altered envelope of the so-called ore-bearing dolomite, as well as of minor occurrences of both stratiform and fissure controlled types. The ore-bearing dolomite encloses metasomatic and cavity-filling ores and is considerably more extensive (Fig. 3). According to Śliwiński (1964, 1969) and Bogacz *et al.* (1972) it differs from early diagenetic dolomite in that it is coarser grained, most small-scale sedimentary features have been obliterated, it is enriched in iron, zinc and lead, and has cross-cutting relations with respect to bedding. Structural relations indicate that the

ore-bearing dolomite is epigenetic and was formed by recrystallization of early diagenetic dolomite and by replacement of limestone.

Metasomatic ore consists of sphalerite and lesser galena which replace ore-bearing dolomite along fronts that locally cross-cut bedding (Sass-Gustkiewicz *et al.*, 1982). Commonly, sphalerite has a ribbon structure that may have resulted from replacement of sedimentary laminations or from a diffusion phenomenon (Sass-Gustkiewicz *et al.*, 1982; Sass-Gustkiewicz, 1985). Cavity-filling ores consist of sphalerite, galena, pyrite and marcasite, and locally minor barite and calcite. These minerals fill open spaces between ore-bearing dolomite clasts in breccias. According to Bogacz *et al.* (1970), Dżułyński & Sass-Gustkiewicz (1980, 1982), Sass-Gustkiewicz *et al.* (1982) and Sass-Gustkiewicz (1985), there is ample textural evidence that the cavity-filling ores were deposited as a result of, and concurrently with, the formation of the hydrothermal karst. The lowermost boundaries of the cavity-filling ore are uneven surfaces that represent former cave floors. Locally, these are covered by clay-bearing internal sediments that contain authigenic sulphides as well as clasts of massive ore-bearing dolomite and metasomatic ore. Upward, there is a gradation from completely disoriented clasts, to crackle breccia, to dolomite with a network of cracks, and finally to undeformed dolomite.

Stratiform mineralization has been noted by Piekarski (1962) who described a 10 cm clayey dolomite layer in the Upper Muschelkalk Boruszowice Beds between Tarnowskie Góry and Chrzanów that carries up to 0.7% Zn and 0.24% Pb. According to Szuwarzyński (pers. comm.) several similar stratiform anomalies are found in the Lower Muschelkalk and in the Keuper. Geochemical anomalies of up to 1000 ppm of Zn and Pb have also been recognized in limestone and early diagenetic dolomite near Chrzanów by Pawłowska & Szuwarzyński (1979) and near Zawiercie by Przeniosło (1974). These anomalies are all on a regional scale, are much more extensive than the epigenetic mineralization, and they are not necessarily enclosed in the ore-bearing dolomite. They are probably of syndimentary origin, though this interpretation is not shared by all Polish geologists.

Finally, minor mineral occurrences are found along steep, tectonically controlled fissures cutting Devonian, Carboniferous and Permian basement underlying some Cracovian-Silesian deposits (Zwierzycki, 1950; Harańczyk, 1979, 1984; Gałkiewicz & Śliwiński, 1983), and locally along faults that displace Jurassic sediments (Harańczyk *et al.*, 1968). These occurrences have similar mineral parageneses to the cavity-fill stratabound deposits (Harańczyk, 1984), and may represent channels along which hydrothermal fluids gained access into the stratabound deposits. Where these fluids transgressed Permian rocks they caused a colour change from the characteristic hematite red to grey, indicating that the fluids were reducing.

#### PARAGENESIS

The most common ore minerals present in the Cracovian-Silesian districts are sphalerite, marcasite, pyrite and galena. Minor amounts of wurtzite, brunckite and lead-arsenic sulphosalts are also locally present (Harańczyk, 1962), and Kucha

& Czajka (1984) have identified primary smithsonite interlayered with sphalerite in the Chrzanów area. Gangue minerals include the ore-bearing dolomite and minor barite, ankerite and calcite. Michalik (1984, 1985) has identified authigenic sphalerite, marcasite and galena together with kaolinite and illite in cave sediments. The kaolinite appears to have formed at the expense of clastic feldspar. According to Bogacz *et al.* (1970), Sass-Gustkiewicz (1975) and Dżułyński & Sass-Gustkiewicz (1985), the sequence of events resulting in the formation of the epigenetic ores was as follows: (i) formation of ore-bearing dolomite which contains minor sphalerite, pyrite and marcasite; (ii) replacement of ore-bearing dolomite by metasomatic sphalerite-rich ore; (iii) formation of hydrothermal karst together with associated cave sediments and karst breccias and (iv) deposition of sphalerite, iron sulphides, galena and local sulpho-salts, barite, smithsonite and calcite in open spaces. The karst forming process and open space-filling mineralization were repeated several times (Sass-Gustkiewicz, 1975, 1985) either because the hydrothermal fluids flowed through the rocks in several pulses, or because of local hydrologic changes during development of hydrothermal karst. In general however, at a given location, galena is later than sphalerite and iron sulphides, and barite and calcite are later than galena. With the exception of galena, hydrothermal crystals are extremely fine-grained and, commonly collophorm, suggesting rapid nucleation from a supersaturated solution.

#### STABLE ISOTOPE GEOCHEMISTRY

The oxygen isotope composition of four medium and coarse grained samples of ore-bearing dolomite (the dolomite most likely to have reached isotopic equilibrium with the hydrothermal fluid), reported by Pawłowska & Szuwarzyński (1979), varies from 23.8‰ to 25.6‰ and averages 24.7‰ relative to SMOW. According to Northrop & Clayton (1966, p. 191) the relationship between dolomite/water fractionation and temperature (°K) is given by:

$$\delta^{18}\text{O}_{\text{dolomite}}/\sim\delta^{18}\text{O}_{\text{water}} = \alpha,$$

$$1000 \ln \alpha = 3.20 \cdot 10^6 T^{-2} - 2.00.$$

Assuming that  $\delta^{18}\text{O}_{\text{dolomite}}$  is 24.7‰,  $\delta^{18}\text{O}_{\text{water}}$  can be calculated for various temperatures. At 100°C, the approximate homogenization temperature of fluid inclusions in sphalerite reported by Karwowski *et al.* (1979),  $\delta^{18}\text{O}_{\text{water}}$  would be 3.7‰, somewhat heavier than the deepest groundwater sampled from the Upper Silesian basin. At 60°C the  $\delta^{18}\text{O}_{\text{water}}$  would be -2.2‰, similar to present day deep seated groundwater (Fig. 7). At 20°C the  $\delta^{18}\text{O}_{\text{water}}$  would be -10.6‰, similar to shallow groundwaters that have been contaminated by meteoric water. It is not possible to choose between these alternatives without knowledge of temperature, however, since coarse-grained dolomite is unlikely to have crystallized at low temperatures, the heavier, more strongly evolved waters are considered to be more likely.

Sulphur isotope studies of the Cracovian-Silesian ores by Harańczyk (1978b) have shown that the ranges in composition for sphalerite, galena and pyrite are

+28 to -15, +15 to -9, and +67 to -22‰ respectively, but the most common values are near zero. Harańczyk suggests that these results indicate that the hydrothermal fluids are of deep, possibly magmatic derivation, and that they have been mixed with some surficial water.

The lead isotopic composition of galena reported by Zartman *et al.* (1979) from ten localities ranges as follows:  $^{206}\text{Pb}/^{204}\text{Pb} = 18.406$  to  $18.444$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.599$  to  $15.634$ , and  $^{208}\text{Pb}/^{204}\text{Pb} = 38.410$  to  $38.434$ . The results plot close to the orogene evolution curve of Doe & Zartman (1979), the lead is extremely homogeneous, and has a model age only slightly older than the enclosing Triassic host rocks. For these reasons, Zartman *et al.* (1979) rule out direct derivation of lead from the mantle, from Precambrian basement, or from sediments derived directly from Precambrian basement, and consider the underlying cratonized Caledonian basement as an unlikely source. The data suggest the derivation of the metals from the Triassic, Permian or Carboniferous basins in which the homogenization of lead isotopes could have been caused by the sedimentary process itself. Zartman *et al.* (1979) favour the Triassic host rocks themselves as the most likely source of the metals, however, as discussed in subsequent parts of this paper, other data suggest that this is unlikely.

#### GEOCHEMICAL ZONATION

According to Przeniosło (1978) the Zn/Pb ratios of mined ores decrease systematically from SSE to NNW, ranging from 5.0 between Bytom and Chrzanów, to 3.1 between Kalety and Olkusz, and 1.7 at Zawiercie. Northwest-striking geochemical anomalies have also been noted by Ridge & Smolarska (1972) on the basis of the As, Sb and Ag contents of 44 samples of galena. Their results suggest that the mean concentrations of As and Sb increase, and the mean concentration of Ag decreases towards the northeast. According to Ridge (*in* Ridge and Smolarska, 1972) these data suggest that the hydrothermal fluids rose along a broad front in the southwest and flowed towards the northeast. Gałkiewicz (1983) noted a northeastward increase in the overall concentration of Ag and Cd (towards Zawiercie) and of Ba (Zawiercie, Olkusz and Tarnowskie Góry), consistent with the southwest-northeast flow of fluids. On the other hand, he found that the concentration of iron sulphides and of associated As and Tl were highest at Tarnowskie Góry and Bytom in the west and decreased eastwards, where according to Gałkiewicz and Harańczyk (*pers. comm.*) ankerite is the most common iron-bearing mineral. This east-west zonation might be accounted for if the gypsiferous beds in the Buntsandstein (which underlie the western part of the Cracovian-Silesian area; see Fig. 3), constituted the source of the sulphur present in the ores.

#### THE HYDROTHERMAL FLUID

Fluid inclusions, mainly in sphalerite, have been studied by Karwowski *et al.* (1979). They are two and three phase inclusions containing water, vapour and oil that homogenize between 92 and 138°C. Since most of the ore deposition took

place during Early Cimmerian (see following section), the depth of mineralization was only 100 to 200 m and trapping temperatures do not differ greatly from observed homogenization temperatures. Karwowski *et al.* (1979) found three inclusions that were sufficiently clear to observe low temperature phase changes. Two inclusions were in calcite, homogenized at 126°C, and had freezing point depressions of 0.0 and 0.2°C showing that this fluid was essentially fresh water. The remaining inclusion was in sphalerite, homogenized at 123°C, had a freezing point depression of -17.6°C, a first melting temperature of -28.6°C. The salinity of this hydrothermal fluid was 22 wt. % NaCl equivalent, similar to present day deep thermal brines in the Upper Silesian basin. The first melting temperature is well below the NaCl-H<sub>2</sub>O eutectic showing that in addition to NaCl other salts are present. Analyses of leachates were also performed by Karwowski *et al.* (1979) and are compared to deep-seated present-day groundwaters from the Upper Silesian basin in Table 1. The Na+K/Ca+Mg ratios in fluid inclusions are variable and low, as would be expected for fluids causing dolomitization and hydrothermal karst formation. The Na+K/Cl ratios in fluid inclusions from sulphides are high and comparable to the evolved thermal brines characteristic of deep groundwaters in the Upper Silesian basin.

The volume of fluid involved in the hydrothermal process can be estimated provided that both the concentration of metals carried in the fluid, and the mass of metals introduced into the host rocks, are known. The concentration of metals in oil field brines may be as high as 500 ppm according to Carpenter *et al.* (1974) and Lydon (1983), whereas Andersen & Macqueen (1982) assume that the metal content of Mississippi Valley-type ore fluids was probably between 1 and 100 ppm. In the present calculation the highest figure of 500 ppm has been assumed. The mass of metals that has been introduced into the host rocks, based on production and reserve figures, has been estimated by Galkiewicz (1967) to be about  $40 \cdot 10^6$  tons. This is a minimum figure because metals present in the stratiform mineralization and dispersed in the ore-bearing dolomite have not been taken into consideration. Assuming then, that the fluid density was 1.12 (22 wt. % at 100°C), the volume of fluid involved with ore deposition was at least 70 km<sup>3</sup>, and may have been much higher.

#### AGE OF MINERALIZATION

The earliest recorded mineralization took place during the Middle and Late Triassic when the stratiform Zn-Pb anomalies were formed. According to Bogacz *et al.* (1970, 1972), the bulk of the epigenetic mineralization took place between the Middle Triassic and Middle Jurassic, during the Early Cimmerian tectonic phase. This is supported by the following lines of evidence: (i) fragments of ore-bearing dolomite have been reported as clasts in Keuper sediments by Ekiert (1959), but this observation has not been confirmed since; (ii) locally Middle Jurassic sediments rest upon a truncated surface of ore-bearing dolomite (Bogacz *et al.*, 1970, 1972); (iii) according to Lipiarski (1971), coals found in paleokarst are of Keuper

or Liassic age, and finally, (iv) if as suggested by Bogacz *et al.* (1970), the Woźniki Limestone is a hot spring precipitate associated with hydrothermal mineralization of the underlying Muschelkalk, then the age of mineralization is Rhaetian.

Evidence for post-Jurassic mineralization is also locally present. Harańczyk *et al.* (1968) document Zn-Pb mineralization along a post-Jurassic reverse fault, which according to Harańczyk (1979), may be associated with Late Cimmerian movements. Finally, widespread but minor, barite-sulphide mineralization occurs along Cretaceous or even Tertiary fractures (Harańczyk, 1979), and is possibly associated with Laramian tectonism.

### ENERGY SOURCE FOR FLUID EMPLACEMENT

Hydrothermal fluids which deposited the Cracovian-Silesian Zn-Pb ores were hot saline brines that penetrated the Triassic host rocks at a time when these were close to the surface. In general, the salinity of groundwaters increases with depth because saline fluids are dense and thus tend to remain deeply buried. Therefore, before such brines can reach high levels in the crust suitable channelways must be present and energy must be supplied. In the Cracovian-Silesian area, the rocks underlying the deposits were intensely faulted during the Caledonian and Variscan orogenies, and channelways providing access to the Triassic carbonate host rocks may have been reactivated during the Cimmerian and Laramian tectonic phases. Possible sources of energy for fluid emplacement may have been heat, hydrostatic head or fluid overpressure. These are tabulated in Table 3, illustrated in Figure 8 and are discussed below.

Table 3

Possible sources of hydrothermal fluids and the energy for their emplacement

	Heat flow	Hydrostatic head	Fluid overpressure
Deep-seated magmas	+	—	+
Underlying Caledonian flysch	+	+	—
Upper Silesian basin	+	+	+
Triassic sediments	—	+	—
Overlying sediments	—	+	—

### HIGH HEAT FLOW

One possible energy source for fluid emplacement is a heat flow anomaly which causes a local decrease in fluid density and an upwelling of deep brines (Fig. 8a). Such a thermal anomaly may be caused by an igneous intrusion and/or by thinning of the underlying lithosphere. It must be high enough to decrease the density of the brine so that it can displace cold, dilute near-surface water.



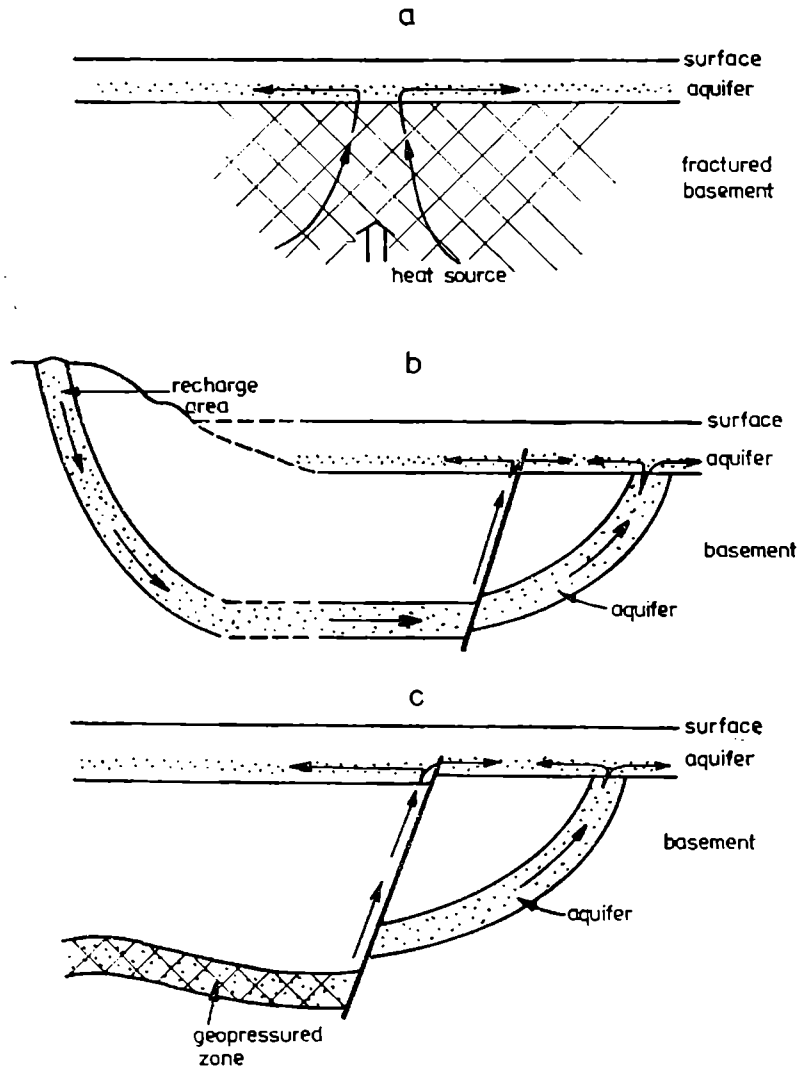


Fig. 8. Schematic diagrams showing possible energy sources for emplacement of saline hydrothermal fluid into ore-bearing strata. *a* — anomalous heat flow; *b* — hydrostatic head; *c* — fluid overpressure; arrows indicate fluid migration paths

In the Cracovian-Silesian area igneous activity took place during the Caledonian and Variscan orogenies, and the latest volcanism and plutonism took place during Early Permian, some 50–60 Ma before the main period of sulphide mineralization. Between Middle Triassic and Middle Jurassic there is no evidence for igneous activity in the Cracovian-Silesian region. During the Cretaceous, tectonic dikes and sills intruded the Carpathian flysch some 50 km to the southwest, and Harańczyk & Gałkiewicz (1970) and Harańczyk (1984), consider that the post-Jurassic mineralization may be related to this igneous episode. However, this is considered unlikely because prior to the Miocene emplacement of the Carpathian nappes, the igneous rocks must have been even further to the south where their effect on the Cracovian-Silesian region would have been negligible. The alternative hypothesis, namely that high heat flow was caused by thinning of the lithosphere, is equally untenable. A decrease in the thickness of the lithosphere is ge-

nerally associated with deepening of sedimentary basins (McKenzie, 1978). In the Cracovian-Silesian region however, there is no evidence for deepening of the sedimentary basin between Middle Triassic and Middle Jurassic. Indeed, this was a time of mild regional uplift (Early Cimmerian) during which terrestrial sediments were deposited.

A further argument against the anomalous heat flow is based on density estimates of the fluids. Between Middle Triassic and Middle Jurassic the Cracovian-Silesian region was above sea level so that shallow ore deposition within the Muschelkalk must have involved displacement of cold near-surface waters. This could only take place if the hydrothermal fluid had a lower density than meteoric water. Assuming after Karwowski *et al.* (1979), that the hydrothermal fluid had a salinity of 22 wt.%, and using the volumetric properties of NaCl solutions of Potter & Brown (1977), it can be shown that at temperatures of ore deposition (mainly between 100 and 125°C), the density of the fluid was in excess of 1.1, clearly too high to displace cold meteoric water. The temperature of the fluid would have to be raised to about 250°C before it could displace cold dilute water with a density of 1.002.

#### HYDROSTATIC HEAD

An alternative mechanism for emplacement of hydrothermal fluids is through the action of an artesian system whereby deep saline water is flushed towards the surface as a result of hydrostatic head (Fig. 8b). This model has been supported by Pelissonier (1965) and Rózkowski *et al.* (1979) for the origin of the Cracovian-Silesian deposits, and by Bethke (1986) for the origin of the Upper Mississippi Valley deposits. In order that fluid emplacement could take place by the above mechanism, the meteoric water recharge area must be elevated and the meteoric water must have access to deep beds where the temperature and salinity of the fluids are high. Such access is most efficient where a permeable horizon is overlain by an impermeable horizon, and extends from the elevated recharge area to deep levels as shown in Figure 8b. However, Toth (1980) has suggested that cross-formational fluid flow may also be important.

In the Cracovian-Silesian region, Rózkowski *et al.* (1979) argue that an uplift of some 2500 m (the pre-Carpathians) about 170 km to the south was the main recharge area during the Early Cimmerian tectonic phase. On this basis they have calculated that the water circulation may have penetrated to nearly 4000 m, at flow rates that are quite adequate ( $9.5 \cdot 10^{-8}$  m/s) to displace deep thermal brines during the Early Jurassic. The main weakness of the above argument however, is the absence of convincing evidence for the presence of a major mountain range to the south of the Cracovian-Silesian area during the Early Jurassic. If such a mountain range was present at this time, one would expect deposition of a thick molasse sequence and the presence of major angular unconformities. In fact, only about 100 m of Early Jurassic Połomia gravels are locally present (Unrug & Calikowski, 1960), and there is an absence of major angular unconformities, suggesting that

hydrostatic head was probably not the dominant mechanism of hydrothermal fluid emplacement. However, it is possible that an elevated region to the south may have contributed towards the northward displacement of basinal brines.

### FLUID OVERPRESSURE

The third mechanism for fluid emplacement involves the generation of fluid pressures greater than hydrostatic. In a sedimentary/metamorphic environment this can take place by seismic pumping, and by compaction and diagenesis associated with burial.

Seismic pumping has been described by Sibson *et al.* (1975), and Dżułyński & Sass-Gustkiewicz (1980) have suggested that it may have played a role in the formation of the Cracovian-Silesian and Eastern-Alpine Zn-Pb deposits. The mechanism involves the generation of extension cracks near the focus of a subsequent earthquake, and the filling of the cracks with fluids from the surrounding rocks. The decrease in stress after the earthquake causes the cracks to close and the fluid to be expelled upwards, mainly along the fault. In the Cracovian-Silesian area it is doubtful whether seismic pumping alone could have generated the large volumes of fluids involved in the formation of the ore deposits. Sibson *et al.* (1975) estimate that an earthquake with a 10 km focal depth, associated with faulting along 10 km strike length and with 10–100 cm of slip would generate  $5 \cdot 10^6 \text{ m}^3$  of fluid. Since conservative estimates indicate that at least  $8 \cdot 10^{10} \text{ m}^3$  of fluid were involved in the ore-forming process, and because tectonism during the Early Cimmerian movements was mild, this mechanism alone, clearly could not have generated sufficient fluid to form the ore deposits.

The alternative way of generating fluid overpressure is through burial of sedimentary rocks (Fig. 8c), during which fluids are generated by compaction and prograde mineral reactions, but their escape to the surface is hindered and only occurs at sporadic intervals. Basinal brines as ore fluids for Mississippi Valley-type deposits have been suggested by Noble (1963), Beales & Jackson (1966) and Anderson & Macqueen (1982), but it was Cathles & Smith (1983) who first quantified the model. They showed that the expulsion of fluids is episodic and must take place during a small fraction ( $< 1/1000$ ) of basin history. The reason for this is that unless fluid expulsion is fast, shallow emplacement of hot brines cannot take place because of excessive cooling during ascent. Conditions that would favour the formation of Mississippi Valley-type deposits by episodic expulsion of basinal brines, modified after Cathles & Smith (1983), are as follows:

1. A deep sedimentary basin must be present. This allows the generation of hot fluids by compaction and/or prograde mineral reactions.
2. The basin must contain impermeable shales that provide a source of fluid and also prevent it from escaping continuously to the surface.
3. The basin should have a complex internal structure that also helps to prevent continuous escape of fluids to the surface.

4. The basin must also contain porous and permeable lithologies that can store and eventually release the geopressured fluid.

5. An efficient access route must be present between the geopressured zone and the site of ore deposition. This may either be a basal aquifer, or a steeply-dipping fault system.

6. The basin should have structural and/or stratigraphic characteristic that focus the expelled brine in a restricted direction

Conditions 1 through 4 appear to be largely fulfilled by the Lower Paleozoic sequence, by the deeper parts of the Upper Silesian Carboniferous basin and by the Permian basin to the north, because all of the above basins are sufficiently large and deep to generate the huge volumes of hot brines necessary for ore formation. The basins are structurally complex and contain both permeable and impermeable lithologies that could both generate and store the geopressured fluids. Conditions 5 and 6 are also probably satisfied because the numerous faults initiated during the Caledonian and Variscan orogenies and reactivated during the Cimmerian and Laramian tectonic phases, may well have provided efficient access and focusing mechanism for the hot brines. Geological evidence for this are the mineral occurrences along faults cutting pre-Triassic rocks underlying some of the stratabound Zn-Pb deposits (Harańczyk, 1984). Furthermore, the extremely fine-grained nature of the ore and the field evidence for numerous mineralizing episodes (both stratiform and stratabound), conform with the model of Cathles & Smith (1983), in which basin dewatering is episodic and short-lived.

In summary then, the most viable mechanism for generation and shallow emplacement of large volumes of hot brines, involves the episodic release of geopressured fluids generated within a deep sedimentary basin. The alternative mechanisms discussed above, cannot alone account for the observed mineralization, however, each may have contributed energy to the hydrothermal system. For instance, enhanced heat flow, increased hydrostatic head, and/or seismic pumping during the Early Cimmerian, Late Cimmerian and Laramian tectonic phases may have contributed to the mineralization process.

## PROVENANCE OF HYDROTHERMAL FLUID

Possible sources of the hydrothermal fluid, and by implication of metals and possibly sulphur, are tabulated in Table 3. They are discussed below in the light of available geological and geochemical data presented above.

### DEEP-SEATED MAGMAS

The association of mineralization with a late phase of the Caledonian-Variscan plutonism in the Cracow-Myszków zone has been suggested by Sass-Gustkiewicz *et al.* (1982) and Harańczyk (1984); with Cretaceous teschenitic magmas in the

Carpathians by Gałkiewicz & Śliwiński (1983) and Harańczyk (1984); and with Tertiary alkali basalts to the west by Gałkiewicz (1978, 1983), Gałkiewicz & Śliwiński (1983) and Harańczyk (1984). The magmatic association of the mineralization has already been criticized on the basis of timing and location. Additional arguments against a magmatic source for the hydrothermal fluid and its dissolved constituents involve fluid volume considerations and lead isotope data.

The volume of hydrothermal fluid needed to form the deposits has been estimated to be at least 70 km<sup>3</sup>. If one assumes that the parent magma contained 5% water, then the intrusive would occupy about 1400 km<sup>3</sup>. The absence of volcanism and major tectonism during the main period of mineralization (Early Cimmerian) argues strongly against the presence of such a large intrusive underlying the Cracovian-Silesian region. The lead isotope data also argue against a magmatic derivation of the metals. The isotopic composition of galena is close to the orogene evolution curve of Doe & Zartman (1979) and quite distinct from the mantle and lower crustal evolution curves. Since the mafic alkaline rocks are most probably of mantle derivation, and the granitic rocks of mantle or lower crustal derivation, it is highly unlikely that the ore lead was derived from such magmatic rocks. A direct derivation of metals from deep levels without the participation of magmas, by some sort of outgassing process hinted at by Harańczyk (1979), can also be excluded for similar reasons.

#### THE CALEDONIDES

The Caledonian metasedimentary rocks lie along the Cracow-Myszków zone to the northwest of the Cracovian-Silesian ore deposits (Figs 2 and 5). Bogacz *et al.* (1975) and Dżułyński & Sass-Gustkiewicz (1985) have suggested that the hydrothermal solutions were derived from deep reservoirs within the Cracow-Myszków zone; they rose along a broad front and spread south and southwest through the Triassic carbonates.

The Lower Paleozoic metasedimentary rocks contain both sandy and shaly lithologies (Fig. 4), and they may have once constituted suitable rocks for generation and storage of hydrothermal fluids. By Triassic time however, these rocks had become steeply folded, faulted and metamorphosed to the greenschist facies. Such rocks are likely to have lost virtually all fluids not combined in mineral structures, and also to have decreased substantially in permeability. Furthermore, it should be pointed out that the Caledonian metamorphic rocks lie to the east and northeast of the Cracovian-Silesian mining districts (Fig. 2) and are separated from them by the axis of Devonian paleoelevations (Fig. 3). If fluids did indeed rise through the Caledonides, as suggested by Bogacz *et al.* (1975), it is difficult to understand why they flowed and formed major ore deposits to the southwest and did not form major ore deposits directly above and to the northeast where Triassic lithologies are similar and no obstructions to fluid flow are known to be present. Finally, the lead isotope composition of galenas argues against the derivation of

metals from the Caledonian basement. According to Zartman *et al.* (1979) the model age is somewhat younger and "it seems unlikely that activation of ore-bearing fluids from deep within this terrain would yield so uniform an isotopic composition" as is present in the Cracovian-Silesian ore deposits.

#### THE UPPER SILESIA BASIN

Over 10 000 m of Cambrian, Devonian and Carboniferous sediments are present in the central part of the Upper Silesian basin (Fig. 4), which lies to the southwest of the Cracovian-Silesian ore districts. Rózkowski *et al.* (1979) have suggested that gravity-fed flow through Namurian and Westphalian sediments during the Liassic gave rise to the bulk of the ore deposits. However, as discussed earlier it is more likely that fluid overpressure was the main energy source for fluid emplacement. Factors that support derivation of fluids from the Upper Silesian basin are as follows:

1. The ore deposits lie along an arc which is parallel to the northeastern margin of the Upper Silesian basin (Fig. 2).

2. The basin is certainly large enough to generate the required volume of fluid.

3. Upper Carboniferous sediments are up to 8000 m thick, so that basinal brines are likely to have reached temperatures in excess of 250°C.

4. The basin contains interbedded clayey and sandy lithologies which could generate and store geopressed fluids. It is underlain by up to 400 m of Cambrian and Devonian sandstones which may have acted as a basal aquifer.

5. A focusing mechanism for fluids appears to be present. In the west, intense Variscan deformation (Fig. 2) may have prevented the escape of fluids in this direction. On the northeastern side of the basin reactivated steep faults near the Cracow-Myszków zone may have provided escape channels for the geopressed fluids. The fluids may also have been "pushed" northward by hydrostatic pressure from the south.

6. The Na+K/Cl ratio of the ore-forming fluid and deep present day groundwaters are similar (Table 2).

7. Basinal fluids derived from the Upper Silesian basin would be reducing because of the widespread presence of coal seams. Indeed, methane is a common constituent of groundwaters in Upper Silesia. The ore fluids were also reducing because at locations where Zn-Pb mineralization cuts Permian red beds, a grey bleached zone develops (Gałkiewicz & Śliwiński, 1983). Furthermore, according to Karwowski *et al.* (1979) fluid inclusions contain hydrocarbons.

8. The oxygen isotope composition of the ore-bearing dolomite is compatible with derivation of the hydrothermal fluid from the Upper Silesian basin.

9. The lead isotope composition of galena after Zartman *et al.* (1979) is compatible with derivation of metals from the Carboniferous basin. The model age is correct, and the orogene composition and the extreme homogeneity of the isotopic ratios can be accounted for by mechanical mixing during molasse sedimentation, followed by leaching of metals by fluids from a large volume of sediments.

A possible difficulty with the derivation of fluids by episodic expulsion of geopressured brines from the Upper Silesian basin is that the bulk of the mineralization took place 50–100 Ma after completion of sedimentation, whereas Cathless & Smith (1983) suggest that in general, mineralization is most likely to take place when basin is subsiding and compacting vigorously. If the above model is correct, geopressured fluid must have survived in the basin at least until Early Jurassic. It is impossible to prove this, but the presence of extensive geopressured zones to this day in the Permian basin to the north (Bojarska *et al.*, 1981) testifies that this is certainly possible.

### THE PERMIAN BASIN

Alternative source rocks for the ore fluids lie in the Permian basin in central Poland. This provenance is supported by the following observations: The deposits lie close to the WNW-striking zone of Lower Permian rocks (see Fig. 2) that are connected to the main Permian basin to the north. This basin contains over 800 m of permeable Rotliegendes (Pokorski, 1981), overlain by up to 900 m of generally impermeable Zechstein (Wagner *et al.*, 1981) and up to 4000 m of Triassic (Ziegler, 1981), a situation favouring periodic expulsion of basinal brines. Indeed, geopressured zones persist to the present day in the Rotliegendes and in the Zechstein (Bojarska *et al.*, 1981). Finally, lead isotopic data are compatible with the derivation of metals from the Permian basin.

There are however, two major difficulties in accepting the Permian basin as the source of the hydrothermal fluids. The first is the fact that the main axis of the Permian basin (the Polish Trough, see Fig. 1) is some 200 km to the north of the deposits, and the Permian sediments in the Cracovian-Silesian area have a clayey matrix and are highly impermeable. This would make it extremely difficult to transport brines to the site of ore deposition sufficiently fast to maintain high temperatures. Secondly, fluids flowing through the Rotliegendes would be oxidizing because of the ubiquitous presence of hematite, whereas evidence in the form of reduced zones surrounding Zn-Pb-bearing shear zones cutting Permian red beds show that the ore fluids were actually reducing.

### THE TRIASSIC AND JURASSIC SEDIMENTS

Finally, it is conceivable that the Triassic host rocks or the overlying Jurassic sediments may have been the sources of the metals. On the basis of the lead isotope data, Zartman *et al.* (1979) propose syngenetic or early diagenetic precipitation of metals within the Muschelkalk. In order to explain the epigenetic character of most ores they suggest that metals may have been redistributed and reconcentrated by circulating connate waters. Bogacz *et al.* (1970) and Dżułyński & Sass-Gustkiewicz (1985) argue against this model by noting that neither Triassic nor Jurassic rocks contained enough syndimentary metals to form the deposits, and there is no evidence of large-scale leaching. A further argument against derivation of the

metals from Triassic or Jurassic sediments rests on fluid inclusion evidence (see Karwowski *et al.*, 1979) which clearly demonstrates that sulphides were deposited from saline brines at temperatures of about 100°C. Since the host rocks were not buried deeply during mineralization, the fluids must have originated considerably deeper and a lateral secretion type origin can be ruled out.

In summary then, it is likely that the source of the hydrothermal fluids lay within the Upper Silesian basin. The ultimate source of the fluid is uncertain. It could contain elements of the original connate water, saline water that infiltrated the basin during Early Permian uplift, as suggested by Pałys (1966, 1971), and water generated by dehydration reactions during diagenesis. The latter is a likely source of at least part of the fluid, because according to Śródoń (1979), the transformation from smectite to illite has largely been completed near the base of the basin.

### CONDITIONS OF TRANSPORT AND DEPOSITION

Conditions of transport and deposition of zinc and lead in the Cracovian-Silesian area are now described in terms of the  $\log fO_2/pH$  diagram shown in Figure 9. In constructing this figure it has been assumed that the temperature was 100°C and the salinity was 3 M NaCl equivalent, values in agreement with fluid inclusion studies of Karwowski *et al.* (1979) and with conditions commonly encountered in Mississippi Valley-type deposits elsewhere (Anderson & MacQueen, 1982). Chemical compositions determined from fluid inclusion studies of Karwowski *et al.* (1979) have not been used here because only one salinity measurement in sphalerite is available, and it may not be representative. It has been assumed that present day deep-seated groundwaters in the Upper Silesian basin are comparable in composition to the hydrothermal ore fluids. As noted earlier, deep groundwaters have been in contact with the enclosing sediments since pre-Miocene time and possibly since the Permian, and they are probably in chemical equilibrium with them. Ranges in chemical composition of deep (> 500 m) brines from the Carboniferous sediments in the Upper Silesian basin are shown in Table 1. They generally fall within the range for Mississippi Valley-type ore deposits and oil field brines. In the following thermodynamic calculations the highest concentrations have been used because they are most likely to represent ancient groundwater, undiluted by younger near surface water. Following Anderson (1977), activity coefficients for doubly charged ions, singly charged ions and neutral species are 0.11, 0.70 and 1.77, respectively, and on these bases the following activities have been calculated:  $a_{Ca^{++}} = 10^{-1.8}$  M,  $a_{Mg^{++}} = 10^{-1.9}$  M,  $a_{K^+} = 10^{-1.6}$  M,  $a_{Ba^{++}} = 10^{-3.3}$  M,  $\Sigma a_S(\text{as } H_2O) = 10^{-1.5}$  M,  $\Sigma a_C(\text{as } H_2CO_3) = 10^{-2.3}$  M. These values, together with equilibrium constants tabulated in Table 4, have been used to construct the phase boundaries in Figure 9.

Hydrothermal fluids in equilibrium with Carboniferous clastic sediments are depicted as area A in Figure 9. These fluids were buffered by the quartz-illite-K feldspar assemblage present in the molasse sediments, and by the presence of aqueous carbonate and methane in the fluids (Rózkowski & Rudzińska-Zapaśnik, 1983).



Table 4

Equilibrium constants at 100°C

Reaction	log $K_{100}$	Reference
$\text{H}_2\text{CO}_3 = \text{HCO}_3^- + \text{H}^+$	-6.41	a
$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$	-10.14	a
$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2$	-113.00	b
$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{++} + \text{Mg}^{++} + 2\text{CO}_3^{2-}$	-19.28	c
$2\text{CaCO}_3 + \text{Mg}^{++} = \text{CaMg}(\text{CO}_3)_2 + \text{Ca}^{++}$	0.50	c
$\text{H}_2\text{S} = \text{HS}^- + \text{H}^+$	-6.49	a
$2\text{H}^+ + \text{SO}_4^{2-} = \text{H}_2\text{S} + 2\text{O}_2$	-94.30	c
$\text{BaSO}_4 = \text{Ba}^{++} + \text{SO}_4^{2-}$	-9.29	a
$3\text{KAlSi}_3\text{O}_8 + 2\text{H}^+ = \text{KAl}_3\text{O}_{10}(\text{OH})_2 + 2\text{K}^+ + 6\text{SiO}_2$	10.20	d
$\text{NaAlSi}_3\text{O}_8 + \text{K}^+ = \text{KAlSi}_3\text{O}_8 + \text{Na}^+$	1.80	c
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-12.26	c

References: a – Naumow *et al.*, 1974; b – Ohmoto, 1972; c – Helgeson, 1969; d – Usdowski & Barnes, 1972.

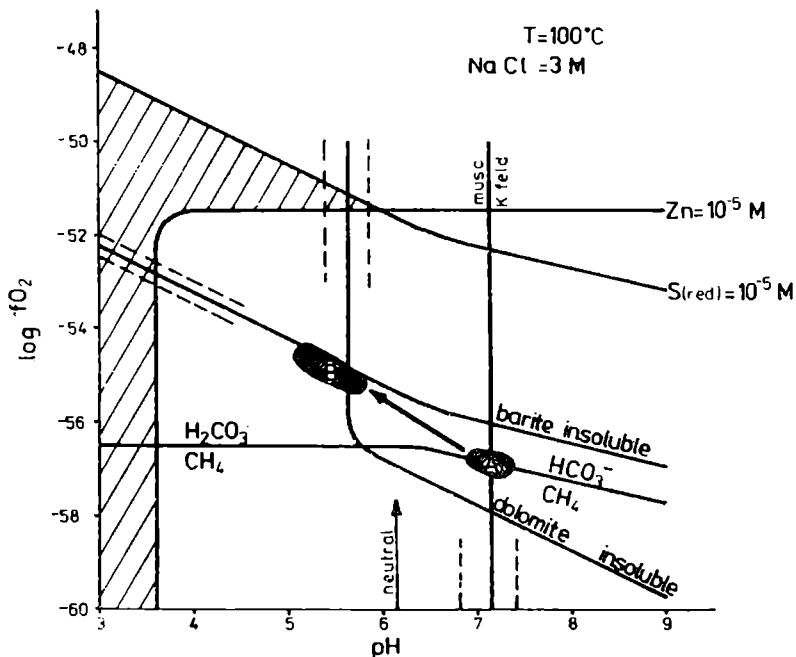


Fig. 9.  $\log f\text{O}_2/\text{pH}$  diagram showing stability fields of aqueous carbonate and methane, dolomite, barite, muscovite and K-feldspar, assuming the following activities:  $\text{Ca} = 10^{-1.8}$  M,  $\text{Mg} = 10^{-1.9}$  M,  $\text{K} = 10^{-1.6}$  M,  $\text{Ba} = 10^{-3.3}$  M,  $\Sigma \text{S}_{\text{H}_2\text{S}} = 10^{-1.5}$  M,  $\Sigma \text{C}_{\text{H}_2\text{CO}_3} = 10^{-2.3}$  M. Dashed lines show the effect of doubling and halving assumed activities. Hatched area marks conditions under which  $10^{-5}$  M (0.6 ppm) of Zn (after Anderson, 1975) can be transported together with sufficient sulphur to form ore. Area A shows fluid in equilibrium with Carboniferous coal measures of the Upper Silesian basin. Area B shows fluid composition during hydrothermal karst formation and ore deposition

The proportion of  $\text{Ca}^{++}/\text{Mg}^{++}$  ( $\log a_{\text{Ca}^{++}} - \log a_{\text{Mg}^{++}} = 0.1$ ) in the fluids emerging from the molasse, was such that dolomitization of limestone was strongly favoured (see equation 5 in Table 4), thus accounting for the widespread development of the ore-bearing dolomite. As the fluids flowed through the carbonate host rocks, conditions changed to those depicted by area *B* in Figure 9. These fluids dissolved dolomite during the formation of hydrothermal karst. It was from these fluids that the ore minerals precipitated, and late in the paragenesis, minor amounts of barite were deposited. The change in conditions from *A* to *B* in Figure 9 represents a decrease in pH from slightly alkaline to slightly acid, and an increase in oxygen fugacity from  $10^{-57}$  to  $10^{-55}$ . The crystallization of kaolinite at the expense of clastic feldspar in hydrothermal karst sediments reported by Michalik (1984, 1985) is supporting evidence for much a drop in pH. The cause of these changes is not entirely clear but may have resulted from mixing of upwelling hydrothermal fluid with small amounts of oxygenated meteoric water. This is supported by fluid inclusion evidence of Karwowski *et al.* (1979) which suggests that both saline and dilute fluids were present during hydrothermal deposition. Addition of oxygen to the upwelling hydrothermal fluid would result in the oxidation of methane to bicarbonate according to the reaction:



which would result in the concomitant generation of bicarbonate ions and a decrease in pH. Both changes would render dolomite more soluble and would result in hydrothermal karst formation for which there is ample field evidence (see Dzułyński & Sass-Gustkiewicz, 1982).

The solubility of sphalerite as bisulphide and chloride complexes after Anderson (1975) is also shown in Figure 9. Significant zinc ( $> 0.6$  ppm) can be taken into solution below a pH of about 3.5 and above an oxygen fugacity of  $10^{-51.5}$ . Conditions under which the fluid contains sufficient reduced sulphur to precipitate sphalerite are even more restricted and are shown as the hachured area in Figure 9. Clearly conditions prevailing during metal transport and deposition (areas *A* and *B* in Figure 9) are far removed from conditions under which zinc can be transported as inorganic bisulphide and chloride complexes. Giordano & Barnes (1981) came to similar conclusions regarding Mississippi Valley-type deposits in general, and concluded that organometallic complexes (in particular the salicylate complex) are probably responsible for metal transport.

One can only speculate regarding the causes of metal precipitation in the Cracovian-Silesian area, but evidently the stability of the metal complexes decreased as a result of changes that took place as the hydrothermal fluids flowed through the carbonate host rocks. These changes may have resulted from the mixing of cool, oxidizing near-surface waters with the hydrothermal brines, and may have included a drop in temperature, a decrease in salinity and pH, and an increase in oxygen fugacity. If the hydrothermal fluids had been in contact with gypsiferous beds found in the Buntsandstein (Fig. 3), addition of sulphur may also have played a role in metal precipitation.

### ORE GENESIS MODEL

The preferred model for the genesis of the Cracovian-Silesian Zn-Pb deposits can be summarized as follows:

1. Geopressured zones developed within the deep parts of the Upper Silesian basin. The fluids were saline and reducing hot brines that may have consisted of connate water, meteoric recharge water emplaced prior to the Miocene, and diagenetic water generated as a result of transformation of smectite to illite.

2. Periodically these fluids were expelled towards the surface mainly as a result of fluid overpressure, but possibly aided by increased heat flow in the Upper Silesian basin and seismic pumping along its tectonically active margin. Hydrostatic head resulting from uplift in the south may have helped focus flow towards the northeast, where a Caledonian and Variscan zone of structural complexity is present.

3. Fluids expelled during Triassic sedimentation gave rise to several synsedimentary concentrations of zinc and lead.

4. After deposition and lithification of Triassic carbonates the area was uplifted above sea level and normal karst developed above the paleo-water table. The karst developed mainly within the Lower Muschelkalk, but locally it also formed in older carbonates where these extended as elevations into the Triassic sediments.

5. Several major expulsions of geopressured fluids took place during Early Cimmerian movement (Late Triassic to Early Jurassic). The hydrothermal fluids were emplaced mainly along paleokarst conduits. These fluids caused regional dolomitization, formation of extensive hydrothermal karst, and deposition of metasomatic and cavity-filling ore. The cavity-filling ore was deposited fast, apparently from supersaturated solutions, possibly as a result of mixing of hot, reducing brines with cold, oxygenated near-surface water.

6. Further mineralization, though probably on a smaller scale, took place during the Late Cimmerian and Laramian tectonic phases.

### EXPLORATION GUIDELINES

The most important factors that favoured the formation of the Cracovian-Silesian Zn-Pb deposits were the presence of an environment allowing the fast, episodic and focused expulsion of deep reducing basinal brines, and the presence of a shallow aquifer into which these brines flowed. Thus, all known economic deposits lie along the northeastern margin of the Upper Silesian basin within a paleo-aquifer that lay mainly in the Lower Muschelkalk. Furthermore all known economic deposits lie within the broad area of ore-bearing dolomite (Fig. 3), the precursor of the main episodes of mineralization; and to the southwest of the chain of pre-Triassic elevations (Fig. 3), which apparently acted as a partial barrier to the flow of hydrothermal fluids. The area to the southwest of the paleoelevations has been explored intensely and major new discoveries of Mississippi Valley-type deposits are unlikely. No major deposits have been discovered to the northeast of the pa-

leoelevations, however, they could be present downstream of a location where the barrier has been massively breached.

Synsedimentary Triassic deposits associated with earlier pulses of fluid from the Upper Silesian basin, might also represent a suitable target for exploration. Synsedimentary occurrences recognized to date are thin and well below ore grade. However, the hydrothermal fluid from which they were deposited was probably denser than sea water and thus would have collected in local depressions of the Triassic sea bottom. It is in such Triassic basins that the search for larger stratiform Zn-Pb deposits could be successful.

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## Streszczenie

**GENEZA ZŁÓŻ CYNKU I OŁOWIU  
REGIONU ŚLĄSKO-KRAKOWSKIEGO**

Antoni Wodzicki

Złóża cynku i ołowiu rejonu śląsko-krakowskiego (Fig. 1–6) występują głównie w utworach węglanowych środkowego triasu, w obrębie strefy przepuszczalnej, która rozwinęła się w późnym triasie i wczesnej jurze, gdy obszar ten znajdował się powyżej poziomu morza. Złóża znajdują się (1) na południowy zachód od strefy Myszków-Kraków, w skład której wchodzi paleozoiczny flisz o miąższości 11 km, sfałdowany i zmetamorfizowany w facji zieleńcowej w czasie orogenezy kaledońskiej, oraz granitoidy kaledońskie i waryscyjskie; (2) wzdłuż północno-wschodniego obrzeżenia basenu górnośląskiego zbudowanego z utworów molasowych o miąższości dochodzącej do 8000 m oraz (3) w obrębie permskiego rowu tektonicznego łączącego się ku północy z głównym basenem permskim Niżu Polskiego. Ruda zawiera sfaleryt, galenę, siarczki żelaza oraz w mniejszej ilości baryt i sole siarkowe. Złóża zawierają: (a) okruszcowanie metasomatyczne zastępujące dolomit kruszczośny, (b) okruszcowanie wypełniające wolne przestrzenie w brekcjach krasu hydrotermalnego, (c) rozległe synsedymencyjne anomalie Zn-Pb w osadach triasowych i (d) niewielkie okruszcowanie rozwinięte wzdłuż uskoku przecinających podłoże niektórych kopalń. Skład izotopowy ołowiu w galenie jest niezwykle jednolity; leży on na krzywej rozwoju izotopowego orogenu i ma wiek modelowy nieznacznie młodszy od wieku skał macierzystych. Okruszcowanie zostało wytrącone z roztworów solnych o objętości co najmniej 70 km<sup>3</sup> w temperaturze około 100°C. Procesy wytrącania nastąpiły w szeregu pulsów, które rozpoczęły się powstaniem anomalii Zn-Pb w triasie, uległy intensyfikacji w fazach wczesnokimeryjskich, kiedy powstała większość złóż metasomatycznych oraz wypełniających próżnie, i zakończyły się słabym okruszcowaniem podczas faz późnokimeryjskich i laramijskich.

Wśród źródeł energii, które mogły spowodować przemieszczanie roztworów hydrotermalnych (Tab. 1, Fig. 8) podwyższony gradient geotermiczny i mechanizm artezyjski nie wchodzi w rachubę z powodu braku przejawów magmatyzmu lub zmniejszenia miąższości skorupy ziemskiej oraz braku dowodów na istnienie pobliskiego, wysokiego pasma górskiego w czasie tworzenia się okruszcowania. Najbardziej prawdopodobnym mechanizmem, jak się wydaje, jest nadciśnienie wód podziemnych, zbliżone do ciśnienia geostatycznego. Wskazuje na to bliskość głęboko pogrzebanych sekwencji skalnych zdolnych do generowania i magazynowania gorących roztworów solnych. Znane są też uskoki reaktywowane w czasie ruchów wczesnokimeryjskich, wzdłuż których mogła zachodzić migracja roztworów do przepuszczalnych utworów triasu.

Prawdopodobne źródła roztworów hydrotermalnych przedstawiono w Tabeli 1. Źródło magmowe można wykluczyć z powodu braku przejawów syngenetycznego magmatyzmu i na podstawie danych izotopowych (Fig. 7). Podobnie nie wchodzi w rachubę flisz kaledoński i utwory permskie. Flisz utracił wodę w trakcie metamorfozy regionalnej, a basen permski jest zbyt odległy od stref złożowych. Ponadto perm rejonu śląsko-krakowskiego składa się z osadów nieprzepuszczalnych. Z kolei utwory triasu nie znalazły się nigdy na dostatecznie dużej głębokości, aby mogły w nich powstać gorące roztwory. Ich źródłem był najprawdopodobniej górnośląski basen węglowy. Jego budowa strukturalna, duże miąższości i skład litologiczny sprzyjały generowaniu i epizodycznemu wypychaniu gorących, zasolonych roztworów ku powierzchni. Skład izotopowy ołowiu w galenie (Fig. 7) jest zgodny z takim źródłem roztworów.

Warunki geochemiczne w trakcie transportu metali przedstawia Figura 9. Skonstruowano ją opierając się na założeniu, że dzisiejsze wody podziemne basenu górnośląskiego mają podobny skład chemiczny do składu, jaki miały roztwory, z których powstało okruszcowanie. Gdy roztwory te znajdowały się jeszcze w utworach zagłębia, były w równowadze chemicznej z układem kwarc—illit—skaleń potasowy oraz metan—dwutlenek węgla (obszar *A* na Fig. 9). Podczas dolomityzacji, powstawania krasu hydrotermalnego i wytrącania okruszcowania aktywność ciśnieniowa tlenu ulegała zwiększeniu, a pH obniżeniu (obszar *B* na Fig. 9), prawdopodobnie w wyniku napływu natleniowych wód meteorycznych. Utlenienie metanu spowodowało obniżenie pH, silne rozpuszczanie węglanów i rozwój krasu hydrotermalnego. Cynk i ołów były transportowane w kompleksach metaloorganicznych, które przechodziły w fazy niestabilne w pobliżu powierzchni ziemi.

Epizodyczne wyciskanie metanonośnych solanek z utworów górnośląskiego basenu węglowego i postępujące ich rozcieńczanie natlenionymi wodami meteorycznymi jest, jak się wydaje, najlepszym wyjaśnieniem genezy epigenetycznej mineralizacji w rejonie śląsko-krakowskim. Wcześniejsze wyparcie roztworów na dno morza triasowego spowodowało powstanie synsedymencyjnych anomalii Zn-Pb. Zatem poszukiwanie złóż typu warstwowego w pobliskich basenach triasowych może okazać się owocne.