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An ore genetic model for the Lubin–Sieroszowice mining district, Poland

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Abstract. The Lubin–Sieroszowice mining district is a world-class copper–silver, stratabound ore deposit that lies near the Lower–Upper Permian boundary. It transgresses the Werra dolomite, the Kupferschiefer organic-rich shale and the Weissliegendes sandstone, which overlie barren Rotliegendes sandstone. On the basis of underground and microscope observations and light stable isotope data, and thermodynamic calculations, a new ore genesis model is proposed whereby ore minerals were deposited in the following stages: Stage 0 was synsedimentary or earliest diagenetic and contains 100s ppm of base metals trapped by clay minerals, and minor sulphides. Stage I was early diagenetic and contains 1000s ppm base metals. It is characterized by bornite and overlying chalcopyrite + pyrite that lie a short distance above the Rotliegendes/Weissliegendes contact. The sulphides were deposited near the interface between an overlying, buffered, reducing fluid (1), largely derived from the Kupferschiefer, and an oxidizing fluid (2) in the Rotliegendes. Stage II is the main ore-forming stage. This stage is late diagenetic, peneconcordant, lies near the Kupferschiefer/Weissliegendes contact, and contains several percent base metals. It is associated with the hematite-bearing Rote Fäule facies and is characterized by vertical zonation. A central chalcocite zone is flanked above and below by bornite and chalcopyrite. Silver occurs with all the above sulphides. Galena and sphalerite occur mainly just above copper zone, whereas pyrite is usually present in the upper part of the copper zone and together with galena and sphalerite. Metals were transported in a copper-rich oxidizing fluid (3), which probably originated deep in the Permian basin, reacted with organic matter in the Kupferschiefer, and mixed with reducing fluid (1) in the Weissliegendes, resulting in the observed mineral zonation. Stage III is late diagenetic, discordant and is represented by massive and dispersed chalcocite ore present on the peripheries and below anhydrite-cemented Weissliegendes sandstone. It resulted from redistribution of earlier copper and silver minerals by descending, reduced, sulphur-rich fluids (4). Stage IV consists of rare polymetallic veins of no economic importance that cut the stratigraphy and are probably related to Alpine tectonism. The richest and thickest ore is in the Weissliegendes, 10–15 km east of the Rote Fäule facies (Fig. 1). It probably occupies structures that trapped fluid (1) which was the main precipitant of metals in the sandstone.

The copper–silver deposits of the Lubin–Sieroszowice district are examples of peneconcordant red bed-associated deposits. They are located about 75 km northwest of Wrocław in southwestern Poland, on the northwest-dipping limb of the Fore-Sudetic Monocline (Fig. 1, 2). The deposit currently being mined extends over nearly 600 km^2, varies in thickness from 0.4 to 26 m, and contains on average about 2% Cu, 40 ppm Ag, 0.2% Pb and 0.1% Zn, as well as anomalous concentrations of As, Ni, Co, Au and PGMs. The deposit limits are undefined down-dip to the northeast and the mine workings will eventually reach maximum economic mining depth. It has been estimated that the entire mining district contains about 68 Mt Cu, 170,000 t Ag, 5.2 Mt Pb and similar amounts of Zn. Therefore, the copper deposit of the district ranks as one of the largest ore deposits in the world.

The ore lies near the Lower (Rotliegendes)/Upper (Zechstein) Permian boundary which it transgresses at low angles. The deposits are similar in many ways to the Zambian copper belt (Annels 1974), White Pine, Michigan (Brown 1971), Spar Lake, Montana (Hayes and Einaudi 1986; Hayes 1990) and the Udokansk and Dzhezkazkan ore fields in Russia (Gablina and Tsepin 1975). These deposits have a similar mineralogical zonation, are associated with continental red beds, and they lie near regional redox boundaries defined by a contact between hematite- and pyrite- ± carbon-bearing sediments.

Two main models have been proposed for the origin of the Lubin–Sieroszowice district, namely syngenetic and diagenetic. According to the first model, metals were

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precipitated within centimeters or meters of the sea water–sediment interface from an anomalous sea water (Harańczyk 1972; Konstantynowicz 1965, 1973; Tomaszewski 1981, 1986; Sawłowicz 1990). According to the diagenetic model the metals were introduced from the underlying Rotliegendes and were deposited at a redox boundary near the Zechstein contact during early diagenesis (Rentzch 1974; Brown 1978; Mayer and Piestrzyński 1985; Haynes 1986a, 1986b; Haynes and Bloom 1987a, 1987b; Oszczepalski 1989) or during late diagenesis (Jowett 1986; Jowett et al. 1987a; Hammer et al. 1990; Oszczepalski and Rydzewski 1991; Bechtel and Püttmann 1991). A variant of this model suggests that the precipitation of metals took place along the interface between the ascending oxidizing fluid and a fluid descending from the overlying Zechstein evaporites (Kucha and Pawlikowski 1986). A similar model was suggested by Davidson (1962). Finally, Vaughan et al. (1989) distinguish four types of Kupferschiefer mineral deposits:

1. Synsedimentary mineralization characterized by framboidal pyrite and about 100 ppm base metals;
2. Early diagenetic 'average mineralization' containing 2000 ppm base metals derived from the immediately underlying lithologies;
3. Late diagenetic 'ore mineralization' with about 3% base metals occurring at the Rotliegende basin margins and derived from oxidizing basinal fluids;
4. Minor post diagenetic structurally controlled veins.

Nevertheless, irrespective of the timing and detailed mechanism of mineralization, most recent workers agree that the deposits are largely diagenetic or post diagenetic in age. Compelling evidence for this is the well-documented fact that the deposits cut stratigraphy in a complex manner (see for instance Rentzsch 1974; Rydzewski 1976; Mayer and Piestrzyński 1985; Kucha and Głuszek 1985; Kucha and Pawlikowski 1986; Jowett et al. 1987a; Oszczepalski 1989) and that replacement of framework grains (Banaś et al. 1982, Kucha 1985), carbonates and clay matrix in the sandstone (Mayer and Piestrzyński 1982), and carbonates of the Werra limestones (Piestrzyński 1991) by sulphides is commonplace.

In the present paper we summarize the geologic setting of the district, describe the succession, zonation, and isotopic composition of the ore minerals, and construct activity diagrams showing stability fields of various Cu, Ag, Pb, Zn and Fe minerals and their solubilities as various chloride and bisuphide complexes. On these bases we suggest a new model for the origin of these deposits that is consistent with the above observations, and involves several stages of ore mineral deposition.

Geologic setting

The Lubin–Sieroszowice district lies close to the southern boundary of the Permian sedimentary basin (Fig. 1). The geology of the district has been described by Krasoń (1967), Tomaszewski (1978, 1981), Rydzewski (1978), Pokorski (1981), Kłapciński et al. (1984) and Oszczepalski (1989). The stratigraphy is shown in Figs. 2, 3a and 4a. Basement consists mainly of Proterozoic gneisses, schists, phyllites and granitoids. It is unconformably overlain by grey to brownish-grey, deformed Carboniferous conglomerates, sandstones and mudstones, and by Permian rocks that are relatively undisturbed.

The Early Permian Rotliegendes contains hematite and/or goethite that rim clastic grains, feldspars that are partly altered to clays, and a matrix that locally contains gypsum (Tomaszewski 1978). It has been subdivided into lower and upper red bed sequences (Kłapciński et al. 1984). The lower red beds are up to 150 m thick and consist of two upwardly fining reddish-brown conglomerate–sandstone–mudstone sequences. They are capped by a few meters to over 250 m of bimodal volcanics–rhyolites and rhyolitic tuffs and trachybasalts, which to the north of the mining district achieve a thickness greater than 1000 m (Ryka 1981; Pokorski 1981). The upper red beds are up to 500 m thick and consist of sandstones and local volcanic-derived conglomerates. The sandstones are fine to medium-grained, moderately well sorted, subangular, and contain about 80% quartz, 20% feldspar and a matrix of carbonate, gypsum and clays. The Rotliegendes are overlain by less than 1 m to over 40 m of white sandstone (Weissliegendes) (Fig. 3) which lacks hematite or goethite and locally contains sulphides. In part it represents the Rotliegendes reworked during the Zechstein transgression (Konstantynowicz 1971; Błaszczyk 1981; Alexandrowicz et al. 1982), but reduction and sulphidation of these rocks probably took place during diagenesis (Konstantynowicz 1971; Alexandrowicz et al. 1982; Kucha and Pawlikowski 1986). The contact between the Rotliegendes and the Weissliegendes is gradational and irregular (Jerzykiewicz et al. 1976; Nemec and Porębski 1981).

The Lower Permian rocks are conformably overlain by Upper Permian evaporitic cyclothems and by Triassic red beds and carbonates. The stratigraphy is summarized by Oberc and Tomaszewski (1963); Jerzykiewicz et al. (1976); Peryt (1978); Tomaszewski (1978); Błaszczyk (1981); Pokorski (1981); Nemec and Porębski (1981); Oszczepalski and Rydzewski (1987). The Basal Limestone overlies the

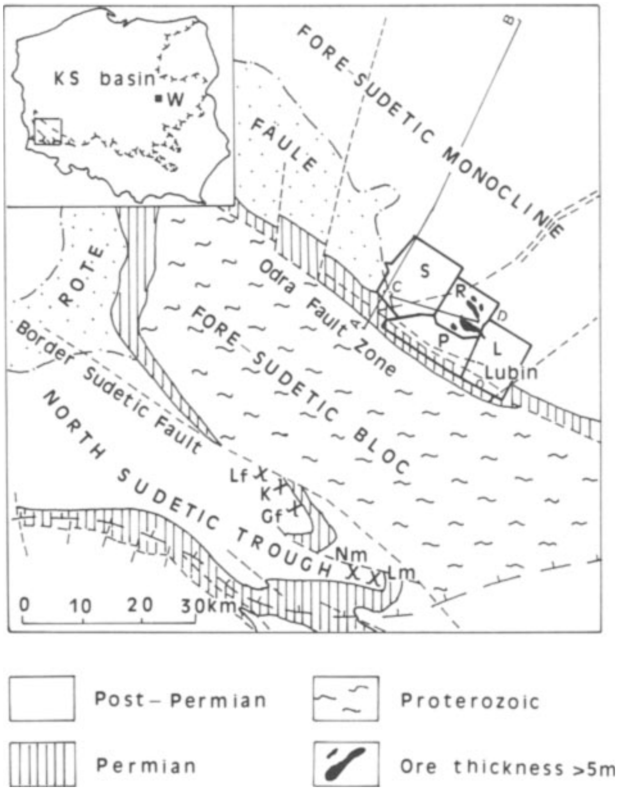

Fig. 1. Location and geologic setting of the Lubin–Sieroszowice district. *S* Sieroszowice; *R* Rudna; *P* Polkowice; *L* Lubin mines; *K* Konrad mine in the North-Sudetic Trough; *Lf* Lubichowa field; *Gf* Grodziec field; *Lm* Lena mine; *Nm* Nowy Kościół mine; *W* Warsaw

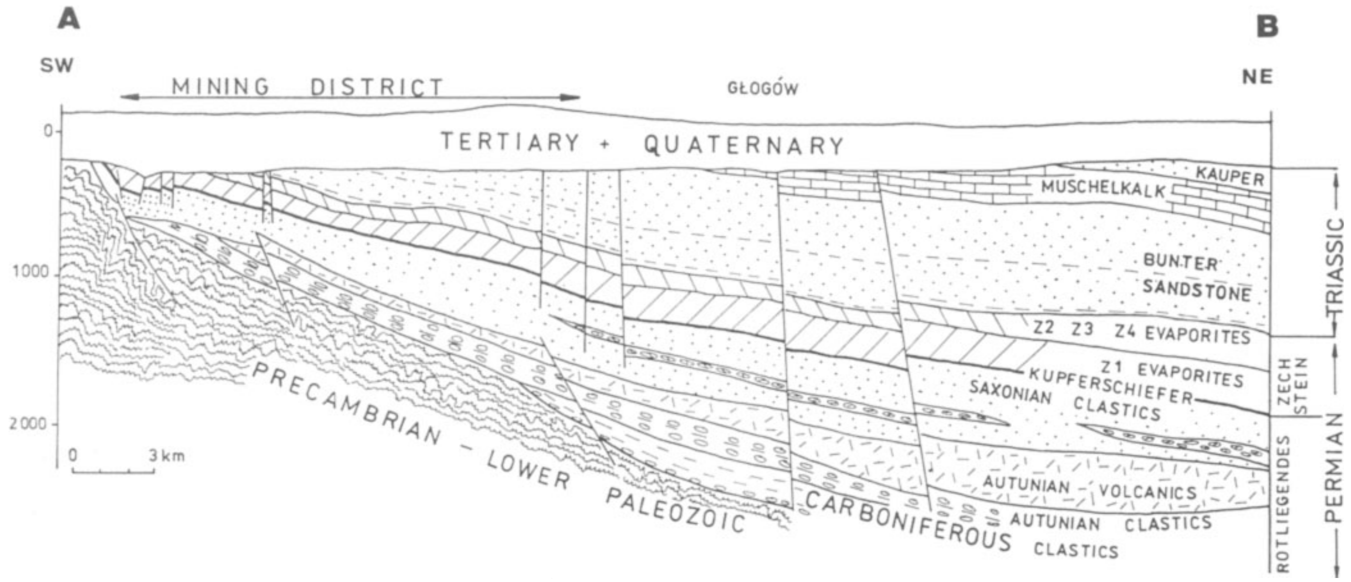

Fig. 2. Geologic cross-section through the district along *line A–B* in Fig. 1. Vertical scale5

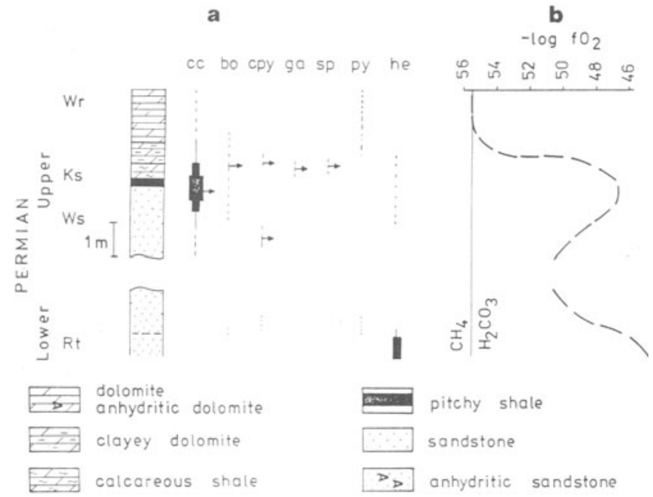

Fig. 3a, b. Stratigraphic column through 'typical' section in the Lubin–Sieroszowice district. **a** Mineral zonation modified after Mayer and Piestrzyński (1985); *Wide bar* > 5%; *Narrow bar* 2–5%; *line* 1–2%; *dashed line* 0.25–1%; *dotted line* present: *Wr* Werra dolomite; *Ks* Kupferschiefer; *Ws* Weissliegendes; *Rt* Rotliegendes. **b** Variation in oxygen fugacity as defined by mineralogy (see interpretation of activity diagrams)

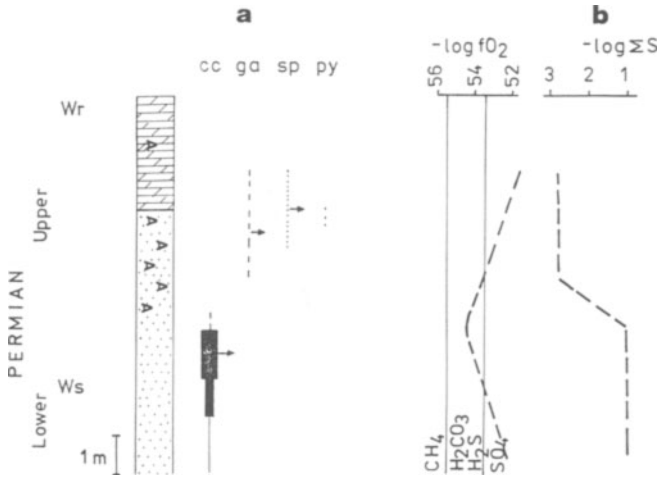

Fig. 4a, b. Stratigraphic column through anhydrite body. **a** Mineral zonation modified after Mayer and Pietrzyński (1982, 1985). Symbols as in Fig. 3. **b** Variation in total sulphur activity and oxygen fugacity as defined by mineralogy (see interpretation of activity diagrams)

Weissliegendes and is 0–0.3 m thick. It is an argillaceous, organic-bearing micrite that is locally sparry. The Kupferschiefer, a black fissile shale, is in sharp contact with the Basal Limestone or the Weissliegendes, and consists of clays, fine-grained dolomite and organic material. It is up to 1 m thick, though most commonly the thickness varies between 0.3 and 0.5 m. The Kupferschiefer is locally missing in several northwest-striking zones, and the overlying dolomite is in direct contact with the Basal Limestone or the Weissliegendes (Błaszczyk 1981). The Kupferschiefer grades upward into a dark-grey organic-bearing dolomitic micrite and sparite that contain lenses of anhydrite and gypsum and are up to 80 m thick. The carbonates grade upward into anhydrite, halite and the remaining Zechstein sequences. According to Jowet et al. (1987a) the Zechstein sediments form an aquiclude which hindered the escape of basinal fluids during diagenesis and helped channel their circulation. The Permian sediments generally dip 3–6° to the northeast, but the dip steepens towards the Odra fault zone (Fig. 2) and the Fore-Sudetic block.

The tectonic development of central Europe (including south-western Poland) has been summarized by Ziegler (1982, 1984). The Carboniferous Hercynian orogeny was followed by a period of erosion leaving only local remnants of Carboniferous rocks in the Lubin area. During the Early Permian, extensional rifting was associated with bimodal volcanism and continental red bed sedimentation in local tectonic depressions. The Late Permian was a tectonically quiet period accompanied by rapid marine transgression and deposition of the Zechstein evaporites. Renewed extensional rifting occurred during Triassic and Early Jurassic, and according to the paleomagnetic data of Jowett (1987b), may have been associated with the mineralization at Lubin. Tilting of the Fore-Sudetic monocline and uplift of the Fore-Sudetic block probably took place during the Laramian phase of the Alpine orogeny (Pokorski 1978).

Form of the deposits

The mineral deposits in the district are mainly stratiform, peneconcordant, and locally discordant, but cross-cutting veins also occur (Mayer and Piestrzyński 1985). The stratiform deposit is restricted to the Kupferschiefer, and according to Wedepohl (1964) and Vaughan et al. (1989), it extends over the entire Kupferschiefer sedimentary basin, and typically contains about 100 ppm base metals.

The peneconcordant ore minerals constitute most of the ore in the district. Typically the ore contains several percent base metals. The ore minerals occur within the Werra Limestone, the Kupferschiefer and the upper part of the Weissliegendes, vary in thickness from 0.4 to several meters and cut across the stratigraphy in a complex fashion (Mayer and Piestrzyński 1985) (Fig. 5). A much less distinct and lower grade band of sulphides is present a few meters above the Rotliegendes/Weissliegendes contact.

The ore minerals that are peripheral to the anhydritic zones (Fig. 5) are in the Weissliegendes and have been described by Mayer and Piestrzyński (1982), and Kucha and Pawlikowski (1986). The anhydritic zones themselves are restricted to those parts of the mining district where the Kupferschiefer is missing. Here the anhydrite extends from anhydrite-rich Werra carbonates to the Weissliegendes in an irregular fashion. Copper ore is peripheral to the anhydrite in the Weissliegendes. It is up to 26 m in thickness and is higher grade in the vicinity of the anhydrite body than is usual for peneconcordant ore. Furthermore, according to the underground mapping of Mayer and Piestrzyński (1982) isolated remnants of peneconcordant ore remain within the anhydrite bodies, showing that the anhydrite event post-dates the peneconcordant mineralization.

The steeply dipping veins occur mainly in the Werra carbonate and locally in the Kupferschiefer and Weissliegendes, and are up to several meters long and up to 80 cm wide. They displace the stratigraphy and, according to Pokorski (1978), are associated with Alpine tectonism.

Ore mineral succession

The ore mineralogy of the Lubin–Sieroszowice district has been extensively studied since the mid 1960s (see for example Jarosz 1966; Harańczyk 1972; Harańczyk and Jarosz 1973; Kucha 1976a, 1976b; Mayer and Piestrzyński 1985; Salamon 1979). Chalcocite is the dominant ore mineral and can constitute up to 90 vol.% of the rock. In addition the ore contains decreasing amounts of bornite, chalcopyrite, digenite, covellite, galena, sphalerite, pyrite, hematite, tennantite and tetrahedrite, and trace amounts of many other Cu, Ag, Ni, Co, Mo, Hg, Bi, U, Au, Pd and

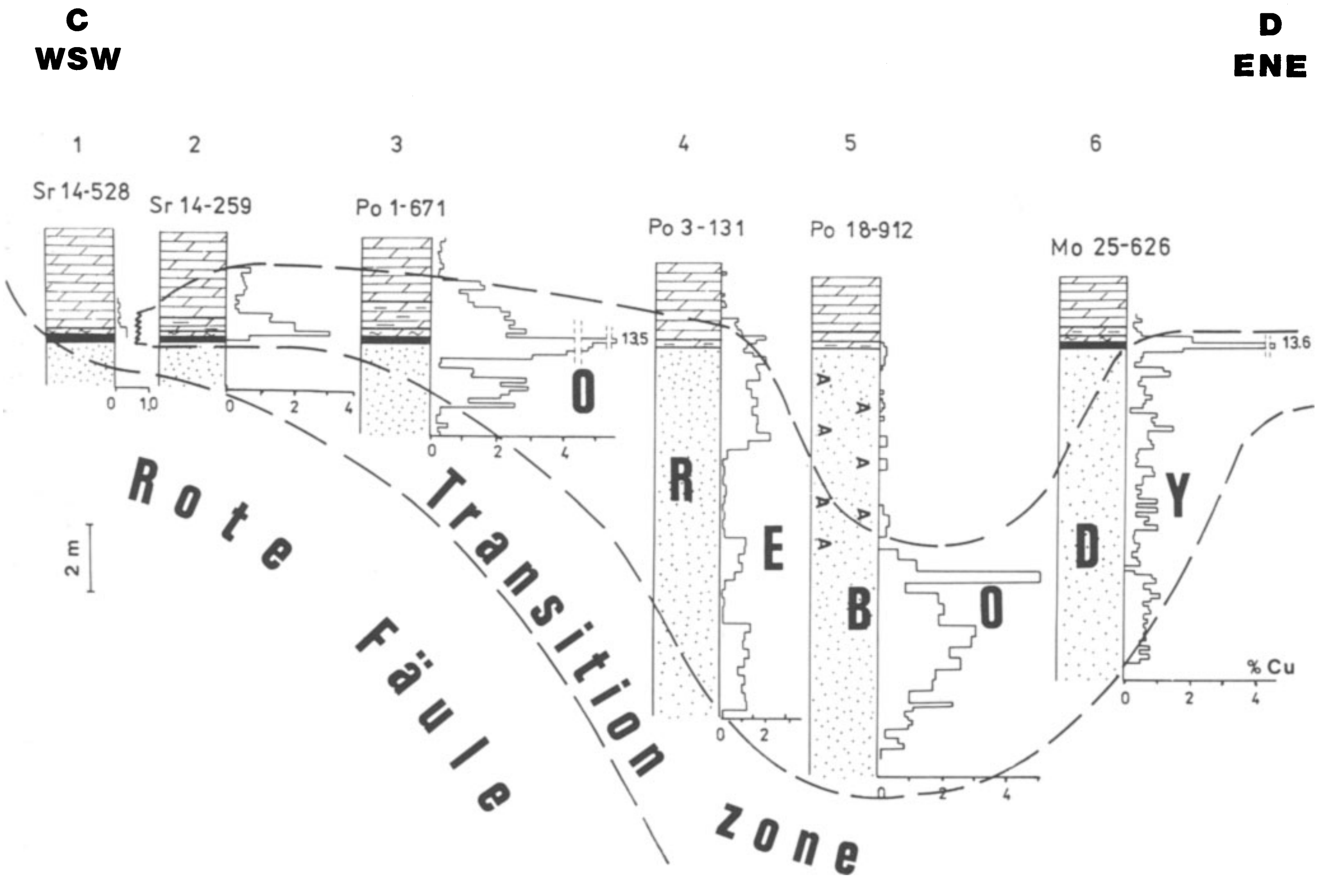

Fig. 5. Stratigraphic columns through Sieroszowice (1 and 2) and Rudna (3, 4, 5 and 6) mines, along profile C–D in Fig. 1, showing quantitative distribution of copper and its relation to the Rote Fäule facies. Columns 4 and 5 are adjacent to, and through anhydrite bodies respectively. Symbols as in Fig. 3

Pt minerals occur locally. In the Werra rocks Zn- and Pb-bearing sulphates and carbonates have been recognized (Piestrzyński 1991). They are usually replaced by sphalerite and galena respectively.

Detailed petrological studies of about 10,000 polished sections by one of us (AP) and a survey of the literature make it possible to establish an overall succession of mineral deposition (Fig. 6). Four main stages of sulphides have been recognized as a result of microscopic analysis.

Stage 0 is synsedimentary and/or earliest diagenetic and contains 100 ppm base metals trapped by clay minerals, and probably trace amounts of stratiform sulphides e.g. bacteriogenic framboidal pyrite and minor disseminated chalcopyrite, digenite chalcocite, bornite, and probably anilite (Rydzewski 1969; Harańczyk 1972; Jung and Knitzschke 1976; Tomaszewski 1978; Sawłowicz 1990). Experimental work of Helios-Rybicka (1991) and Helios-Rybicka et al. (1991) suggest that base metals may also have accumulated in clay minerals. In the Lubin–Sieroszowice district the stratiform sulphides have been masked by later mineralization. Stage 0 was followed by dolomitization of Werra carbonates with local crystallization of idiomorphic dolorhombs and minor xenomorphic sulphide aggregates.

Stage I ore minerals are peneconcordant, consist of bornite and overlying chalcopyrite + pyrite, and occur a short distance above the Rotliegendes/Weissliegendes contact (Mayer and Piestrzyński 1982).

Stage II consists mainly of chalcocite and lesser amounts of digenite, covellite, silver-bearing minerals, bornite, chalcopyrite, sphalerite, galena, pyrite and hematite (Salamon 1979; Kucha 1981, 1982; Mayer and Piestrzyński 1985). These minerals were deposited more or less contemporaneously, though not at the same location (see section on mineral zonation). In the Kupferschiefer and the overlying Werra carbonates, they consist of disseminated ore and both horizontal and vertical veinlets which, according to Jowett (1987), formed as a result of hydrofracturing during Kimmerian tectonism. This is associated with progressive oxidation of organic matter, especially near the Rote Fäule facies (Bechtel and Püttmann 1991). In the Weissliegendes Stage II ore is disseminated and locally it occurs as sets of up to 60 sulphide bands that are generally discordant to the bedding (Jerzykiewicz et al. 1976; Mayer and Piestrzyński 1990; Sawłowicz and Wedepohl 1992). The bands are up to 1.5 cm apart and have one sharp (lower) and one diffuse (upper) border, except for the bottom band which has two diffuse borders. They probably result from diffusion of H_2S and metal complexes from opposite directions (Mayer and Piestrzyński 1990), which implies that two hydrothermal fluids were present during this stage. Petrographic relations do not indicate temporal relations between Stages I and II, but interpretation of mineral zonation (see section on interpretation of activity diagrams) suggests that Stage I is earlier.

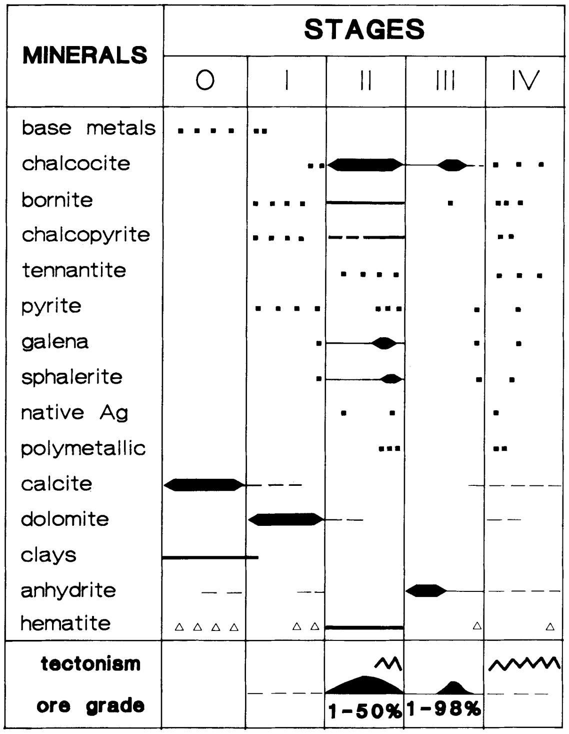

Fig. 6. Generalized mineral succession in the Lubin–Sieroszowice district. Hematite from the Rote Fäule is not included

Stage III is associated with anhydritization whereby anhydrite fills intergranular spaces, and replaces sulphides, framework grains and matrix in the Weissliegendes (Mayer and Piestrzyński 1982). Stage II copper minerals have been replaced by anhydrite and only galena, sphalerite and marcasite remain in the anhydritic bodies but have been displaced downward from their earlier elevation. Outside the anhydrite bodies and within the Weissliegendes, chalcocite and minor digenite replace all pre-existing phases including feldspar, quartz, carbonates and clays (Banaś et al. 1982; Kucha 1985). Stage III represents remobilization of earlier minerals.

Stage IV consists of steeply dipping veins associated with Alpine tectonism (Vaughan et al. 1989). The veins contain barite, anhydrite, gypsum, carbonates, bornite, chalcopyrite, tennantite, galena, sphalerite, Fe–Ni–Co sulphides and arsenides, and represent earlier ore remobilized during tectonism. This stage is not of economic importance.

Mineral zonation

Both horizontal and vertical zonation have been noted from the district. Horizontal zonation has been reported on the mining district, regional (southwestern Poland) and on the Polish Permian basin scales. On the mining district scale (200 km^2) and on the basis of about 200 drill holes, Konstantynowicz (1971, see Fig. 74) and Tomaszewski (1978, see Fig. 34) report a mineralogical zonation as follows: from the WSW to the ENE characteristic ore minerals are: hematite (Rote Fäule facies); chalcocite; bornite; chalcopyrite. On a regional scale of southwest Poland (20,000 km^2), and on the basis of up to 200 drill holes, Rydzewski (1978), Jowett et al. (1987a, see Fig. 6) and Oszczepalski (1989, see Fig. 8) report a zonation as follows: hematite (Rote Fäule facies); copper; lead; zinc; pyrite. A similar zonation has been reported from the

Mansfeld mining district in Germany by Rentzch (1974). On the scale of the polish Permian sedimentary basin (174,000 km^2), and on the basis of about 800 drill holes (one hole per 216 km^2) Oszczepalski (1989, see Fig. 9) and Oszczepalski and Rydzewski (1991, see Fig. 5) note a similar basin-wide zonation, with the hematitic Rote Fäule occurring mainly in west-central Poland, and giving way to copper, zinc and lead, and pyrite towards the east and north.

The most detailed study regarding zonation in the district has been carried out by Mayer and Piestrzyński (1985) at the Rudna mine. Their study is based on the point count analysis (1000–3000 points) of 1321 samples from 109 profiles collected over an area of approximately 15 km^2. This study is particularly important because the Rudna mine coincides with the chalcocite/bornite boundary as reported by Konstantynowicz (1971) and Tomaszewski (1978), and the copper/lead boundary as reported by Jowett et al. (1987a) and Oszczepalski (1989). Within the Kupferschiefer (Fig. 7 of Mayer and Piestrzyński 1985) chalcocite is the dominant mineral throughout the mine, the distribution of bornite, chalcopyrite, galena and sphalerite appears quite random, and no horizontal zonation is evident. Within the top 0.5 m of the Weissliegendes (see Fig. 6 of Mayer and Piestrzyński 1985), the highest chalcocite concentration lies in the southwest part of the mine, and the ratio of bornite to chalcocite and the galena concentration increase towards the northeast. It should be stressed that galena even here remains a minor constituent of the ore. Moreover, these patterns are ill-defined and it is not certain whether they reflect the mineralogical zonation reported by Konstantynowicz (1971) and Tomaszewski (1978), and the transition from copper to lead-rich zones noted by Jowett et al. (1987a) and Oszczepalski (1989).

Vertical zonation has been recognized by Konstantynowicz (1971), Banaś (1980), Banaś et al. (1983), Kucha and Głuszek (1985), Mayer and Piestrzyński (1985), Kucha (1990) and others. There are two distinct patterns that are present in the district, namely, a 'typical' pattern characteristic of areas where the Kupferschiefer is present, and a pattern associated with the anhydrite zones which occur only in Kupferschiefer-free parts of the district. The 'typical' pattern is shown in Fig. 3a. It is characterized by a central copper-rich chalcocite zone which generally lies within the Kupferschiefer and the underlying Weissliegendes, and is flanked above and below by bornite and chalcopyrite. Galena and sphalerite are present above the copper-rich ore zone but are not present below it. Below the copper-rich zone, close to the underlying hematite-bearing rocks (Rote Fäule), lies lower-grade copper mineralization characterized by chalcopyrite and bornite. Pyrite is present above the main copper-rich chalcocite zone and within the lower copper zone. Silver is found in the main copper zone in crystalline solution in chalcocite and bornite, as stromeyerite, acanthite and locally as native silver. The highest concentration of native silver is observed in the transition zone between the copper and the lead–zinc zones where it lies in the Kupferschiefer. Hematite is intergrown with bornite (Kucha 1980) and also is characteristic of the Rote Fäule (Fig. 3a).

The distribution of minerals near the anhydritic zones is shown in Fig. 4a. Galena and sphalerite are present in the anhydritic rocks, though at a stratigraphically lower level than in the 'typical ore'. Chalcocite is present below and peripherally to the anhydritic zones. Silver is present in crystalline solution, locally as acanthite, but not as native silver. Some of the richest and thickest ore in the district lies below and adjacent to the anhydritic bodies (Figs. 1 and 5) (Mayer and Piestrzyński 1982; Kucha and Pawlikowski 1986).

Light stable isotope composition

The sulphur-isotope composition of the district has been investigated by Harańczyk (1984), Sawłowicz (1989), Jowett et al. (1991a), Jowett et al. (1991b) and the present study for which isotopic determinations were carried out by Professor St. Hałas, Physics Department, Maria Curie-Skłodowska University, Lublin. The results are summarized in Fig. 7 and can be divided into three groups: disseminated sulphides (average $\delta^{34}S = -34.8$); vein sulphides (average $\delta^{34}S = -30.5$); and 'massive' sulphides associated with anhydritic bodies (average $\delta^{34}S = -18.1$).

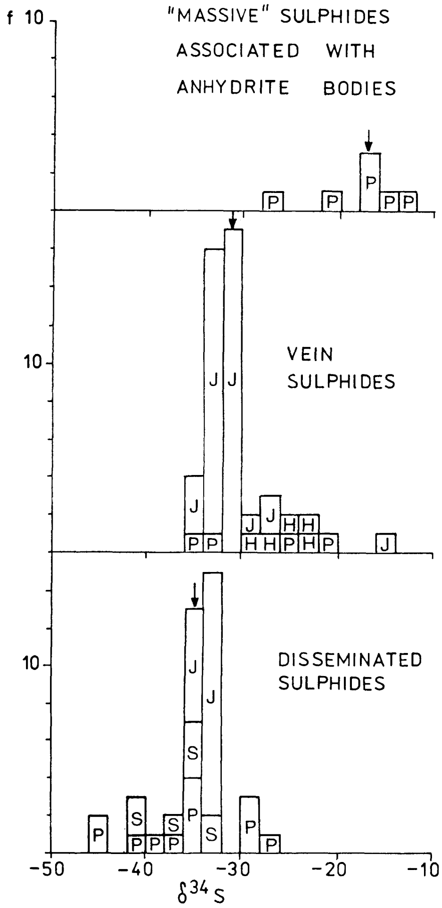

Fig. 7. Sulphur-isotope composition of disseminated and vein sulphides, and 'massive' sulphides associated with anhydrite bodies. *Arrows* indicate mean values for each group. Data from the following sources: *H* Harańczyk (1984); *S* Sawłowicz (1989); *J* Jowett et al. (1991a); *P* present study

The negative $\delta^{34}S$ values and the progressive enrichment in $\delta^{34}S$ with time have been intepreted by Sawłowicz (1989) as resulting from bacterial reduction of sulphate in an open system which gradually changed into a closed system during early diagenesis. Alternatively, the data can be interpreted as representing three separate sulphur sources. Following Jowett et al. (1991a), the difference between the disseminated and vein sulphur can be explained by postulating two sulphur sources: a light sulphur from the Kupferschiefer, and a $\delta^{34}S$-enriched sulphur from the Rotliegendes. Furthermore, the sulphide sulphur associated with the anhydritic bodies constitutes a distinct population representing a third sulphur source, probably related to the overlying anhydritic evaporites.

Oxygen- and carbon-isotope composition of carbonates from the Kupferschiefer have been investigated in the district by Sawłowicz (1989), and in Germany by Hammer et al. (1990) and Bechtel and Püttmann (1991). The carbonates become isotopically lighter as the Rote Fäule facies are approached. This is explained by interaction of the carbonates with ascending, oxidizing, isotopically light fluids associated with the mineralization.

Construction of activity diagrams

Activity diagrams which show phase boundaries and the solubilities of various complexes, are useful in describing hydrothermal systems. If the correct assumptions are made and the thermodynamic data used are reliable, it is possible to place limits on the chemical environment prevailing during mineral deposition, and thus place some constraints on the ore genesis model. This was previously attempted by Jasiński (1978a, 1978b, 1979) who constructed Eh–pH diagrams at 25 °C on the assumption that metals were deposited syngenetically. In the present study the epigenetic hydrothermal origin is accepted. The assumptions needed to construct activity diagrams are based on chemical analyses of present-day deep formation waters from the Permian basin, on reported fluid inclusion homogenization data, on calculated activities based on observed mineralogical composition in presumed source rocks, and on the sulphur-isotope composition of coexisting phases.

The average chemical composition (g/l) of deep formation waters from the Polish Permian basin is as follows: $Na^+ = 53.3$ ($\sigma = 23.98$, $V = 44\%$ for $n = 70$); $Ca^{++} = 27.3$ ($\sigma = 14.53$, $V = 52\%$ for $n = 77$); $Mg^{++} = 2.2$ ($\sigma = 1.53$, $V = 71\%$ for $n = 71$); $Cl^- = 137.1$ ($\sigma = 48.36$, $V = 35\%$ for $n = 77$); $SO_4^{--} = 1.0$ ($\sigma = 1.62$, $V = 163\%$ for $n = 74$); $HCO_3^- = 0.7$ ($\sigma = 1.21$, $V = 180\%$ for $n = 75$); pH = 6.3. ($\sigma = 0.97$, $V = 15\%$) (unpublished oil industry data) (see also Bojarska et al. 1978). The temperature prevailing during hydrothermal deposition is estimated to have been 100 °C. This is close to present-day deep Permian basin formation temperatures of 45–110 °C (Lubaś 1986), the preliminary fluid inclusion homogenization temperature of 120 °C in the German Kupferschiefer-type deposits (Tonn et al. 1987) and sulphur-isotope fractionation temperatures of 60–90 °C (Jowett et al. 1991b). Furthermore, because only low-temperature orthorhombic chalcocite is present, the temperature must have been below 105 °C (Roseboom 1966). The activities of Cl^- and Na^+ are estimated to have been 1.55 m and 0.92 m respectively. These estimates are based on the average concentrations in present-day formation waters and activity coefficients calculated using the extended Debye-Huckel equation of Helgenson et al. (1981) at a temperature of 100 °C and an ionic strength of 4.67. The activity of K^+ is estimated to have been 0.014 m. This estimate is based on the assumption of chemical equilibrium between albite and K-feldspar (see Appendix) in the Rotliegendes, at a temperature of 100 °C and Na^+ activity of 0.92 m. The activity of $SO_4^=$ is estimated to have been 0.0016 m, on the assumption that it was controlled by anhydrite solubility (gypsum, probably retrogressive after anhydrite, is present in the Rotliegendes). This is in reasonable agreement with the activity of 0.0005 m calculated from the analytical data. The pH is estimated to have been 6.3, based on the average pH of present-day formation waters. Furthermore, assuming equilibrium between K-feldspar and muscovite (see Appendix) in the Rotliegendes, and a K^+ activity of 0.014 m, the pH is calculated to be 6.36, in close agreement with the above estimate.

The activity diagram shown in Fig. 8 has been constructed on the bases of the above estimates and using the

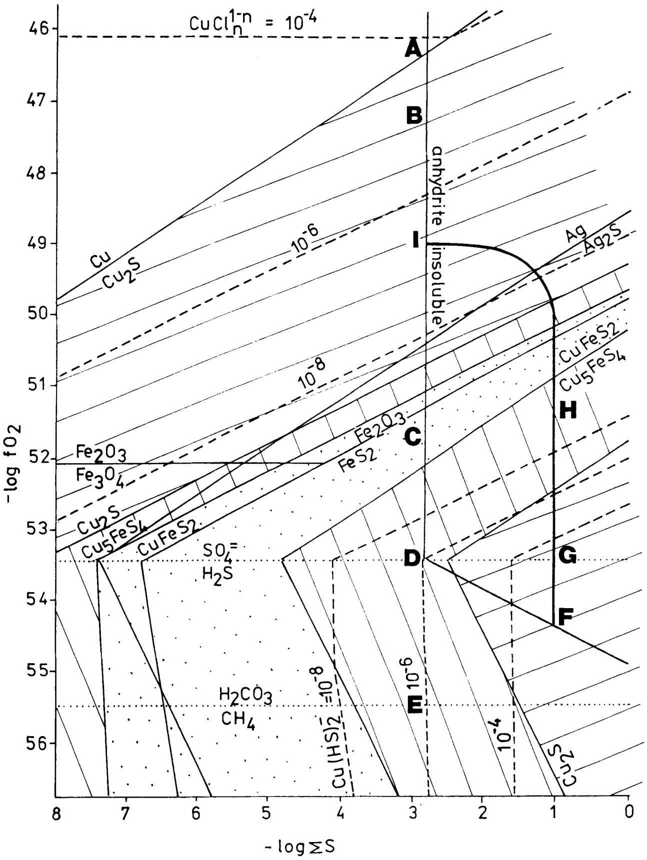

Fig. 8. Oxygen fugacity – total sulphur activity phase diagram showing stability fields of ore minerals and anhydrite, and the solubility of copper as chloride and bisulphide complexes. It is assumed that T = 100 °C, $a_{Cl^-} = 1.55$ m, $a_{Na^+} = 0.92$ m, $a_{K^+} = 0.014$ m, $a_{SO_4^{-2}} = 0.0016$ m, pH = 6.3, *Line A–B–C–D–E* represents mixing of fluids composition *A* and *E*, or reduction of fluid composition *A* by organic matter. *Line F–G–H–I* represents mixing of fluids compositions *F* and *I*

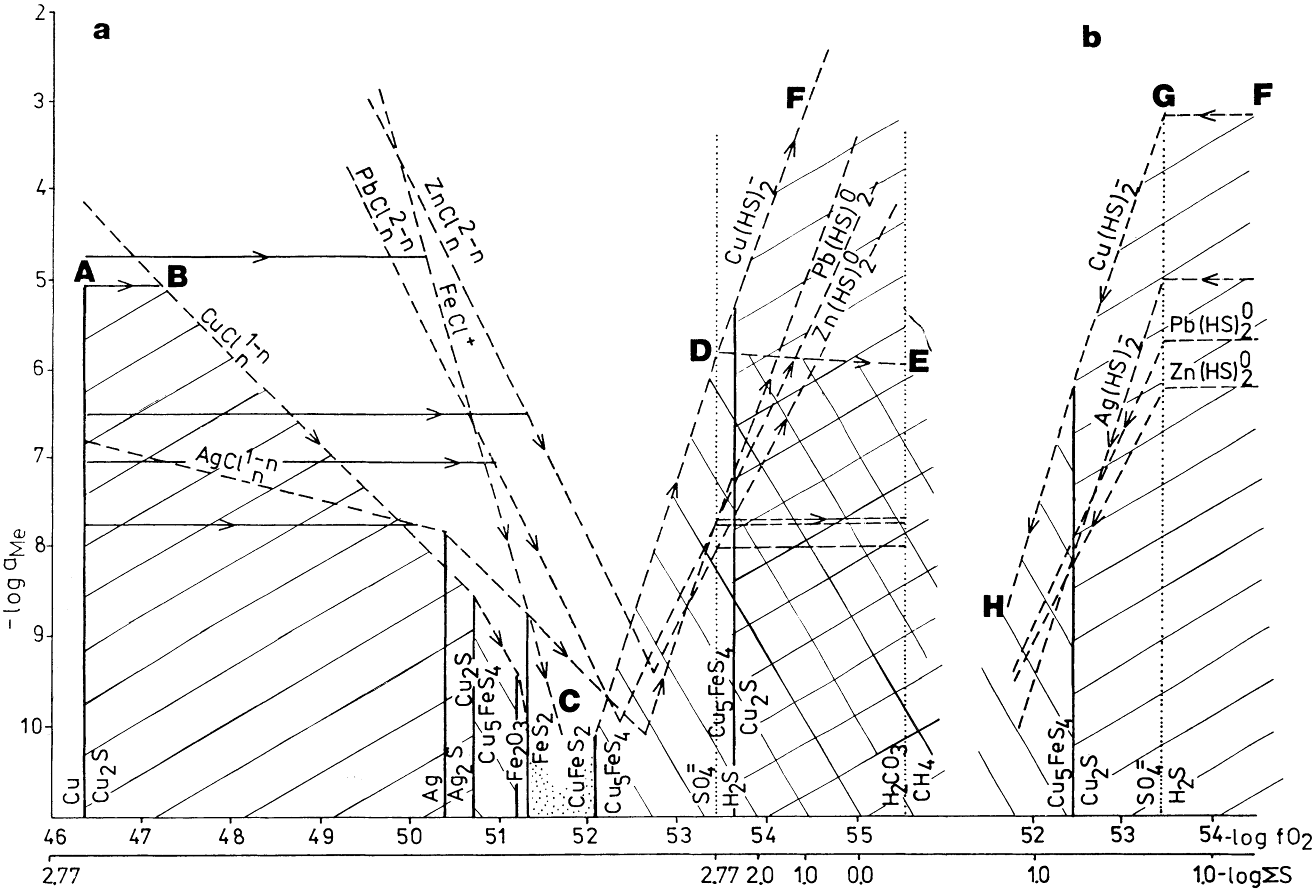

Fig. 9a, b. Metal activity – oxygen fugacity phase diagram showing stability fields of ore minerals and the solubility of metals as chloride and bisulphide complexes. Assumptions as for Fig. 8. **a** Solubility of metals along transect *A–B–C–D–E* in Fig. 8, represents mixing of fluids with compositions *A* and *E*, or reduction of fluid composition *A* by organic matter. Solubility of metals along transect *A–B–C–D–F* in Fig. 8 represents reduction of fluid composition *A* in equilibrium with anhydrite. **b** Solubility of metals along transect *F–G–H* in Fig. 8 represents mixing of fluids composition *F* and *I*

thermodynamic data shown on the Appendix. Figure 8 shows stability fields of iron, copper and silver minerals and anhydrite, the boundary between $SO_4^=/H_2S$ and H_2CO_3/CH_4 fields, as well as solubility contours of copper chloride and copper bisulphide complexes. Phase boundaries and solubilities of copper, silver, lead and zinc as chloride and bisulphide complexes, are shown in Fig. 9 as a function of log fO_2 and log total S along selected transects through Fig. 8. Phase boundaries and solubilities for silver, lead and zinc are based on reliable thermodynamic data at 100 °C. For copper and iron thermodynamic data are extrapolated from 200 °C and are less reliable. In the following section we interpret these activity diagrams in terms of the observed mineral zonation and the geologic setting of the district.

Interpretation of activity diagrams

The activity diagrams (Figs. 8, 9) assume constant temperature and chemical equilibrium. This is a simplification, but as shown below, the diagrams can be used to interpret the observed mineralogical zonation. The activity diagrams are interpreted separately for the 'typical' mineral zonation developed throughout most of the mining district (Fig. 3a), and separately for the mineral zonation developed near the anhydritic bodies (Fig. 4a).

Hydrothermal fluids responsible for the 'typical' mineralization flowed through the Rotliegendes where they equilibrated with feldspar, clays, hematite and anhydrite. The fluids were thus near neutral (pH = 6.3), oxidizing and saturated with respect to anhydrite. These fluids interacted either directly or indirectly with organic matter in the lower Zechstein rocks. Thus, during mineralization resulting in the 'typical' ore, fluid composition probably lay along line A–E in Fig. 8.

The vertical mineral zonation shown in Fig. 3a can be interpreted in terms of the activity diagrams in Figs. 8 and 9 as follows: the main ore horizon, characterized by chalcocite + hematite, was precipitated in an oxidizing environment. In both upward and downward directions the relative proportion of bornite and chalcopyrite increases, representing more reducing conditions. At a still lower level, near the Rotliegendes/Weissliegendes contact, bornite and hematite are present, representing a return to more oxidizing conditions. The vertical variation in oxygen fugacity shows three changes in slope (see Fig. 3b). These can best be interpreted as resulting from the successive mixing of three fluids, here labeled as fluids 1, 2 and 3, and by reaction of fluid 3 with the organic material in the Kupferschiefer and overlying carbonates.

Fluid 1 occupied intergranular space in the Weissliegendes and overlying Werra rocks. It contained isotopically light sulphur which was probably derived mainly from the Kupferschiefer (see section on stable isotopes). It was reducing and probably lay near point E on Fig. 8. Fluid 2 lay in the Rotliegendes. It was oxidizing (in equilibrium with hematite), contained sulphur as sulphate (in equilibrium with anhydrite), and contained copper in solution as chloride complexes. Interaction of fluids 1 and 2 near the Rotliegendes/Weissliegendes boundary resulted in precipitation of bornite and overlying chalcopyrite and pyrite. The activity of copper and iron in the oxidizing fluid solution (fluid 1) was low (less than 10^{-8} m), because the solubility of copper was intersected in the bornite field and that of iron in the pyrite field (see Fig. 9). Thus, only minor copper was precipitated at this stage, and it resulted in the formation of the weakly mineralized, stratigraphically lower bornite and chalcopyrite zone shown in Fig. 3a.

Fluid 3 was injected into fluid 1 along the Kupferschiefer/Weissliegendes contact. It was oxidizing, contained sulphur that was isotopically lighter than the sulphur in fluid 1, and was probably derived from the deep parts of the Permian basin. It rose to the top of the Weissliegendes aquifer and was less dense than fluids 1 or 2 probably because it was hotter. Above this level fluid 3 slowly penetrated through the Kupferschiefer, became progressively more reducing, and successively precipitated chalcocite, bornite, chalcopyrite, galena, sphalerite and pyrite. The widespread but minor presence of lead- and zinc-bearing carbonates and sulphates probably represents local conditions where there was insufficient reduced sulphur to crystallize galena and sphalerite. However, according to Roberts (1973), Mayer and Piestrzyński (1985) and Piestrzyński (1991) some of the base-metal-bearing carbonates and sulphates may have been precipitated during sedimentation or early diagenesis and are thus unrelated to fluid 3 emplacement. Within the Weissliegendes, fluid 3 mixed with fluid 1 (which was buffered at a low oxygen fugacity by CH_4/H_2CO_3, and $H_2S/SO_4^{=}$) and chalcocite, bornite and chalcopyrite were deposited successively. Conditions were not reducing enough to precipitate galena, sphalerite and pyrite below the main copper ore horizon, but may have become sufficiently reducing to the east-northeast of the district where Rydzewski (1978), Jowett et al. (1987a) and Oszczepalski (1989) report enrichment in lead, zinc and pyrite. Silver was coprecipitated with copper in the chalcocite and bornite zones, locally as native silver, but mainly in crystalline solution in sulphides. Thus the activity of the silver chloride complexes was probably about $10^{-7.7}$ m, intersecting the solubility curve just above the acanthite/native silver phase boundary (see Fig. 9). The activity of copper chloride complexes in solution was probably about 10^{-5} m, reflecting the 500-fold higher concentration of copper than silver in the ore.

The ore associated with the anhydritic zones (Fig. 4a) represents a distinct and later hydrothermal episode involving fluid 4. Downward migration of this fluid into the Weissliegendes resulted in the crystallization of anhydrite, and in the redistribution of the mineralization. The solubility of anhydrite decreases rapidly with increasing temperature (Blount and Dickson 1969), and its precipitation may have resulted from a rise in temperature as fluid 4 reached the Weissliegendes. The metals were redistributed as follows: copper was displaced out of the anhydritic zones and reprecipitated as chalcocite around the peripheries; silver followed copper and was precipitated as sulphides or as crystalline solutions in copper sulphides and not as native silver; galena and sphalerite were displaced downward but remained within the anhydritic bodies (Fig. 4) (Mayer and Piestrzyński 1982). Variation in oxygen and total sulphur (Fig. 4b) and the zonation can be explained in terms of the activity diagrams in Figs. 8 and 9 as follows: hydrothermal fluid 4, in equilibrium with anhydrite, became progressively reducing as it descended through organic-bearing Werra rocks. In contact with the anhydrite fluid composition changed along line I–C–D and then line D–F, resulting in a rapid increase in total sulphur (Fig. 8) and a rapid increase in the solubility of metals as bisulphide complexes (Fig. 9). At point F the solubilities of copper ($10^{-3.2}$ m) and silver (10^{-5} m) were sufficiently high to remove these metals entirely from the anhydritic bodies, whereas the solubilities of galena ($10^{-5.7}$ m) and sphalerite ($10^{-6.2}$ m) were lower and these minerals remained largely within the anhydritic bodies. As this evolved fluid 4 (point F, Fig. 8) flowed out of the anhydritic bodies it mixed with evolved fluid 3 (point I, Figs. 8, 9) and the composition changed along curve F–G–H–I. The solubilities of copper and silver fell steeply past point G and chalcocite was reprecipitated together with sulphide silver. The sulphur present in these deposits represents a mixture of anhydrite and earlier sulphide sulphur.

Genetic model

The ore deposits of the Lubin–Sieroszowice district have had a long and complex history of mineralization which included a synsedimentary or early diagenetic stage, three late diagenetic stages and a tectonic stage (Fig. 10).

Stage 0 (Fig. 10a) is synsedimentary or earliest diagenetic. It is the most extensive but economically the least important. It is characterized by framboidal pyrite (Vaughan et al. 1989; Sawłowicz 1990), and the accumulation of 100s ppm base metals mainly in clay minerals (Kucha et al. 1990) but also as minor base metal sulphides that were precipitated by bacterial reduction of sulphates. In the district this stage has been largely masked by lateral sulphide deposition.

Stage I mineralization took place near the boundary between fluids 1 and 2 (Fig. 10b). It is characterized by bornite and overlying chalcopyrite and pyrite, and contains a few 1000 ppm base metals. Fluid 1 was reducing and was probably derived from the overlying Kupferschiefer during diagenesis. It may have been restricted to structural traps in the permian strata but this has not been established. Fluid 2 lay within the Rotliegendes in equilibrium with hematite, anhydrite, feldspars and clays and carried minor copper in solution as chloride complexes.

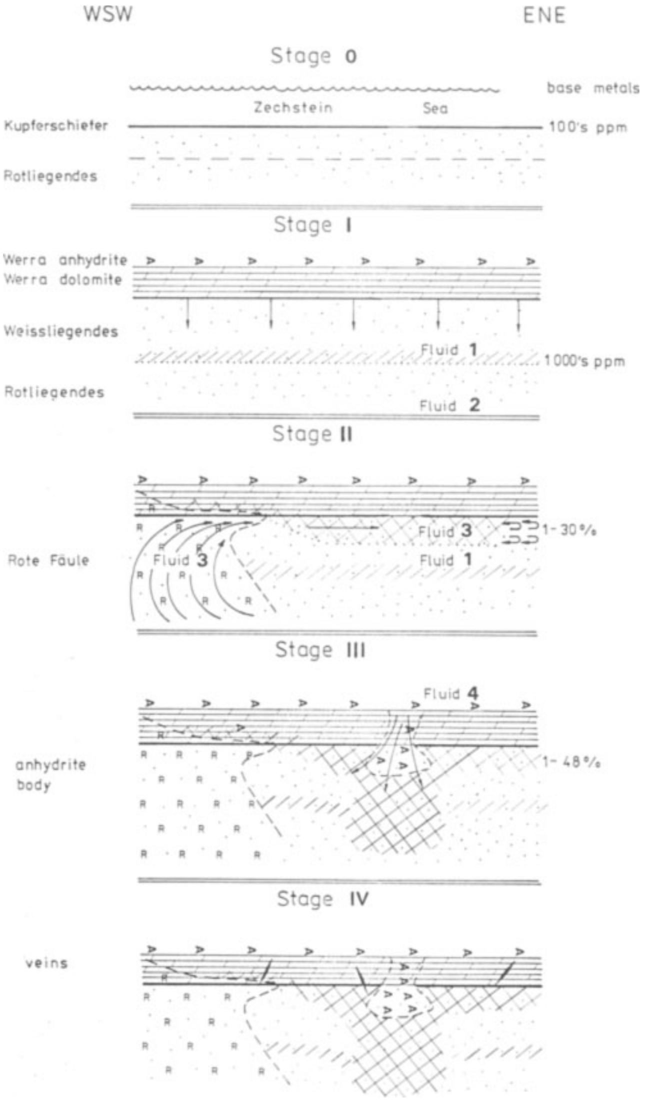

Fig. 10. Genetic model for the mineralization in the Lubin–Sieroszowice district. *Stage 0* Synsedimentary or earliest diagenetic deposition. *Stage I* Precipitation of metals near interface between oxidizing fluid 2 and reducing fluid 1. *Stage II* Injection of copper-rich, oxidizing fluid 3 along base of Kupferschiefer. Precipitation of metals by interaction of fluid 3 with organic matter in the Kupferschiefer and by mixing of fluid 3 with fluid 1. *Stage III* Downward expulsion of fluid 4 which is in equilibrium with anhydrite, and displacement of copper and silver to the peripheries of the anhydrite bodies. *Stage IV* Deposition of polymetallic veins along tectonic fractures

Copper precipitation occurred near the interface between these two fluids, bornite precipitating under slightly more oxiding conditions than the chalcopyrite and pyrite. Stage I mineralization may be related to the 'average mineralization' described by Schmidt and Friedrich (1988) and Vaughan et al. (1989), which according to these authors was early diagenetic and was strongly influenced by the nature of the underlying lithologies.

Stage II mineralization took place as a result of mixing of fluid 3 and fluid 1 in the Weissliegendes, and as a result of reduction of fluid 3 as it came in contact with the overlying organic-bearing Zechstein rocks (Fig. 10c). It represents the bulk of the ore in the district and contains on average 2% copper. Fluid 3 flowed through the Rotliegendes and thus was in equilibrium with hematite, anhydrite, feldspars and clays. According to Jowett (1986) and Jowett et al. (1987a), the ore-forming fluid may have leached base metals from the bimodal Autunian volcanics and then flowed upwards towards basin margins. Fluid 3 had a lower density than fluids 1 and 2, probably because it was hotter, and thus reached the basal Zechstein where the bulk of the mineralization took place. In these regions of upwelling the Rote Fäule facies reached the Kupferschiefer and from here spread laterally. It reacted with the Kupferschiefer and the overlying organic-bearing carbonates, became progressively more reducing and precipitated hematite (Rote Fäule facies)–chalcocite–bornite–chalcopyrite and pyrite–galena–sphalerite successively. This zonal pattern in the Kupferschiefer is similar to that predicted by Sverjensky (1987) for oil-field brines equilibrated with anhydrite-bearing red beds, and reacted with graphitic shales. Within the Weissliegendes, fluid 3 became progressively more reducing as it mixed with fluid 1. The oxygen fugacity of fluid 1 was buffered by CH_4/H_2CO_3, and $H_2S/SO_4^=$ enhancing its capacity to reduce fluid 3. With progressive reduction of fluid 3, hematite–chalcocite–bornite–chalcopyrite were successively deposited. Conditions here were not reducing enough to precipitate galena and sphalerite. It is possible that mixing of fluids 3 and 1 took place only locally, where structural conditions were favourable for the trapping of fluid 1. For instance such conditions may have existed at the Rudna mine and the western part of the Lubin mine where the bulk of the ore is in the Weissliegendes.

Stage III mineralization took place as a result of mixing between a descending fluid 4 which was in equilibrium with anhydrite, and an evolved fluid 3 (Fig. 10d). This only took place in regions where the Kupferschiefer was missing. Fluid 4 may have originated in the Werra anhydrite horizon as a result of gypsum dehydration. As it migrated downward towards the permeable Weissliegendes, it became increasingly reducing, and below the SO_4/H_2S boundary, it became strongly enriched in H_2S. This increased the solubility of copper and silver as bisulphide complexes, causing their solution and reprecipitation under more oxidizing conditions present beyond the anhydrite boundaries. Strong evidence for such a process is the presence of local Stage II copper remnants within the anhydrite bodies (Mayer and Piestrzyński 1982). Such mixing of descending and ascending fluids as a mechanism of metal precipitation has previously been suggested by Kucha and Pawlikowski (1986). Locally, Stage III overprints Stage II.

Stage IV mineralization occurs only locally along minor faults and joints (Fig. 10e). It consists of carbonate, anhydrite barite and sulphide veinlets that are of no economic importance. They are structurally controlled and are possibly related to Alpine tectonism (Harańczyk 1972). They may be coeval to the 'structurally controlled late diagenetic' mineralization of Vaughan et al. (1989).

The most important episode of mineralization in the district was Stage II. In contrast, Stages 0, I and IV are never in themselves economic, and Stages III and IV mainly represent redistribution of earlier mineralization.

According to Jowett et al. (1987b), paleomagnetic studies show that the main episode of mineralization (Stage II) occurred between 250 and 220 Ma. This coincided with continental rifting and was associated with the opening of the Tethys ocean. According to Jowett (1986), lateral temperature gradients at this time drove convection cells within the Rotliegendes and the Autunian volcanics, and ore deposition took place at basin margins during some 20 cycles.

As a result of the present study it is possible to calculate the volume of the main metal-carrying fluid needed to form the deposits because the activity of silver chloride complexes in fluid 3 is well constrained (Fig. 9). Under the assumptions that $T = 100\,°C$; $a_{Cl^-} = 1.55$ Mm $a_{Ag} = 10^{-7.75}$ m; ionic strength = 4.67, the concentration of silver in fluid 3 was 0.028 ppm. Thus, if 170,000 t of silver are present in the district, about 5000 km^3 of fluid 3 was necessary to form the Lubin deposits. Thus, manyfold recycling of basinal brines, as suggested by Jowett (1986), seems likely during the ore-forming process at Lubin.

Conclusion

As noted in Polish geological literature (Harańczyk 1972; Rydzewski 1976; Mayer and Piestrzyński 1982, 1985; Kucha and Pawlikowski 1986; Oszczepalski and Rydzewski 1991; and many others) the ore deposits are located near the margin of the Early Permian sedimentary basin (the likely source of the fluids), which contain volcanics (the likely source of the metals), and near the Kupferschiefer (the likely source of most of the reduced sulphur). The region of upwelling is marked by the Rote Fäule facies penetrating to the level of the Kupferschiefer. However, contrary to Jowett et al. (1987a), the richest ore does not lie immediately adjacent to the Rote Fäule, but is located some 10–15 km downstream (see Figs. 1, 5). Furthermore, the lead–zinc zones postulated by Jowett et al. (1987a) and Oszczepalski (1989) to lie outboard of the copper zone are not clearly defined in the one area which has been studied in detail (the Rudna mine) (Mayer and Piestrzyński 1982 and 1985). Thus the supposed horizontal zonal pattern of Cu-Pb-Zn may not be helpful in regional prospecting.

Three types of ore deposits are present in the district: peneconcordant ore in the Kupferschiefer and to a lesser extent in the overlying carbonates (Polkowice and Sieroszowice mines); peneconcordant ore in the Weissliegendes (Rudna and western Lubin mines); and discordant ore that is peripheral to anhydritic zones in the Weissliegendes (Rudna and western Lubin mines). Synsedimentary and early diagenetic (Stage 0) and tectonic mineralization (Stage IV) are of no economic importance in the district.

Ore of the Kupferschiefer-type occurs where upwelling, oxidizing, copper-bearing fluids came into direct contact with the organic shale. Here metals precipitated as a result of reduction by organic carbon in the Zechstein rocks.

Ore of the Weissliegende-type occurs where the oxidizing, copper-rich fluids came into contact with an earlier, reducing, buffered fluid that was trapped beneath the Kupferschiefer, possibly in structural traps. Here metals were precipitated as a result of reduction by the earlier fluid.

Ore of the anhydrite association occurs peripherally to anhydrite bodies in the Weissliegendes where descending, reducing, sulphur-rich fluids displaced and reconcentrated earlier copper/silver ore. This only occurs at locations where the Kupferschiefer is missing, and the descending fluid could penetrate from the overlying evaporites to the Weissliegendes.

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Appendix

	$\log K_{100}$	Reference
$Cu + H^+ + 1/4CO_2 + Cl^-$ $= 1/4C + 1/2H_2O + CuCl$	-0.1^{a}	4
$1/4Cu_5FeS_4 + HS^- + 1/2H_2S$ $= 1/4CuFeS_2 + Cu(HS)_2^-$	-1.6^{a}	4
$Cu_2S + 4Cl^- + 2O_2 = 2CuCl_2^- + SO_4^{-2}$	77.09^{b}	13
$Cu_2S + 6Cl^- + 2O_2 = 2CuCl_3^{-2} + SO_4^{-2}$	77.20^{b}	13
$5CuFeS_2 + S_2 = 4FeS_2 + Cu_5FeS_4$	16.86	14
$2Cu + 1/2S_2 = Cu_2S$	17.09	8
$Cu_5FeS_4 = 4Cu^+ + Cu^{+2} + Fe^{+2} + 4S^{-2}$	-133.4	8
$Cu^{+2} + 1/2H_2O = Cu^+ + 1/4O_2 + H^+$	-12.4	8
$Cu_2S = 2Cu^+ + S^{-2}$	-39.37	8
$FeS_2 = Fe^{+2} + S^{-2} + 1/2S_2$	-30.17	8
$5CuFeS_2 + 2H^+ + 1/2O_2 + Cl^-$ $= 3FeS_2 + Cu_5FeS_4 + H_2O + FeCl^+$	27.0^{a}	4
$3FeS_2 + 2O_2 = Fe_3O_4 + 3S_2$	44.57	8
$2FeS_2 + 3/2O_2 = Fe_2O_3 + 2S_2$	38.39	8
$2Fe_3O_4 + 1/2O_2 = 3Fe_2O_3$	26.02	8
$Ag_2S + H_2 = 2Ag + H_2S$	-2.34	3
$Ag + H^+ + 1/4O_2 = Ag^+ + 1/2H_2O$	6.01	8
$Ag^+ + 2Cl^- = AgCl_2^-$	4.46	15
$Ag^+ + 3Cl^- = AgCl_3^{-2}$	3.85	15
$Ag^+ + 4Cl^- = AgCl_4^{-3}$	1.94	15
$Ag_2S + H_2S + 2HS^- = 2Ag(HS)_2^-$	-4.18	7
$PbS + 2H^+ = Pb^{++} + H_2S$	-5.69	11
$Pb^{+2} + Cl^- = PbCl^+$	1.67	16
$Pb^{+2} + 2Cl^- = PbCl_2^0$	2.67	16
$Pb^{+2} + 3Cl^- = PbCl_3^{-1}$	2.21	16
$Pb^{+2} + 4Cl^- = PbCl_4^{-2}$	1.93	16
$PbS + H_2S_{(g)} + HS^- = Pb(HS)_3^-$	-6.9	6
$PbS + H_2S_{(g)} = Pb(HS)_2^0$	-6.4	6
$ZnS + 2H^+ = Zn^{+2} + H_2S$	-4.17	2
$Zn^{+2} + 2Cl^- = ZnCl_2^0$	1.89	2
$Zn^{+2} + 3Cl^- = ZnCl_3^-$	2.34	2
$Zn^{+2} + 4Cl^- = ZnCl_4^{-2}$	1.36	2
$Zn^{+2} + 2HS^- = Zn(HS)_2^0$	12.3	2
$Zn^{+2} + 3HS^- = Zn(HS)_3^-$	14.2	2
$H_2S = H^+ + HS^-$	6.61	10
$HS^- = H^+ + S^{-2}$	12.00	16
$H_2S + 2O_2 = SO_4^{-2} + 2H^+$	99.13	10
$H_2S + 1/2O_2 = H_2O + 1/2S_2$	23.14	8
$H_2S = H_2S_{(g)}$	1.42	5
$CaSO_4 = Ca^{+2} + SO_4^{-2}$	-5.63	8
$H_2CO_3 = H^+ + HCO_3^-$	-6.35	8
$HCO_3^- = H^+ + CO_3^{-2}$	-10.1	8
$CO_2 + H_2O = H_2CO_3$	-1.97	8
$C + O_2 = CO_2$	54.5^{a}	12
$CaCO_3 = Ca^{+2} + CO_3^{-2}$	-9.57	1
$H_2CO_3 + H_2O = CH_4 + 2O_2$	-111^{c}	12
$H_2O = H_2 + 1/2O_2$	-31.8	8
$3K\text{–}fd + 2H^+ = Ms + 6SiO_2 + 2K^+$	-9.0	9
$K\text{–}fd + Na^+ = Ab + K^+$	-1.9	9

1. Bourcier (1983)
2. Bourcier and Barnes (1987)
3. Cobble et al. (1982)
4. Crerar and Barnes (1976)
5. Drummond (1981)
6. Giordano and Barnes (1979)
7. Gammons and Barnes (1989)
8. Helgeson (1969)
9. Helgenson et al. (1978)
10. Murray and Cubicciotti (1983)
11. Naumov et al. (1974)
12. Ohmoto (1972)
13. Rose (1976)
14. Schneeberg (1972)
15. Seward (1976)
16. Seward (1984)
17. Stephens and Cobble (1971)

[a] Extrapolated from 200 °C

[b] Calculated

[c] Extrapolated from 150 °C

[d] Extrapolated from 150 °C