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Oxidative alteration of the Kupferschiefer in Poland: oxide-sulphide parageneses and implications for ore-forming models*

The Kupferschiefer ore series, between the Lower Permian (Rotliegendes) terrestrial redbeds/volcanics and the Upper Permian (Zechstein) marine sequence, is developed as dark grey organic matter rich and metal sulphide containing deposits (reduced areas) and as red-stained organic matter depleted and iron oxide-bearing sediments (oxidized areas = Rote Fäule). A distinctive feature of the Kupferschiefer mineralization is the presence of a transition zone from oxidized to reduced rocks, both vertically and horizontally. This zone is characterized by sparse, disseminated copper sulphides within hematite-bearing sediments, oxide pseudomorphs after framboidal pyrite, and replacements of copper sulphides by iron oxides and covellite. These textural features and copper sulphide replacement of pyrite in reduced sediments imply that the main oxide/sulphide mineralization postdated formation of an early-diagenetic pyrite. The Kupferschiefer mineralization resulted from upward and laterally flowing fluids which oxidized originally pyrite containing organic matter rich sediments to form hematitic Rote Fäule areas, and which emplaced base metals into reduced sediments. It is argued that long-lasting and large-scale lateral fluid flow caused the crosscutting relationships, expansion of the hematitic alteration front, the vertical and regional horizontal mineral zoning patterns, and the location of copper orebodies directly above and around oxidized areas.

INTRODUCTION

The Kupferschiefer mineralization occurs in the strata between the uppermost Lower Permian (Rotliegendes) terrestrial redbeds/volcanics and the Upper Permian (Zechstein) marine siliciclastics, shales, carbonates, and evaporites. Polymetallic ore-bearing sediments are developed in the central-European Permian basin in two magnafacies, as black (dark grey) organic matter rich and metal sulphide containing deposits (reduced areas); and as red-coloured organic matter deficient and iron oxide containing sediments (oxidized areas = Rote Fäule).

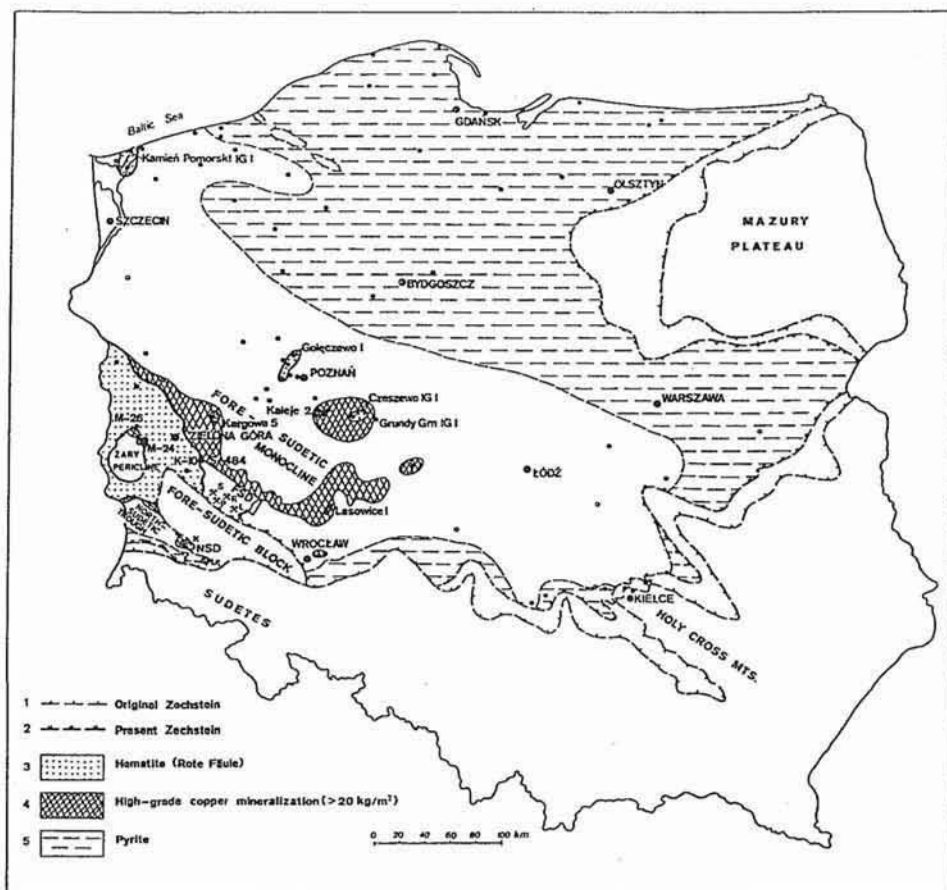


Fig. 1. Ore-grade copper mineralization in relation to hematitic Rote Fäule areas; of over 400 studied wells, only those situated off Sudetic Foreland and mentioned in the text are shown

FSD — Fore-Sudetic deposit, S — Sierszowice mine, P — Polkowice mine, R — Rudna mine, L — Lubin mine; NSD — North-Sudetic deposit, K — Konrad mine, Le — Lena — Nowy Kościół mines

Występowanie rud miedzi w stosunku do obszarów utlenionych (Rote Fäule); spośród 400 zbadanych otworów, zaznaczono jedynie lokalizację niektórych otworów spoza obszaru przedsudeckiego oraz otwory wspomniane w tekście

FSD — złożo przedsudeckie, S — kopalnia Sierszowice, P — kopalnia Polkowice, R — kopalnia Rudna, L — kopalnia Lubin; NSD — złożo północnosudeckie, K — kopalnia Konrad, Le — kopalnie Lena — Nowy Kościół; 1 — pierwotny zasięg cechsztynu, 2 — współczesny zasięg cechsztynu, 3 — hematyt, 4 — bogata mineralizacja miedziowa ($> 20 \text{ kg/m}^3$), 5 — piryt

The Kupferschiefer copper deposits are located in the southwest part of Poland — in the North-Sudetic Trough and Fore-Sudetic Monocline (Fig. 1). These two units are separated by the uplifted Fore-Sudetic Block and Żary Pericline, bordered in the South by the Marginal Sudetic Fault, and in the North by the Middle Odra Fault System. These units

developed essentially during the Laramide phase of the Alpine orogeny as foreland structures to the Sudeten Mts. Permian and Mesozoic strata were probably deposited over the Fore-Sudetic Block, but were eroded during the Lower Tertiary when Laramide movements uplifted the Fore-Sudetic Block, rejuvenated old structures, and created new fault systems.

The ore series consists of Weissliegendes, Basal Limestone, Kupferschiefer and Zechstein Limestone (Fig. 2). Locally, small amounts of sulphides occur at the base of the Lower Anhydrite. The principal ore minerals are chalcocite-type sulphide minerals (i.e. Cu-S type sulphides of the chalcocite – covellite – digenite – djurleite and anilite series), bornite, chalcopyrite, galena, and sphalerite. Pyrite and marcasite are ubiquitous constituents in the basal Zechstein.

Geological studies of the red-stained basal Zechstein sediments in relation to the ore mineralization were initiated in the North-Sudetic Trough (e.g. E. Konstantynowicz, 1965; C. Skowronek, 1968). The discovery in 1957 of the Lubin deposit enabled the ore/Rote Fäule system to be investigated on a regional scale (J. Wyżykowski, 1958; A. Rydzewski, 1964, 1969). The largest hematitic areas have been recognized in the region of western Fore-Sudetic Monocline and Żary Pericline (Fig. 1; A. Rydzewski, 1978; S. Oszczepalski, 1979, 1980; S. Oszczepalski, A. Rydzewski, 1983), as well as in SE Germany (J. Rentzsch, G. Knitzschke, 1968). Recently, continuing studies carried out in the remaining part of Poland established further occurrences of the hematitic facies, in the areas of Lasowice, Czeszewo, Kargowa, Gołęczewo and Kamień Pomorski (Fig. 1).

Important features of the sulphide mineralization in the Fore-Sudetic Monocline have been described in detail in numerous papers (S. Lisiakiewicz, 1969; C. Harańczyk, 1972; J. Niśkiewicz, 1980; W. Mayer, A. Piestrzyński, 1985; Z. Sawłowicz, 1990; H. Kucha, 1990; and many others), however, too little attention has been paid to the Rote Fäule and its transition to the sulphidic zone. Detailed studies show (A. Rydzewski, S. Oszczepalski, 1984; S. Oszczepalski, 1989; S. Oszczepalski, A. Rydzewski, 1991) that investigations of mineral assemblages at the contact between oxidized and reduced rocks appear to be very important for promoting understanding of the origin of the Kupferschiefer mineralization.

This paper presents the results of geological and petrographical studies of iron oxide/sulphide mineralization in Poland. Special attention has been given to the transition from the hematitic Rote Fäule to sulphidic rocks. Mineralogical and textural relationships observed within this transition zone appear to be a key to the problem of the origin of the Kupferschiefer mineralization.

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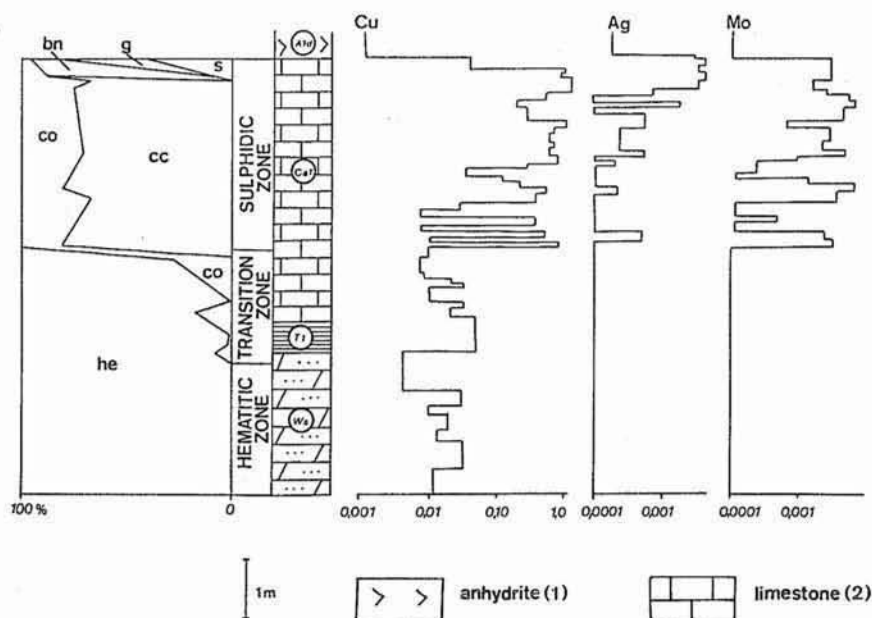


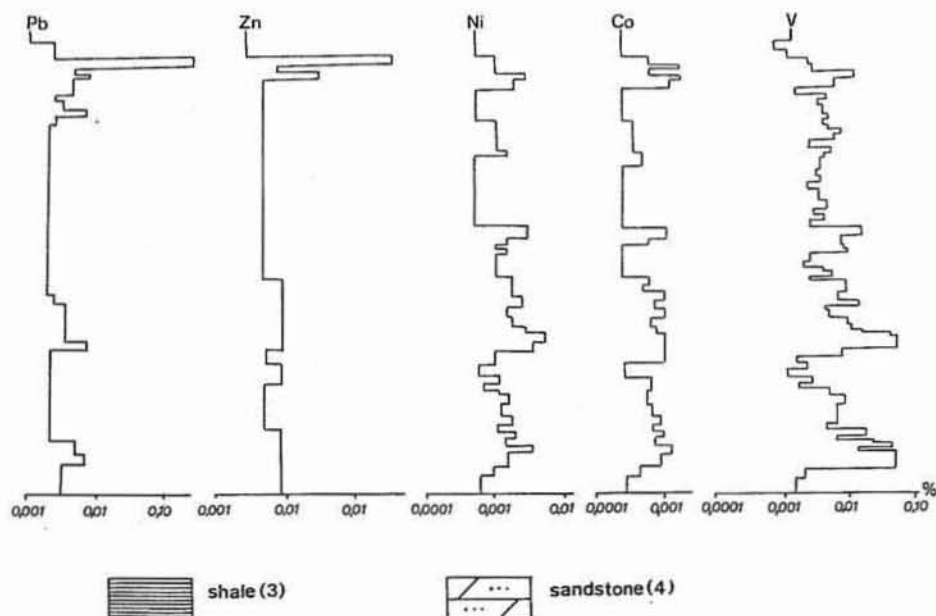
Fig. 2. Mineral zonation and distribution of metals observed along the M-24 drill section through the Kupferschiefer ore series; see Fig. 1 for location

A1d — Lower Anhydrite, Ca1 — Zechstein Limestone, T1 — Kupferschiefer, Ws — Weissligendes; he — hematite, co — covellite, cc — chalcocite, bn — bornite, g — galena, s — sphalerite

TRANSITION FROM HEMATITIC TO SULPHIDIC ROCKS

A distinctive feature of the Kupferschiefer mineralization in Poland is the presence of an intermediate zone between oxidized and reduced sediments, termed here "the transition zone" (Fig. 2). This transition zone cuts across the stratigraphy at an angle of less than 1° , occurring in particular sections in one lithostratigraphic unit or comprising more units. Its thickness varies from some millimetres in the Kupferschiefer horizon to several metres in the Weissligendes, Basal Limestone and Zechstein Limestone (S. Oszczepalski, 1989; S. Oszczepalski, A. Rydzewski, 1991).

The upward transition of iron oxide-bearing rocks into metal sulphide containing sediments is characterized by a gradual change from reddish-brown rocks through grey ones with red spots, streaks and bands, to dark grey and black sediments. This change in colour is accompanied by a distinct decrease in ferric iron content as well as an increase in C_{org} and S_{total} content and an increase in MgO/CaO ratio. Locally, the zone of transition contains small quantities of glauconite. The copper content is 0.1% or less in the Weissligendes, Basal Limestone and Zechstein Limestone and 0.1–0.4% in the Kupferschiefer. Locally, sediments in the transition zone may contain considerable amounts of organic matter (e.g. where this transition crosses the Kupferschiefer bed), but they are commonly barren in both



Mineralna strefowość i rozkład zawartości metali w cechsztyńskiej serii miedzionośnej otworu M-24; lokalizacja otworu na fig. 1

A1d — anhydryt dolny, Ca1 — wapień cechsztyński, T1 — łupek miedzionośny; Ws — biały spągowiec; he — hematyt, co — kowelin, cc — chalkozyn, bn — bornit, g — galena, s — sfaleryt; 1 — anhydryt, 2 — wapień, 3 — łupek, 4 — piaskowiec

iron oxides and metal sulphides. Compared to the sulphide zone, oxidized sediments are characterized by the predominance of calcite over dolomite, high Fe_2O_3/C_{org} (> 2) ratios, small amounts of organic matter ($< 0.9\%$ TOC) and the lack of amorphous kerogen (only scarce refractory recycled carbonaceous particles occur), low content of bitumen ($< 0.06\%$), isoprenoids ($< 0.01\%$ of bitumen), and Ni+VO porphyrins (< 0.1 mg/100 g of rock), as well as by low S_{total} content ($< 0.2\%$) (S. Oszczepalski, 1989). Furthermore, organic matter in the oxidized Rote Fäule is of higher coal rank (low H/C and O/C ratios) than in the sulphidic zone and it is characterized by low ratios of C/N in kerogen and an increase of asphaltene concentration (Z. Sawłowicz, 1989), as well as by the high ratio of phenantrene/sum methylphenantrenes and high content of unsubstituted aromatic compounds (naphthalene, biphenyl, dibenzofuran, dibenzothiophene) (S. Speczik, W. Püttmann, 1987).

Above the transition zone, successive enrichments in chalcocite-like phase sulphides, bornite, chalcopyrite, galena and sphalerite occur, as seen in Fig. 2. As in vertical sections, a pronounced mineral zonation as well as the transition between the hematitic and sulphidic rocks is repeated horizontally. In general, this transition occurs within a lateral distance of 100's of metres to some kilometres, according to the local thickness of this zone (A. Rydzewski, S. Oszczepalski, 1984). Because this zone is too narrow to appear on the map, the extent of oxidized areas is arbitrarily placed at the contact of hematitic and sulphidic sediments in the Kupferschiefer bed. Likewise in vertical sections, in a plan view the

transition zone has intermediate characteristics compared with hematitic and sulphidic zones.

MINERALOGY, TEXTURES, PARAGENETIC SUCCESSIONS

Oxidized zone. In red-coloured sediments, iron oxides (hematite, goethite) occur as microcrystals (submicroscopic red pigment), aggregates (opaque or brown irregular grains), and spherules (< 50 μm in size). These iron oxide particles are dispersed throughout the sediments or concentrated to form red spots, bands or earthy masses. The most abundant are spherules which principally occur in the Kupferschiefer bed, making up 1–5% of the shale. Spherules tend to concentrate in the dark interlaminar matrix of the shales (Pl. I, Figs. 1, 2). The shape, size and mode of occurrence of these spheres strongly suggest that they are oxide pseudomorphism by oxidation of pyrite framboids. Notable are iron oxide pseudomorphs after very early diagenetic framboidal pyrite filling chambers of skeletons. Iron oxide spherules can be translucent reddish-brown granules consisting of microcrystalline hematite with admixture of iron hydroxides (Pl. I, Fig. 1), or they are composed of well-crystallized hematite and goethite (Pl. I, Fig. 2). Red-stained sediments contain only locally small amounts of sulphides (mostly pyrite, marcasite, chalcocopyrite, and covellite). Calcite nodules contain inclusions of hematite in zoned calcite crystals that are comprised of alternating layers enriched and depleted with hematite pigment; some outer zones are built with goethite. Rare remnants of sulphides corroded by iron oxides are also found. Calcite, anhydrite, gypsum, and dolomite veinlets contain neither iron oxides nor metal sulphides.

Thus, it is reasonable to conclude that most iron oxides occurring in reddened sediments resulted from oxidation of pre-existing early diagenetic pyrite. Some well-crystallized forms could have been formed by precipitation from iron-bearing solution.

Transition zone. In the transition zone mineralization is predominated by the following paragenesis: hematite+goethite and covellite with other minor chalcocite-like phase sulphides, bornite, chalcocopyrite, pyrite, and marcasite. Coexisting iron oxides occur in a few textural varieties, such as microcrystals, aggregates, spherules, and composites. Coarser composite grains of iron oxides with copper sulphides are of particular importance. Hematite forms intergrowths with digenite (Pl. I, Fig. 3). The most remarkable are textures indicating replacement of copper sulphides by iron oxides. The most abundant replacement textures are partial substitutions of chalcocite, covellite, and chalcocopyrite by hematite and goethite. Chalcocite grains are commonly veined, invaded or rimmed by iron oxides, or partially corroded by hematite (Pl. I, Figs. 4, 5). In the latter case an intermediate zone between hematite crystals and chalcocite grains is found. Covellite grains are corroded by iron oxides in similar way (Pl. I, Fig. 6). Locally, iron oxides have altered grains of covellite, leaving only remnant cores of covellite surrounded by replacement oxides. In some places goethite partly substitutes chalcocopyrite (Pl. I, Fig. 7) and bornite.

Sulphides occur mostly as finely scattered grains, less commonly as mutual composites. Textures indicating covellitization of copper sulphide grains are common. Covellite generally takes the form of lamellar intergrowths with chalcocite and bornite, or complex intergrowths with carbonate material. Carbonate grains and laminae contain sparse,

disseminated covellite and pyrite microcrystals clearly occur as reduced remnants within oxidized shales. Residual covellite is also retained as minute grains dispersed in hematite-bearing shales, indicating that sulphidation predated oxidation. In the North-Sudetic Trough, bornite and chalcopyrite grains have been identified within red spots as well as diffused sulphide aureoles around red spots (C. Skowronek, 1968).

In summary, textural relationships appear to suggest the following paragenetic succession: pyrite – chalcopyrite, bornite, chalcocite – covellite – iron oxides.

Reduced zone. In reduced lithologies adjacent to the transition zone the dominant sulphide minerals are copper sulphides of Cu-S type. Moving away from this transition, sulphides of Cu-Fe-S type (in turn bornite and chalcopyrite) appear to be much more common; and then galena and sphalerite. Pyrite is the most widespread of the sulphides, mostly in areas off the copper enrichment, making up 1–6% of the shales. This contrasts with the Cu-S phase-bearing areas where the pyrite content is typically less than 0.5%.

The bulk of base-metal mineralization is represented by very fine (< 50 μm in size) anhedral disseminated grains, comprising more than 80% of the sulphides. Less commonly, sulphides occur as coarser-grained aggregates, lenses and streaks, as well as fillings of fractures and vein openings. In the sandstone, sulphides occur as cement to detrital grains, rhythmic ore banding and large ore concretions discordant to bedding. Sulphides form anhedral and euhedral grains (20–300 μm in size) which impregnate carbonate cement. Commonly, sulphides replace clastic grains (Pl. II, Fig. 1). In the shale ore, disseminated ores are concentrated mainly in the organic-rich interlaminar matrix and are aligned parallel to the sedimentary laminae or grouped to form thin bands concordant with lamination. In places, soft-sediment bending of clay laminae around sulphide blobs is seen, implying precompactional formation (Pl. II, Fig. 2). Disturbance of laminae by the growth of sulphide grains is also common. Fillings of open spaces are also present (Pl. II, Fig. 3). Ores typically impregnate carbonate grains and laminae; this texture is defined by irregular remnants of carbonates present within sulphides (Pl. II, Fig. 4). In the carbonate ore, base-metal sulphide grains are mostly large and anhedral. The most common textures are random disseminations, open space fillings, and replacements of dolomite rhombs (Pl. II, Figs. 5, 6), impregnations in burrow fillings, concretions, and incrustations of carbonate/sulphate nodules. Sulphides also substitute carbonate minerals in spaces between anhydritic blades of the Lower Anhydrite (Pl. II, Fig. 7).

Pyrite in the mineralized sequence occurs in the form of framboids — spheroidal aggregates 5–50 μm in size consisting of equal sized (1–5 μm) euhedral (mainly octahedral) pyrite microcrystals, dispersed or clustered in organic-rich lithologies; some of them are overgrown with equant crystals of pyrite or marcasite to form sunflower framboids or larger aggregates in which framboidal remnants can only rarely be detected; single crystals — tiny (less than 20 μm in diameter) and coarse (up to 500 μm in size) individual euhedra (mainly cubes), often fractured and invaded by marcasite; and aggregates — irregular large grains occurring mostly as impregnations of carbonates, fossil replacements, nodules or burrow fillings (particularly at the base of Zechstein Limestone).

Both fine- and coarse-grained base-metal sulphides commonly form complex mutual-boundary textures, therefore, a simple mineral succession is hard to construct. Generally, however, chalcopyrite is preferentially replaced by bornite, and bornite by Cu-S type ores. Crucial in constructing the paragenetic sequence are studies of the mineralization in the

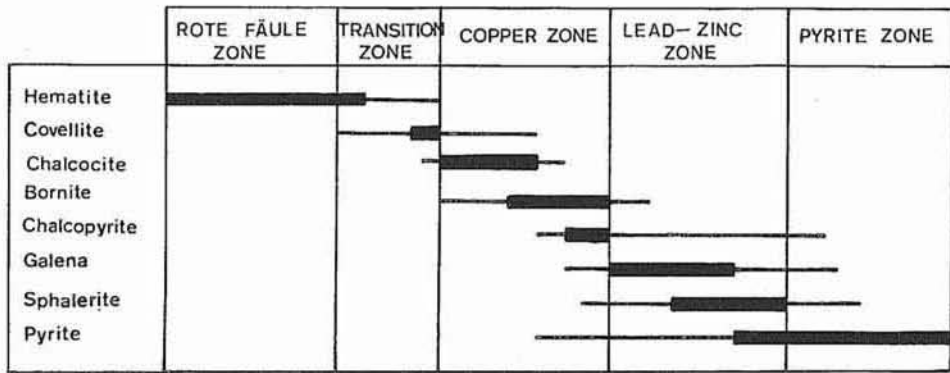


Fig. 3. Paragenetic sequence of iron oxides and metal sulphides in the transition from oxidized to reduced rocks
 Sukcesja mineralna tlenków żelaza i siarczków metali w strefie przejściowej między utworami utlenionymi i redukcyjnymi

chalcocite-bornite zone, where numerous chalcocite, digenite, covellite, bornite, and chalcopyrite grains pseudomorphic after framboidal pyrite are fairly common (Pl. III, Figs. 1–4). Some irregular blobs of chalcocite have grown at the expense of pyrite clusters, and chalcopyrite at the expense of pyrite aggregates (Pl. III, Figs. 5, 6).

Replacement of pyrite by copper sulphides indicates that the formation of framboidal pyrite predated copper precipitation. Since pyrite is replaced by copper sulphides, and sulphur-rich copper-poor sulphide (chalcopyrite) is followed successively by sulphur-poor copper-rich sulphides (bornite, chalcocite), it may be assumed that the generalized succession is: pyrite – sphalerite, galena – chalcopyrite – bornite – chalcocite (Fig. 3).

IMPLICATIONS FOR GENETIC INTERPRETATIONS

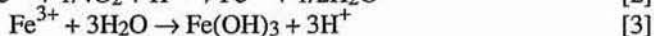
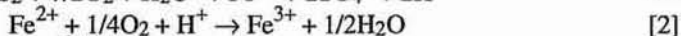
Many aspects of ore genesis have very recently been reviewed by A. Rydzewski (1969), E. C. Jowett (1986), S. Speczik, W. Püttmann (1987), E. C. Jowett *et al.* (1987), F. -P. Schmidt, G. Friedrich (1988), S. Oszczepalski (1989), D. J. Vaughan *et al.* (1989), H. Kucha (1990), S. Oszczepalski, A. Rydzewski (1991). They maintain that the formation of ores should be regarded as an overall product of the Permian basin evolution. Lower Permian volcanic rocks and pre-Permian rocks have been postulated to have provided the source sediment in the form of the Rotliegendes redbeds. Metals may have been leached to form cuprous chloride complexes by the convectionally driven oxidizing and near neutral brines of Na-Ca-Cl type (E. C. Jowett, 1986; S. Oszczepalski, 1989).

Mineralization of the Kupferschiefer ore sequence originated when metalliferous basinal brines were channelled updip up the flanks of palaeohighs into Zechstein sediments. Ore-fluid migration proceeded along the reactivated fault systems separating palaeohighs from depressions. This passage was probably enhanced by a higher than normal heat flow in the regions of magmatic Permian activity and by the tectonic instability of the Permian

intracontinental rift basin. In areas of upward movement of mineralizing fluids, pyritic and organic-rich basal Zechstein sediments have been strongly altered. This is demonstrated by the presence of hematitic spherules pseudomorphic after framboidal pyrite, remnants of oxidized copper sulphides, and relics of strongly degraded organic matter in reddened sediments. Highly characteristic are halos of hematite surrounding Cu-sulphide grains, intergrowths of iron oxides with copper sulphides as the by-products of pyrite substitution by copper, rims and partial replacements of copper sulphides by iron oxides, as well as partial replacements of chalcocite and Cu-Fe-S type sulphides by covellite. These replacements by covellite can be interpreted as indicative of the step-wise process of oxidation resulting in a loss of copper and an effective gain in sulphur (cf. M. Sato, 1960). Note, that in this case much covellite, anilite, djurleite and digenite, which occur proximally to the oxidized areas, could have been formed as intermediates in the oxidation of chalcocite.

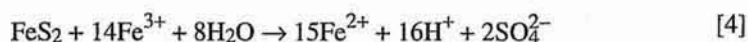
The most important factor which could have influenced the hematite/ore system formation was the long-distance brine transport. It is clearly evidenced by the overlapping character of hematite emplacement, high-grade (> 40 kg/m² Cu) copper mineralization belts rimming the oxidized areas, and the concentric pattern of mineral parageneses (Figs. 1, 2). As a further result of oxidative alteration by flowing fluids, sulphates were precipitated as gypsum and anhydrite within surrounding carbonates, with $\delta^{34}\text{S}$ values from -21 to 20‰ (E. C. Jowett *et al.*, 1991). This range may be partly related to the oxidation of isotopically light pyrite. These fluids also removed trace metals from the hematized areas, such as Ag and Mo, concentrating them at the redox interface (Fig. 2). A fraction of iron might have been also removed from the transition-chalcocite zone to the bornite-chalcocopyrite zone, as is indicated by a minimum iron content within the first mentioned zone. Also, the noble metals, U and Th accumulated at the boundary between oxidized and reduced sediments as a result of the oxidation of organics catalyzed by noble metals and gamma radiation (H. Kucha, 1990).

Potential oxidants. It seems evident that the oxidized facies resulted from the inorganic post-depositional oxidation of pyrite containing organic-rich basal Zechstein. In areas of the most intensive ascent of altering fluid, reactions of this fluid with pyrite and organics precipitated iron oxides. Some of the oxygen needed to destroy pyrite and organics may have originated from gases dissolved in Rotliegendes waters. More oxygen would have been supplied to the Rotliegendes aquifer due to the mixing of meteoric waters with ascending formational brines, but not to such extents as to limit the solubility of copper as cuprous chloride complexes (cf. A. W. Rose, 1989). In oxygen-poor waters pyrite was preferentially oxidized by Fe²⁺ and Cu⁺, and less so by dissolved oxygen. Oxidation of pyrite by oxygen may be described as follows:



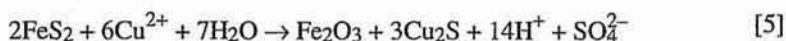
Hematite is a final product of goethite (FeOOH) and iron hydroxide dehydration (U. Schwertmann, E. Murad, 1983). Oxidation of pyrite at pH < 4 is very rapid because of the mediation of iron-oxidizing bacteria. However, these bacteria grow poorly above pH 4 and, furthermore, above pH 5 the inorganic oxidation of Fe²⁺ to Fe³⁺ is so fast that bacteria play

only a minor role in catalyzing the process (C. O. Moses *et al.*, 1987). Therefore, taking into account the inferred chemistry of mineralizing fluids, it is likely that in the presence of oxygen, inorganic oxidation of the Kupferschiefer pyrite was presumably of greater importance when compared with microbial oxidation. Pyrite could have also been oxidized by ferric iron transported by mineralizing fluids and/or produced by reaction [2]:

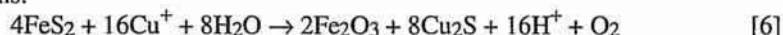


The solubility of Fe^{3+} is very low at $\text{pH} > 4$, nevertheless some ferric iron remains in solution. As experimentally demonstrated (C. O. Moses *et al.*, 1987), low concentrations of ferric iron can oxidize pyrite, and dissolved oxygen is not required for pyrite oxidation in the pH range where the solubility of Fe^{3+} is low.

Other potential oxidants might have been radicals (H_2O_2 , OH) produced during radiolysis of aqueous fluids (cf. I. F. Vovk, 1981), as well as cupric ions:



and cuprous ions:



Note, that this reaction [6] also produces a little O_2 for further oxidation. Furthermore, in weakly oxidizing and circumneutral solutions, which are expected to have percolated through the redox transition before entering the reducing environment, intermediate sulphur oxyanions (sulphite, SO_3^{2-} ; thiosulphate, $\text{S}_2\text{O}_3^{2-}$; polythionates, $\text{S}_n\text{O}_6^{2-}$) might have been formed in addition to sulphate, as has been experimentally verified (H. C. Granger, C. G. Warren, 1969; M. B. Goldhaber, 1983). Sulphoxy species can be involved in sulphide mineral oxidation (C. O. Moses *et al.*, 1987). Ubiquitous thiosulphate relics (H. Kucha, 1990) suggest that the $\text{S}_2\text{O}_3^{2-}$ anion played a crucial role in metal accumulation and redistribution.

Contemporaneously, oxidation processes created initial acidity of the fluid, which caused leaching of framboidal pyrite, as supported by local absence of hematite framboids in low-energy reddened shales. However, in an alkaline carbonate environment hydrogen ions released during oxidation are neutralized and the pH remains near neutral (R. V. Nicholson *et al.*, 1988). Such chemistry of the migrating fluid enhanced incomplete iron dissolution resulting in the formation of iron oxides which mimic the morphology of precursor pyrite (cf. M. B. Goldhaber, 1983). This same fluid was also responsible for local dissolution and calcitisation of oxidized carbonates (S. Oszczepalski, 1989).

Potential sources of sulphur. Metal zoning and textural relationships of oxide and sulphide minerals suggest that altering Cu-bearing fluids spreading outward from the feeder areas emplaced copper into reduced sediments, precipitating Cu to form successive copper assemblages as the ore fluids became progressively depleted in copper in response to increased H_2S fugacity (cf. E. M. Ripley *et al.*, 1985; D. W. Haynes, M. S. Bloom, 1987; A. W. Rose, 1989). The framboidal habit of the majority of pyrite and $\delta^{34}\text{S}$ values ranging from -3 to -44% (e.g. C. Harańczyk, 1972) are indicative of formation within some metres of the sediment surface during bacterial sulphate reduction. Chalcocite-

like phase and sulphur isotopes of disseminated Cu-sulphides from -2 to -44% , with a maximum between -31 and -36% (E. C. Jowett *et al.*, 1991 with references), suggest that disseminated ores were deposited by bacterially-produced sulphide (incorporating, like pyrite, ^{34}S -enriched biogenic sulphide) at temperatures less than about 100°C , i.e. at a burial depths less than ca. 600 m (S. Oszczepalski, 1989). Some copper could have been fixed by reaction with early-diagenetic pyrite. We should, however, take into account the fact that the pyrite-replacement model alone cannot clearly explain the formation of high-grade copper orebodies, because of insufficient amounts of pyrite in the basal Zechstein to supply enough sulphur. The fact that chalcocite enrichments do not usually contain pyrite testifies the intensity of the replacement-type reactions of Cu-bearing fluids with iron sulphides, or alternatively, there is the possibility that cupriferous solutions locally penetrated sediments and deposited copper before the formation of pyrite. The other potential S source could have been organic sulphur derived from early-diagenetic decomposition of organically bound reduced sulphur, or supplied during subsequent diagenesis, by thermal degradation of organic sulphur compounds. At slightly elevated temperatures pyrite may be hydrolyzed to become the source of sulphur as H_2S (H. Ohmoto, 1986). Some additional sulphur could have been provided by disproportionation of oxyanions to aqueous sulphide (H. C. Granger, C. G. Warren, 1969), by an extrinsic reducing agent (e.g. H_2S -containing hydrocarbons), and as SO_4^{2-} supplied by the Rotliegendes brines or from the oxidation of pyrite and organic sulphur with subsequent abiologic sulphate reduction. Characteristically, sulphides in coarse aggregates and veinlets are isotopically heavier than sulphides in disseminations, having $\delta^{34}\text{S}$ values generally ranging between -25 and -35% . ^{34}S -enriched sulphur within coarse-grained ores and veinlets indicates that some isotopically heavy sulphur was introduced to the Kupferschiefer from the underlying Rotliegendes and reduced by thermochemical reaction with organic matter in the Kupferschiefer (E. C. Jowett *et al.*, 1991).

CONCLUDING REMARKS

The textural and paragenetic data strongly suggest that the main Kupferschiefer hematite and base metal sulphide mineralization originated after the formation of pyrite. Textural evidence for pre- and post-lithification precipitation of the sulphide/oxide parageneses indicates that a syngenetic model, in which metals and sulphur are both sedimentary is untenable. Instead, the mixing model, in which ore metals are imported to sediments and precipitated by chemical reactions between mineralizing solutions and pore water containing reduced sulphur, appear to be easily accepted. The replacement textures present within the transition from oxidized to reduced rocks, the discordant position of the Rote Fäule to the stratigraphy, the fundamental link between hematite and sulphide mineralization, and zonation patterns collectively suggest that the Kupferschiefer hematite/sulphide mineralization originated from upward and laterally flowing fluids. Passage of these fluids through the basal Zechstein sediments caused the oxidation of organic matter, oxidation of pyrite to iron oxides, oxidation of copper sulphides, precipitation of metals by sulphide, and successive precipitation of other base metals as the fluids gradually lost their oxidation potential. Further petrographical, geochemical and S isotope studies are required to deter-

mine whether, besides a mixing mechanism, other models for transportation and precipitation of base metals and sulphur contributed to ore-forming process.

It is conceivable that processes leading to the formation of the Kupferschiefer ore pattern were long-lived and lasted presumably over a time span from 250 (the Kupferschiefer deposition age) to about 220 Ma, as is suggested by the age of hematite (E. C. Jowett *et al.*, 1987) and precompactational timing of the bulk of ores (S. Oszczepalski, 1989). After the early-diagenetic period of disseminated-ore formation, probably before complete lithification of the enclosing sediments, complex processes of dissolution-migration-reprecipitation operated, as is evidenced by numerous copper sulphide replacements of carbonates and detrital grains as well as mutual intergrowths of copper sulphides. Coarse-grained and veined ores have generally been considered to have originated during later diagenesis after some lithification of the host sediments (E. C. Jowett, 1986), although it is still hard to distinguish whether this was as a result of remobilization of early-formed sulphides, additional late introduction of ore fluids and hydrofracturing or as a consequence of joint action of the above mechanism, as was maintained by S. Oszczepalski (1989). Quantitative mass balance evaluation implies that superposition of early- and late-diagenetic mineralization must be appealed to in order to account for the observed Lubin deposit (L. M. Cathles *et al.*, 1993).

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REFERENCES

- BANAŚ M., SALAMON W., PIETRZYŃSKI A., MAYER W. (1982) — Replacement phenomena of terrigenous minerals by sulphides in copper-bearing Permian sandstones in Poland. In: Ore genesis — the state of the art (eds. G. C. Amstutz *et al.*), p. 3–9. Springer Verlag, Berlin, Heidelberg.
- CATHLES L. M. III., OSZCZEPALSKI S., JOWETT E. C. (1993) — Mass balance evaluation of the late diagenetic hypothesis for Kupferschiefer Cu mineralization in the Lubin basin of southwestern Poland. *Econ. Geol.*, **88**, p. 948–956.
- GOLDHABER M. B. (1983) — Experimental study of metastable sulphur oxyanion formation during pyrite oxidation at pH 6–9 and 30°C. *Am. J. Sc.*, **283**, p. 193–217.
- GRANGER H. C., WARREN C. G. (1969) — Unstable sulphur compounds and the origin of roll-type uranium deposits. *Econ. Geol.*, **64**, p. 160–171.
- HARAŃCZYK C. (1972) — Ore mineralization of the Lower Zechstein euxinic sediments in the Fore-Sudetic Monocline (in Polish with English summary). *Arch. Miner.*, **30**, p. 13–173, no. 1–2.
- HAYNES D. W., BLOOM M. S. (1987) — Stratiform copper deposits hosted by low-energy sediments: IV. Aspects of sulphide precipitation. *Econ. Geol.*, **82**, p. 875–893.
- JOWETT E. C. (1986) — Genesis of Kupferschiefer Cu-Ag deposits by convective flow of Rotliegende brines during Triassic rifting. *Econ. Geol.*, **81**, p. 1823–1837.
- JOWETT E. C., PEARCE G. W., RYDZEWSKI A. (1987) — A Mid-Triassic paleomagnetic age of the Kupferschiefer mineralization in Poland, based on a revised apparent polar wander path for Europe and Russia. *J. Geophys. Res.*, **92**, p. 581–598.

- JOWETT E. C., RYE R. O., OSZCZEPALSKI S., RYDZEWSKI A. (1991) — Isotopic evidence for the addition of sulphur during formation of the Kupferschiefer ore deposits in Poland. *Zbl. Geol. Paläont.*, **4**, p. 1001–1015, Teil I.
- KONSTANTYNOWICZ E. (1965) — Signs of mineralization of the Zechstein of the North Sudetic syncline. *Pr. Geol. Komis. Nauk Geol. PAN, Kraków*, **28**.
- KUCHA H. (1990) — Geochemistry of the Kupferschiefer, Poland. *Geol. Rundsch.*, **79**, p. 387–399.
- LISIAKIEWICZ S. (1969) — Geological structure and mineralogical analysis of a copper deposit in the Grodziec Basin (in Polish with English summary). *Biul. Inst. Geol.*, **217**, p. 5–109.
- MAYER W., PIESTRZYŃSKI A. (1985) — Ore minerals from Lower Zechstein sediments at Rudna mine, Fore-Sudetic Monocline, SW Poland. *Pr. Miner. Komis. Nauk Miner. PAN, Kraków*, **75**.
- MOSES C. O., NORDSTROM D. K., HERMAN J. S., MILLS A. L. (1987) — Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochim. Cosmochim. Acta*, **52**, p. 1561–1571.
- NICHOLSON R. V., GILLHAM R. W., REARDON E. J. (1988) — Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings. *Geochim. Cosmochim. Acta*, **54**, p. 395–402.
- NIŚKIEWICZ J. (1980) — Metasomatic phenomena in the Zechstein copper ore deposits of Lower Silesia (in Polish with English summary). *Geol. Sudetica*, **15**, p. 7–82, no. 2.
- OHMOTO H. (1986) — Stable isotope geochemistry of ore deposits. *Rev. Miner.*, **16**, p. 491–559.
- OSZCZEPALSKI S. (1979) — Polymetallic mineralization of basal Zechstein rocks in the Węglińiec – Żary area (in Polish with English summary). *Kwart. Geol.*, **23**, p. 563–578, no. 3.
- OSZCZEPALSKI S. (1980) — Paleogeography, sedimentation and mineralization of the Z1 carbonate series (Zechstein) in the western part of the Fore-Sudetic Monocline (western Poland). *Contr. Sed.*, **9**, p. 307–323.
- OSZCZEPALSKI S. (1989) — Kupferschiefer in southwestern Poland: sedimentary environments, metal zoning, and ore controls. *GAC Spec. Paper*, **36**, p. 571–600.
- OSZCZEPALSKI S., RYDZEWSKI A. (1983) — Copperbearing of Permian rocks in areas adjoining the Lubin – Sieroszowice deposit (in Polish with English summary). *Prz. Geol.*, **31**, p. 437–444, no. 7.
- OSZCZEPALSKI S., RYDZEWSKI A. (1991) — The Kupferschiefer mineralization in Poland. *Zbl. Geol. Paläont.*, **4**, p. 975–999, Teil I.
- RENTZSCH J., KNITZSCHKE G. (1968) — Die Erzmineralparagenesen des Kupferschiefers und ihre regionale Verbreitung. *Freib. Forsch.-H.*, **C231**, p. 189–211.
- RIPLEY E. M., MERINO M., MOORE C., ORTLOLEVA P. (1985) — Mineral zoning in sediment-hosted copper deposits. In: *Handbook of strata-bound and stratiform ore deposits* (ed. K. H. Wolf), **13**, p. 237–260.
- ROSE A. W. (1989) — Mobility of copper and other heavy metals in sedimentary environments. *GAC Spec. Paper*, **36**, p. 97–110.
- RYDZEWSKI A. (1964) — Petrography and mineralization of the Zechstein deposits in the areas of Fore-Sudetic monocline and of pericline of Żary (in Polish with English summary). *Prz. Geol.*, **12**, p. 476–480, no. 12.
- RYDZEWSKI A. (1969) — Petrography of the copper-bearing Zechstein shales in the fore-Sudetic monocline (Lower Silesia) (in Polish with English summary). *Biul. Inst. Geol.*, **217**, p. 113–167.
- RYDZEWSKI A. (1978) — Oxidated facies of the Zechstein copper-bearing shale in the Fore-Sudetic Monocline (in Polish with English summary). *Prz. Geol.*, **26**, p. 102–108, no. 2.
- RYDZEWSKI A., OSZCZEPALSKI S. (1984) — Występowanie stref utlenionych i ich znaczenie w poszukiwaniu cechstyńskich złóż rud miedzi. *Arch. Państw. Inst. Geol. Warszawa*.
- SATO M. (1960) — Oxidation of sulphide ore bodies — II. Oxidation mechanisms of sulphide minerals at 25°C. *Econ. Geol.*, **55**, p. 1202–1231.
- SAWŁOWICZ Z. (1989) — Organic matter in the Zechstein Kupferschiefer from the Fore-Sudetic Monocline (Poland). *I. Bitumen. Miner. Pol.*, **20**, p. 69–86.
- SAWŁOWICZ Z. (1990) — Primary copper sulphides from the Kupferschiefer, Poland. *Miner. Deposita*, **25**, p. 262–271.
- SCHMIDT F.-P., FRIEDRICH G. (1988) — Geologic setting and genesis of Kupferschiefer mineralization in West Germany. *SGA Miner. Deposits Spec. Publ.*, **5**, p. 25–59.
- SCHWERTMANN U., MURAD E. (1983) — The effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays Miner.*, **31**, p. 277–284.
- SKOWRONEK C. (1968) — Taches rouges dans les formations du Zechstein bas (in Polish with French summary). *Rudy Metale Nieżel.*, **13**, p. 134–137.
- SPECZIK S., PÜTTMANN W. (1987) — Origin of Kupferschiefer mineralization as suggested by coal petrology and organic geochemical studies. *Acta Geol. Pol.*, **37**, p. 167–187, no. 3–4.
- VAUGHAN D. J., SWEENEY M., FRIEDRICH G., DIEDEL R., HARAŃCZYK C. (1989) — The Kupferschiefer: An overview with an appraisal of the different types of mineralization. *Econ. Geol.*, **84**, p. 1003–1027.

- VOVK I. F. (1981) — Radiolytic model of formation of brine composition in the crystalline basement of shields. *Geochem. Intl.*, 18, p. 80–93.
- WYŻYKOWSKI J. (1958) — Research of copper ores in the fore-sudetic zone (in Polish with English summary). *Prz. Geol.*, 6, p. 17–22, no. 1.

Sławomir OSZCZEPALSKI

UTLENIAJĄCE PRZEOBRĄŻENIE ŁUPKU MIEDZIONOŚNEGO W POLSCE: TLENKOWO-SIARCZKOWE PARAGENEZY I IMPLIKACJE GENETYCZNE

Streszczenie

Cechsżyńskie rudy miedzi typu łupku miedzionośnego występują w SW Polsce (fig. 1) i leżą w strefie kontaktowej między lądowymi utworami czerwonego spągowca i morskimi utworami cechsztynu, tworzącej tzw. serię miedzionośną (fig. 2).

W obrębie serii miedzionośnej stwierdzono osady noszące charakter redukcyjny i utleniony („rote Fäule”). Tego rodzaju dwufacjalność osadów ujawniono zarówno w niecce północnosudeckiej, jak i na monoklinie przedsudeckiej oraz w NW Polsce (fig. 1). Facja utleniona obejmuje utwory o czerwonej lub szarobrunatnej barwie, zawierające hematyt i uwodnione tlenki żelaza (brak siarczków, obecne tlenkowe pseudomorfozy po framboidalnym pirycie; tabl. I, fig. 1, 2) oraz znikome zawartości w łupku miedzionośnym zdegradowanej materii organicznej ($< 0,9\% C_{org}$), bituminów, izoprenoidów, porfirin, metylfenantrenów i S_{calc} ($< 0,2\%$), przy bardzo wysokim stosunku Fe_2O_3/C_{org} (> 2). Najczęściej cechy facji utlenionej wykazują osady białego spągowca oraz wapienia podstawowego i łupku miedzionośnego (w niecce północnosudeckiej pod nazwą margli plamistych), rzadziej utwory wapienia cechsżyńskiego lub — w skrajnym przypadku — spągowe partie anhydrytu dolnego.

Kontakt strefy utlenionej i redukcyjnej (zarówno pionowy, jak i lateralny) nie jest granicą ostrą, lecz stanowi strefę przejściową od utworów zawierających tlenki żelaza do utworów osiarczkowanych. Strefa przejściowa przemieszcza się od białego spągowca do spągu anhydrytu dolnego (ku centrum strefy utlenionej) pod kątem $0,5-1^\circ$, tnąc granice jednostek litostratygraficznych serii miedzionośnej (S. Oszczepalski, 1989; S. Oszczepalski, A. Rydzewski, 1991). Cechą charakterystyczną tej strefy są cechy pośrednie do facji utlenionej i redukcyjnej. W szczególności strefę tę cechuje: (1) współwystępowanie rozproszonych tlenków żelaza i siarczków metali (głównie typu Cu-S); (2) obecność reliktywów siarczków z otoczkami pigmentu hematytowego oraz struktur zastępowania siarczków miedzi przez hematyt i getyt (tabl. I, fig. 3–7); oraz (3) nieznacznie podwyższona — w stosunku do utworów całkowicie utlenionych — zawartość miedzi (w granicach od 0,1 do 0,4%). W pionie strefę przejściową cechuje zmienna miąższość, od kilku milimetrów lub centymetrów w łupku miedzionośnym do kilku lub kilkunastu metrów w białym spągowcu i wapieniu cechsżyńskim. Lateralnie, szerokość strefy przejściowej nie przekracza kilku kilometrów.

Stwierdzone dotychczas prawidłowości w obrazie rozmieszczenia i zróżnicowania omawianej mineralizacji — a zwłaszcza: (1) występowanie strefy przejściowej (o zmiennej miąższości) między osadami facji utlenionej i redukcyjnej (fig. 2); (2) występowanie siarczków miedzi bezpośrednio ponad osadami utlenionymi (liczne wypełnienia wolnych przestrzeni oraz zastąpienia węglanów i framboidalnego pirytu przez siarczki) (tabl. II i III); (3) przecinanie granic litologicznych i stratygraficznych przez nieregularną powierzchnię graniczną strefy przejściowej; (4) przemieszczanie się najbogatszej mineralizacji siarczkowej z białego spągowca do anhydrytu dolnego, wzdłuż kontaktu ze strefą przejściową; (5) występowanie bogatej mineralizacji miedziowej (o zasobnościach powyżej 40 kg/m^2) wyłącznie w najbliższym otoczeniu obszarów utlenionych (fig. 1); (6) pozioma i pionowa strefowość występowania metali (jej wyrazem jest stopniowy wzrost zawartości — kolejno — cynku, ołowiu i miedzi w stronę utworów zawierających tlenki żelaza); (7) występowanie ciał rudnych w pobliżu lineamentów oddzielających permskie paleowyniesienia od paleodepresji — świadczą o tym, że powstanie systemu hematytowo-siarczkowego i złóż rud miedzi jest wynikiem procesów utleniania i redukcji, zachodzących pod wpływem ascencji z utworów czerwonego spągowca niskotemperaturowych roztworów chlorkowych, zawierających metale, oraz ich przepływu przez spągowe utwory cechsztynu, ulegające beztlenowej diagenecie.

Przepływ tych roztworów powodował utlenienie materiału organicznego i wczesnodiagenetycznego pirytu w łupku miedzionośnym. Do potencjalnych utleniaczy należy zaliczyć: tlen rozpuszczony w solankach, tlen dostarczany do solanek przez wody meteoryczne, Fe^{3+} , Cu^{2+} , Cu^+ oraz produkty radiolizy. Możliwymi źródłami siarki potrzebnej do zredukowania metali były: siarkowodór biogeniczny, piryt, siarka związana z materią organiczną, siarkowodór wchodzący w skład węglowodorów, oxyaniony siarki (powstałe w trakcie utleniania osadów redukcyjnych) oraz siarczany (pochodzące z czerwonego spagowca, jak i powstałe wskutek działania procesów utleniających) — poprzez ich termochemiczną redukcję. Takie czynniki jak: wysoki postwaryscyjski strumień cieplny oraz tektoniczna niestabilność związana z tworzeniem się intrakontynentalnego ryftu w permie, ułatwiały cyrkulację roztworów mineralizujących. Konwekcyjny przepływ mógł istnieć przez długi okres, powodując ekspansję obszarów utlenionych oraz tworzenie się ciał rudnych i żył kruszcowych.

PLATE I

Reflected light photomicrographs of iron oxides and copper sulphides (in oil)

Mikrofotografie (w świetle odbitym) tlenków żelaza i siarczków metali (w imersji)

Fig. 1. Goethite pseudomorphic after pyrite spherules; Kupferschiefer, K-10 borehole

Getytowe pseudomorfozy po kulkach pirytu; łupek miedzionośny, otwór wiertniczy K-10

Fig. 2. Hematite pseudomorphs after framboidal pyrite; Kupferschiefer, K-10 borehole

Pseudomorfozy hematytu po framboidalnym pirycie; łupek miedzionośny, otwór wiertniczy K-10

Fig. 3. Digenite (grey) intergrown with hematite laths (light grey, high relief); Zechstein Limestone, Koźuchów IG 1 borehole (near K-10 borehole)

Digenit (szary) przerośnięty listewkowym hematytem (jasnoszary, wysoki relief); wapień cechsztyński, otwór wiertniczy Koźuchów IG 1 (w pobliżu otworu K-10)

Fig. 4. Chalcocite (white) invaded and rimmed by goethite (dark grey) and hematite (white, high relief); Zechstein Limestone, Sieroszowice mine

Chalkozyn (biały) penetrowany i otoczony getytem (ciemnoszary) i hematytem (biały, wysoki relief); wapień cechsztyński, kopalnia Sieroszowice

Fig. 5. Chalcocite (white) partially replaced by hematite (tiny white crystals with high relief); submicroscopic masses of iron oxides separate hematite crystals from chalcocite; Zechstein Limestone, Koźuchów IG 1 borehole (near K-10 borehole)

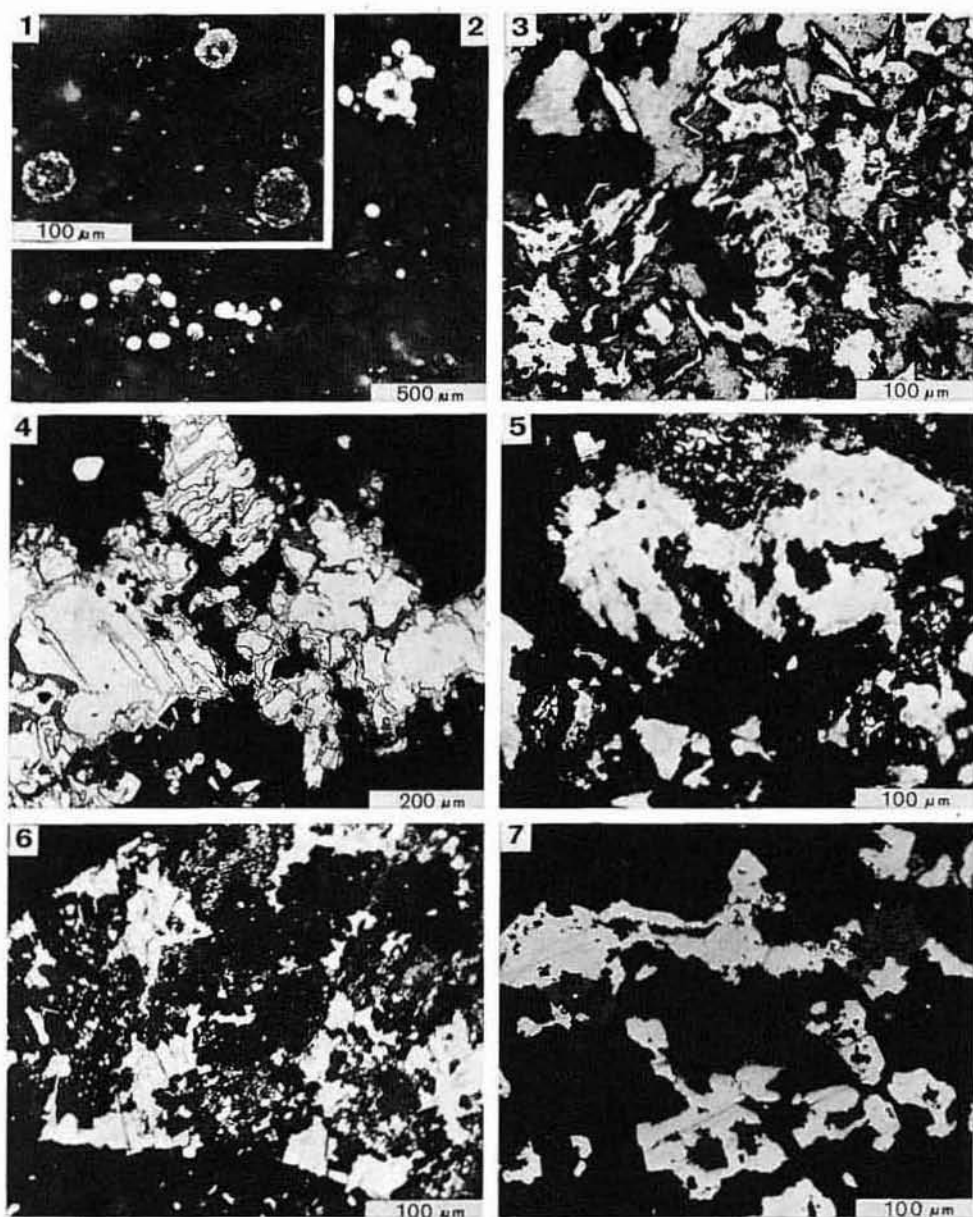
Chalkozyn (biały) częściowo zastąpiony hematytem (drobne białe kryształy o wysokim reliefie); submikroskopowe tenki żelaza oddzielają kryształy hematytu od chalkozynu; wapień cechsztyński, otwór wiertniczy Koźuchów IG 1 (w pobliżu otworu wiertniczego K-10)

Fig. 6. Covellite (white) replacing fragment bryozoa skeleton, later on replaced by clumps of iron oxides; Kupferschiefer, S-484 borehole

Kowelin (biały) zastępujący fragment szkieletu mszywiola, podstawiony kępami tlenkami żelaza; łupek miedzionośny, otwór wiertniczy S-484

Fig. 7. Chalcopyrite (light grey) partially replaced by goethite (grey); Kupferschiefer, Konrad mine

Chalkopiryt (jasnoszary) częściowo zastąpiony getytem (szary); łupek miedzionośny, kopalnia Konrad



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PLATE II

Reflected light photomicrographs of sulphide mineral textures (in oil)

Mikrofotografie (w świetle odbitym) tekstur minerałów siarczkowych (w imersji)

Fig. 1. Replacements of quartz and lithic grains by bornite (bn) and chalcocite (cc), Weissliegendes, Rudna mine
Tekstury zastąpienia kwarcu i ziarn litycznych przez bornit (bn) i chalkozyn (cc); biały spągowiec, kopalnia Rudna

Fig. 2. Chalcopyrite grains wrapped by clay laminae, Kupferschiefer, Grundy Górne IG 1 borehole

Ziarno chalkopirytu otoczone laminami ilastymi; łupek miedzionośny, otwór wiertniczy Grundy Górne IG 1

Fig. 3. Francolithic fragments of lingula shells cracked and cemented by sphalerite (s) and chalcopyrite (cp); finely disseminated chalcopyrite grains in shale; Kupferschiefer, M-1 borehole

Frankolitowe fragmenty skorupki lingul, porozrywane i scementowane sfalerytem (s) i chalkopirytem (cp), rozproszone ziarna chalkopirytu w obrębie łupku; łupek miedzionośny, otwór wiertniczy M-1

Fig. 4. Carbonate laminae replaced by galena (g) and sphalerite (s); note relics of carbonates (dark grey); Kupferschiefer, M-1 borehole

Laminy węglanowe zastąpione galeną (g) i sfalerytem (s); zwracają uwagę relikty węglanów (ciemnoszare); łupek miedzionośny, otwór wiertniczy M-1

Fig. 5. Galena infilling vug in the Zechstein Limestone; note partial replacement of dolomite rhomb by galena; Lubin mine

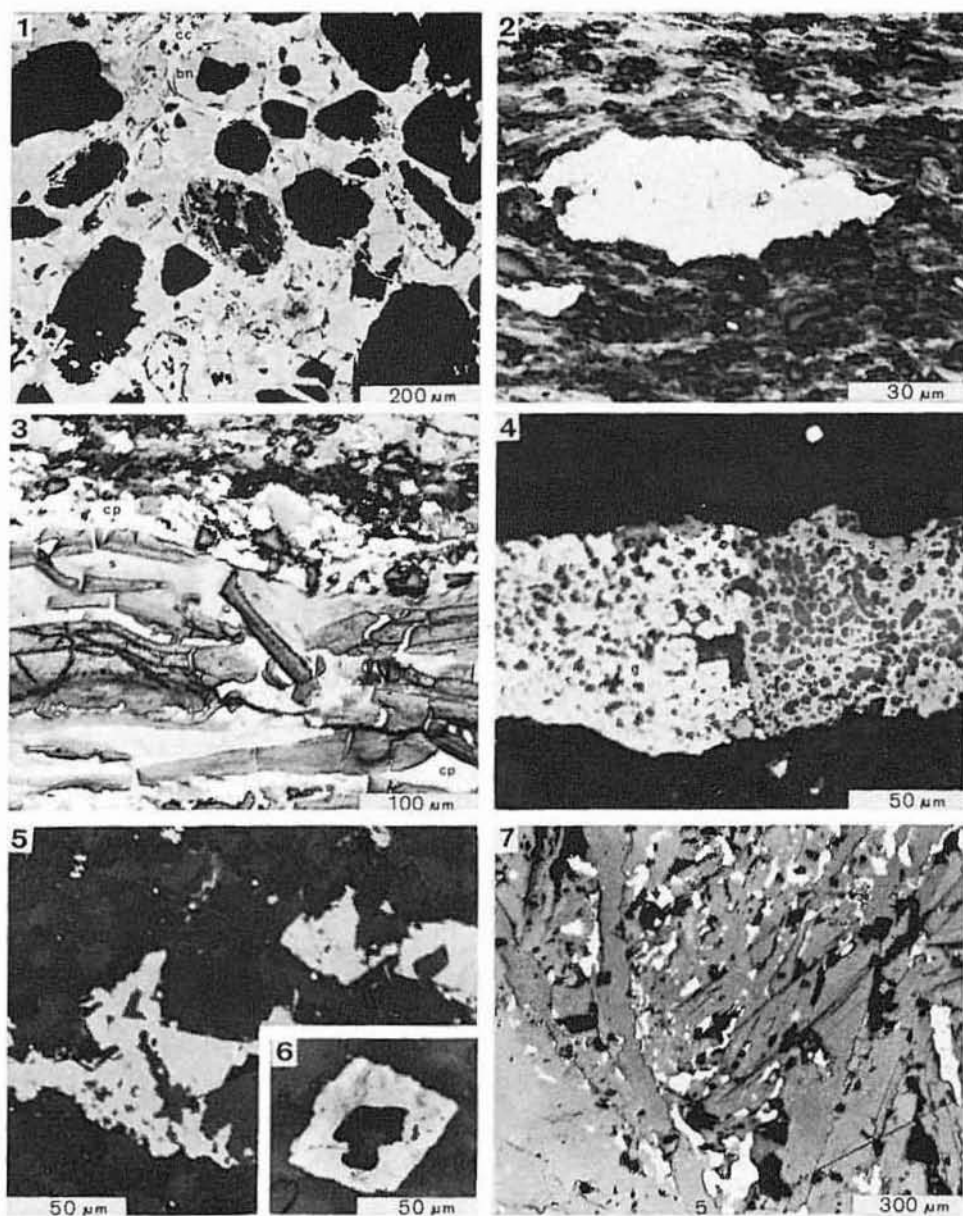
Galena wypełniająca pustkę w wapieniu cechsztyńskim; zwraca uwagę częściowe zastąpienie romboedru dolomitowego galeną; kopalnia Lubin

Fig. 6. Dolomite rhomb partially replaced by covellite; Zechstein Limestone, M-24 borehole

Romboedr dolomitu częściowo zastąpiony kowelinem; wapień cechsztyński, otwór wiertniczy M-24

Fig. 7. Chalcopyrite replacing carbonate cement of anhydrite blades; Lower Anhydrite, M-26 borehole

Chalkopirynt zastępujący węglanowy cement pomiędzy listewkowym anhydrytem; anhydryt dolny, otwór wiertniczy M-26



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PLATE III

Reflected light photomicrographs of pyrite-copper sulphide replacement textures (in oil)

Mikrofotografie (w świetle odbitym) tekstur zastępowania pirytu przez siarczki miedzi (w imersji)

Fig. 1. Mimic replacement of framboidal pyrite (py) by chalcopyrite (cp); remnants of corroded pyrite are visible in microcrystals of chalcopyrite; Kupferschiefer, Polkowice mine

Piryt framboidalny (py) mimicznie zastąpiony chalkopirytem (cp); relikty korodowanego pirytu widoczne w obrębie mikrokryształów chalkopirytu; łupek miedzionośny, kopalnia Polkowice

Fig. 2. Pyrite (py) framboid mimically replaced by bornite (bn); chalcocite inclusions in bornite; Kupferschiefer, Polkowice mine

Framboid pirytu (py) mimicznie zastąpiony bornitem (bn); inkluzje chalkozynu w bornicie; łupek miedzionośny, kopalnia Polkowice

Fig. 3. Digenite (di) pseudomorphs after pyritic framboids cemented with chalcocite (cc); Kupferschiefer, Polkowice mine

Pseudomorfozy digenitu (di) po framboidach pirytowych, zcementowane chalkozynem (cc); łupek miedzionośny, kopalnia Polkowice

Fig. 4. Almost complete replacement of pyrite framboids by chalcocite; digenite (dark grey) inclusions in chalcocite; Zechstein Limestone, Kaleje 2 borehole

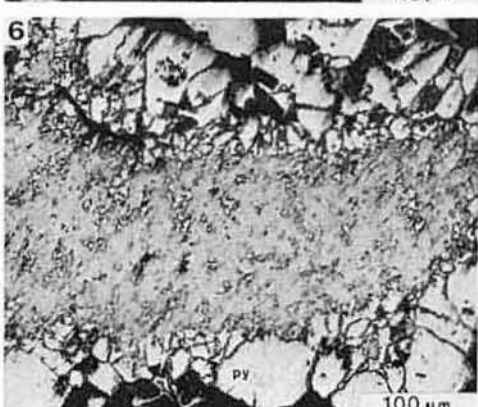
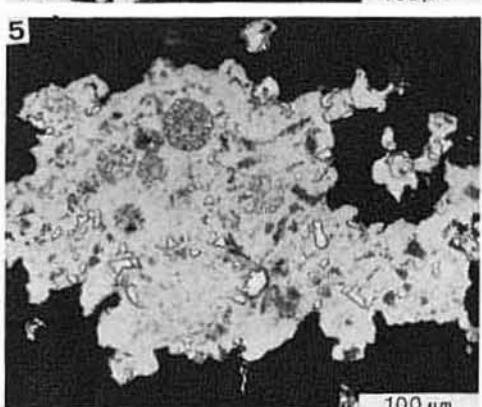
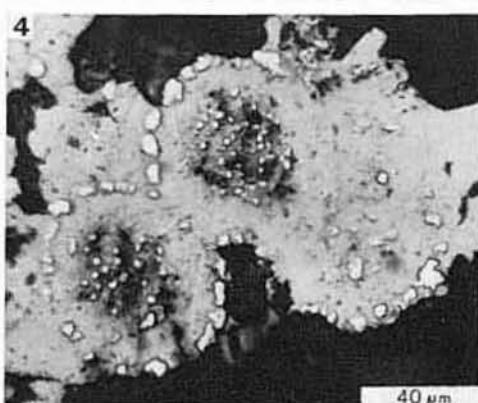
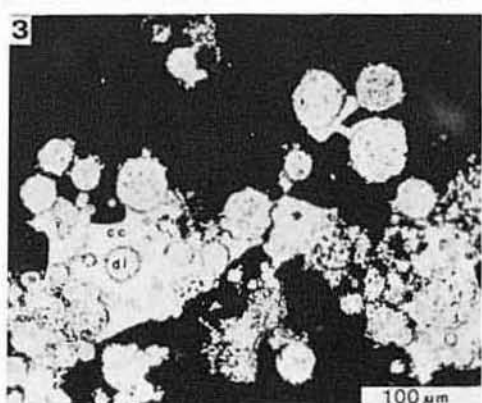
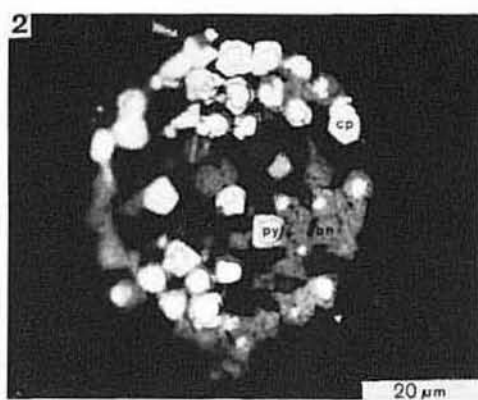
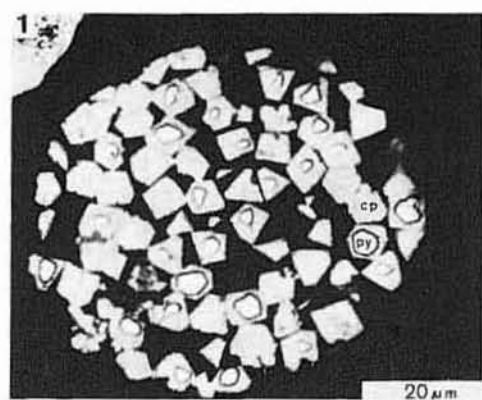
Niemal kompletne zastąpienie framboidów pirytu przez chalkozyn; inkluzje digenitu (ciemnoszare) w chalkozynie; wapień cechsztyński, otwór wiertniczy Kaleje 2

Fig. 5. Remnant pyrite framboids and corroded pyrite microcrystals (white) within chalcocite (grey); Kupferschiefer, Polkowice mine

Reliktowe framboidy pirytu i korodowane mikrokryształy pirytu (białe) w chalkozynie (szary); łupek miedzionośny, kopalnia Polkowice

Fig. 6. Successive replacement of pyrite (py) by chalcopyrite; Zechstein Limestone, Grundy Górne IG 1 borehole

Sukcesywne zastępowanie pirytu (py) chalkopirytem; wapień cechsztyński, otwór wiertniczy Grundy Górne IG 1



Ślawomir OSZCZEPALSKI — Oxidative alteration of the Kupferschiefer in Poland: oxide-sulphide parageneses and implications for ore-forming models