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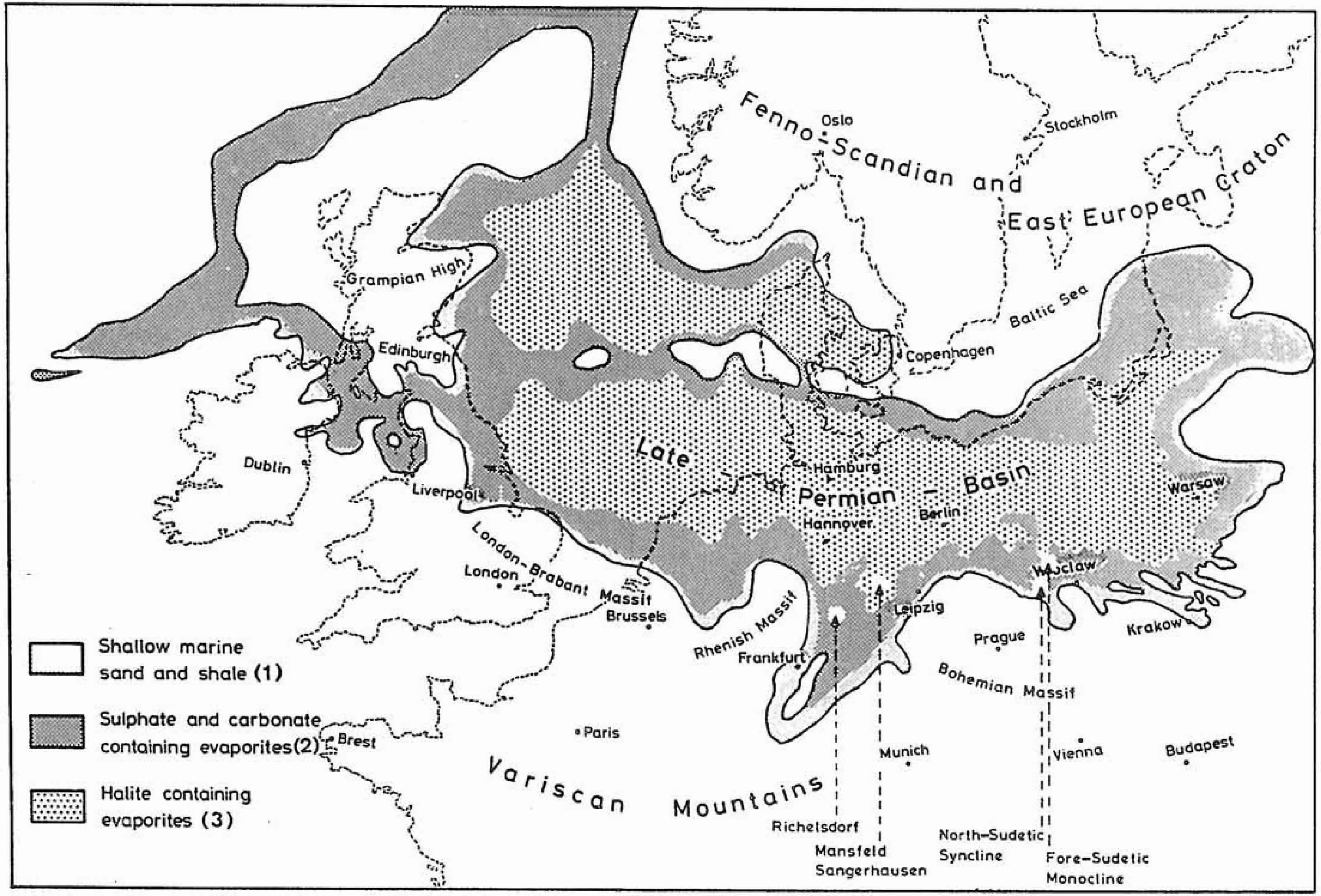
Composition and origin of the Kupferschiefer bed*

The Kupferschiefer of Upper Permian age sampled in Poland, Germany, the Netherlands and England has been investigated for its mineral, chemical and (S, Pb, O and C) isotopic composition. Rate of deposition of the sapropelic marly shale (rarely more than half a metre in thickness) was very low. This is indicated by high V/C, Mo/C and U/C ratios. Galena and sphalerite mineralization in the sediment, exceeding 0.5% metal, occurs over relatively large areas. Mineralization of chalcocite, bornite and chalcopyrite with more than 0.5% Cu is restricted to small regions which occur on top of voluminous Rotliegendes sediments. Economic grades for former and present copper mining in the latter areas are due to additional mineralization of the footwall (Weissliegendes) and/or hanging wall (Zechstein Limestone) of the Kupferschiefer bed. Late diagenetic remobilization of Cu into the hanging wall is usually indicated by adjacent zones of secondarily oxidized metal barren "Rote Fäule". The isotopically very light sulphur ($\delta^{34}S$ –24 to –40‰) in the majority of the syngenetically, early and late diagenetically formed sulphides is explained as a product of bacterial sulphate reduction. Precipitation of sulphides from seawater does not cause high Cu concentrations or even moderate Pb concentrations in sapropelic sediment. Seawater of closed nearshore basins and diagenetic fluids received their high metal concentrations from the porous Rotliegendes sediments in the Kupferschiefer footwall. Because Zn-Pb-Cu sulphides and pyrite contain different and not equilibrated sulphur isotopes, the former sulphides cannot have generally replaced the latter mineral. Vertical and lateral zonation of Cu (plus Ag), Pb and Zn sulphides in this sequence is controlled by their solubility and by the rate of bacterial sulphide production. The lead isotopic composition of the Kupferschiefer from Germany is intermediate between that of galena from the Middle Devonian Rammelsberg ore and from Jurassic vein deposits of the Harz Mts. The majority of properties of the Kupferschiefer bed can be explained by a syngenetic (indicated by framboids) to diagenetic (and not epigenetic) mineralization with metals mainly derived from soaked Rotliegendes sediments.

INTRODUCTION

The Kupferschiefer is a laminated marly shale, dark grey to black in colour due to a high content of degraded organic carbon. It is usually less than a metre thick and can be sampled at numerous surface, drilling and mining exposures in England, the Netherlands, Germany and Poland. This sediment was formed in a marine basin of Late Permian age. Its palaeogeography is drawn in Figure 1. It occurs in the footwall of the well known evaporite


Fenno-Scandian and East European Craton
Oslo
Stockholm
Grampian High
Edinburgh
Copenhagen
Baltic Sea
Dublin
Liverpool
Late Permian Basin
Hamburg
Hannover
Berlin
Warsaw
Wrocław
London-Brabant Massif
London
Brussels
Rhenish Massif
Frankfurt
Leipzig
Prague
Krakow
Bohemian Massif
Paris
Brest
Variscan Mountains
Munich
Vienna
Budapest
Richelsdorf
Mansfeld Sangerhausen
North-Sudetic Syncline
Fore-Sudetic Monocline
Shallow marine sand and shale (1)
Sulphate and carbonate containing evaporites(2)
Halite containing evaporites (3)

series. A specific feature of this black shale is its mineralization of sphalerite, galena, cholcocite, bornite and chalcopyrite in certain areas of deposition. The copper minerals are mainly restricted to regions not far from the shore (densely stippled area of Fig. 1). The four deposits of former and present mining at Richelsdorf, Mansfeld – Sangerhausen, the North-Sudetic Syncline and the Fore-Sudetic Monocline are marked by arrows in Figure. 1. The present author has investigated samples from these localities in Germany and Poland, and from numerous areas covered by Kupferschiefer grading from low to high Zn, Pb, Cu concentrations. Chemical, isotopic and microscopic methods were applied.

Controversial models exist of a syngenetic-diagenetic or an epigenetic formation of the Zn-Pb-Cu mineralization. Conclusions on the genesis should not be exclusively based on investigations from the mining areas. They should rather consider the different varieties of the Kupferschiefer bed and its footwall ranging from background to economic metal concentrations.

GEOLOGY AND PALAEOENVIRONMENT

At the beginning of the Zechstein period a marine transgression flooded parts of Central Europe extending from northern England and the North Sea to large parts of Poland (Fig. 1). By this time the pre-existing Variscan mountains were eroded to a large extent and deep depressions were filled with Lower Permian detritus. The Zechstein transgression hit an almost flat topography in northern Germany and Poland and a hilly topography surrounding the preserved parts of the Variscan mountains. The hilly region caused the formation of separate basins with a few hundred metres water depth. Erosion did not contribute much detrital material because of the dry climate. The latitudinal position of the Central European part of the Upper Permian basin was about 20 to 30 degrees North (C. R. Scotese *et al.*, 1979). Vanadium, molybdenum and uranium are elements, which typically accumulated in sapropelic sediments in amounts which correlate inversely with the rate of sediment accumulation. V/C, Mo/C and U/C ratios as high as 0.03, 0.005 and 0.001, respectively, indicate very low rates of detrital deposition of Kupferschiefer sapropels (U/C ratio from H. Tonndorf, 1994). They may be compared with sapropels from the Black Sea with V/C = 0.003 and Mo/C = 0.001 (H. -J. Brumsack, 1988). The rate of deposition in the Black Sea is about 30 cm per thousand years (L. A. Nazarkin, 1960). At the much lower rate of deposition in the North Atlantic of about 1 cm per thousand years V/C and Mo/C ratios as high as 0.01 and 0.005, respectively, could be observed in C_{org}-rich clays of Cenomanian/Turonian age in this ocean (H. -J. Brumsack, 1980, 1986). This comparison indicates

Fig. 1. Map of Zechstein deposition based on information from S. Depowski (1978), W. Jung (1968) and P. A. Ziegler (1982)

Position of the four mining localities of Kupferschiefer is marked by arrows

Mapa cechsztyńskiego systemu depozycyjnego, na podstawie prac S. Depowskiego (1978), W. Junga (1968) i P. A. Zieglera (1982)

1 — płytkomorskie piaskowce i łupki, 2 — siarczany i węglany z ewaporatami, 3 — sól kamienna z ewaporatami; usytuowanie kopalń cechsztyńskich rud miedzi wskazano strzałkami

a very low rate of detrital accumulation for the sampled Kupferschiefer basin, as low as in the present North Atlantic.

Sedimentation in the major part of the early Zechstein basin is characterized by a cyclic alternation of clay rich and carbonate rich material forming distinct laminations. This cyclic change was probably caused by different organic production with a seasonal optimum followed by a minimum of plankton growth and carbonate deposition. A recent formation of such seasonal lamination of biogenic and nonbiogenic components can be observed in the present Gulf of California (D. Donegan, H. Schrader, 1982). The thickness of the laminae in Kupferschiefer samples is ≤ 0.1 mm. For an average thickness of the Kupferschiefer bed of 30 to 40 cm its time of formation can be extrapolated as ranging between 10^4 and 10^5 years which is identical with the above estimate based on V and Mo accumulation. The agreement between the two estimates suggests that the lamination is due to seasonal changes in sedimentation.

The preservation of the lamination indicates the absence of bioturbation. Fossils of benthic organisms do not occur in the sediment (J. Paul, 1982). Their absence and the preservation of a large proportion of the original organic carbon (average $\approx 6\%$ C) indicates the existence of anoxic deep waters in the basins of the Kupferschiefer sea. Stagnant conditions in the water body might have been caused by vertical gradients in density related to temperature and/or salinity. The average boron concentration in the illitic mica of about 30 Kupferschiefer samples, as analyzed by K. H. Wedepohl (1964), is about 400 ppm B which is apparently related to almost normal seawater salinity and not to highly saline brines (for calibration see H. Harder, 1974).

Reducing conditions in sapropelic mud and anoxic deep waters cause the bacterial reduction of seawater sulphate and the precipitation of sulphides. The products of reduced seawater sulphate are pyrite by the reaction of H_2S with sedimentary iron oxides (R. A. Berner, 1984), and chalcocite, sphalerite and greenockite by precipitation from the anoxic part of the water column (L. Jacobs *et al.*, 1985, 1987). L. Jacobs (*op. cit.*) observed a dramatic decrease of Cu, Zn and Cd concentrations across the O_2/H_2S interface in the water column of the Framvaren Fjord in Norway and the Cariaco Trench North of Venezuela, and accumulation of these elements in the Framvaren sediment relative to the lithogenic components by factors of 11, 105 and 420, respectively. Silver would be additionally precipitated because of the very low solubility of its sulphide, but this was not investigated by L. Jacobs *et al.* (1985). The sulphur isotopic composition of Zn-Pb-Cu sulphides and of pyrite from Kupferschiefer of 19 localities in the Netherlands, NW Germany and the Mansfeld – Sangerhausen region, as analyzed by G. Marowsky (1969), clearly indicates its bacterial origin. C. Harańczyk (1986) and Z. Sawłowicz (1989) have reported comparable results from the deposits in Poland. This sulphide sulphur is isotopically very light with the most frequent values in the $\delta^{34}S$ range from –24 to –40‰, indicating sulphate reduction at low temperature. Such low values have to be explained by the kinetic fractionation effect of bacterial sulphate reduction. The degree of fractionation relative to Upper Permian seawater is about 40‰ or a little more. Such values are comparable to the sulphur fractionation observed in recent reduced sediments of the Baltic Sea by M. Hartmann and H. Nielsen (1969) and in anoxic seawater of the Framvaren Fjord in Norway (L. G. Anderson *et al.*, 1988). G. Marowsky (1969) has additionally observed a systematic difference between the $\delta^{34}S$ maximum of Zn-Pb-Cu sulphides (from –25 to –37‰) and the maximum of pyrites (from –32 to –39‰). The large fraction of isotopically lighter pyrite was consequently not formed in equilibrium with Zn-Pb-Cu sulphides because in case of coprecipitation pyrite sulphur is isotopically heavier than sulphur of Zn-Pb-Cu sulphides (c.f. Fig. 16-B-3b in H. Nielsen, 1978). This fact requires different sources or stages for the formation of the two groups of sulphides and does not allow the author to assume that Zn-Pb-Cu sulphides have generally replaced pyrite. Our microscopic observation of highly and moderately mineralized Kupferschiefer samples and results published by J. Niśkiewicz (1980) on material from the Polish deposits suggest that pyrite partly replaced by sphalerite, galena or Cu sulphides is not very abundant. In the Polish deposits the abundance of Cu is often higher than that of Fe which excludes a general replacement of pyrite by Cu sulphides.

The most abundant carbonate in the Kupferschiefer sediment is dolomite (K. H. Wedepohl, 1964; R. Erzberger, 1965). An early diagenetic formation of this carbonate is conformable with its content of about 400 ppm Sr. On the basis of experimental results R. L. Jacobson and H. E. Usdowski (1976) suggested that the concentration of Sr in seawater-equilibrated dolomite should be about one half of the Sr abundance in marine calcite. The concentration in recent marine calcite is close to 1000 ppm Sr (J. Veizer, 1978). The average oxygen isotopic composition of the majority of samples of Kupferschiefer dolomite, as investigated by G. Marowsky (1969), is close to $\delta^{18}O$ –2‰ relative to SMOW which reflects an origin from fluids being close to seawater oxygen isotopic composition. Calcite instead of dolomite occurs in various samples from the Kupferschiefer bed. Its low Sr concentration ($\leq$ 400 ppm Sr) and light oxygen isotopic composition ($\delta^{18}O$ from 0 to –9‰) indicates a secondary origin (replacement of dolomite etc.). The deposits of the Fore-Sudetic Monocline, Richelsdorf and Sangerhausen contain a larger fraction of carbonates with light oxygen. Their average of $\delta^{18}O$ is between –4 and –6‰ (J. Hammer *et al.*, 1990; A. Bechtel, S. Hoernes, 1993) and indicates higher proportions of meteoric waters in the diagenetic fluids.

The radiogenic age of silicate minerals in the Kupferschiefer bed is not conformable with the age of sediment deposition because of their detrital origin. A rough estimate of the age of mineralization and some indication about its source might be derived from the lead isotopic composition of the galena fractions in Zechstein sediments (including the Kupferschiefer) in relation to the upper crustal lead development as calculated by J. S. Stacey and J. D. Kramers (1975). J. Lévêque and U. Haack (1993) have published $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios of galena in Zechstein Limestone and Kupferschiefer from the SW border of the Harz Mts., and also of hydrothermal ore veins and the syngenetic Rammelsberg ore deposit, both in the Harz Mts. The vein deposits of the Harz Mts. are mainly of Jurassic age (J. Lévêque, U. Haack, 1993) and the Rammelsberg mineralization is of Middle Devonian age (380 Ma). We present the plots of $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios of the respective mineralizations published by J. Lévêque and U. Haack (1993) in Figure 2. The average lead isotopic data on 8 Kupferschiefer samples from Germany (K. H. Wedepohl *et al.*, 1978) and on 10 Kupferschiefer samples from Sangerhausen (south of the Harz Mts.) (J. Hammer *et al.*, 1987) also plot in the Zechstein (Z) area of Figure 2. The model age of the syngenetic Rammelsberg (R) deposit is about 300 Ma on the J. S. Stacey and J. D. Kramers (1975) curve which indicates a higher U/Pb ratio of their source relative to the upper continental crust. The model age of the major vein mineralization of the Harz Mts. (H) is about 180 Ma on the J. S. Stacey and J. D. Kramers (1975) curve which is conformable with a Jurassic

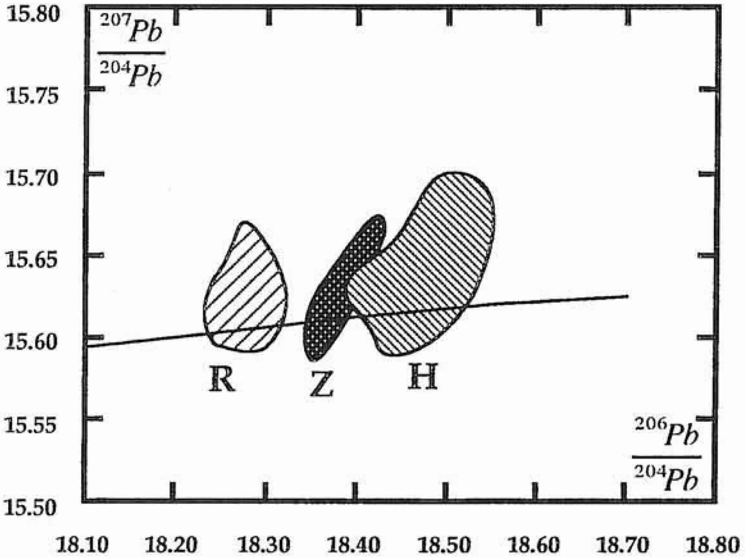


Fig. 2. Areas of lead isotopic composition of Zechstein deposits including Kupferschiefer at the SW border of Harz Mts. (Z) which occur intermediate between galena composition from Middle Devonian syngenetic Rammelsberg ore (R) and mainly Jurassic vein type ore from the Harz Mts. (H) (according to J. Lévêque, U. Haack, 1993); the upper crustal lead evolution curve by J. S. Stacey, J. D. Kramers (1975) is included

Obszary o ustalonym składzie izotopów ołowiu, włącznie z łupkiem miedzionośnym występującym na SW krańcu Harzu (Z), który cechuje skład pośredni między galeną ze środkowodewońskich syngenetycznych rud Rammelsbergu (R) i jurajskimi rudami żyłowymi z Harzu (H) (według: J. Lévêque, U. Haack, 1993); krzywa ewolucji górnoskorupowego ołowiu według: J. S. Stacey, J. D. Kramers (1975)

age. Galena from the Zechstein sediments plots intermediate between R and H, indicating a model age intermediate between 380 and 180 Ma. The boundary between the Permian and Triassic is 245 Ma (G. S. Odin, 1982). The Kupferschiefer sedimentation, which gives the maximum age of that system, must be close to that boundary because of the short duration of the Late Permian (≤ 5 Ma: M. Menning, 1986). E. G. Jowett *et al.* (1987*a*) have published palaeomagnetic ages of the "Rote Fäule" hematitization of the Kupferschiefer in Poland at 230±10 and 240±10 Ma. These authors probably underestimated the error of the palaeomagnetic method. Figure 2 clearly demonstrates that the Kupferschiefer lead is isotopically separate from the lead of the vein deposits of the Harz Mts. which excludes assumptions about a general hydrothermal mineralization of Mesozoic age of the Kupferschiefer bed in Germany.

SULPHIDE PRECIPITATION AND ITS LATERAL AND VERTICAL ZONATION

Genetic interpretations of structures of sulphide ores often suffer from remobilization and recrystallization of fine-grained minerals. Our microscopic and microprobe studies of Kupferschiefer samples from Drente, Groningen (the Netherlands), Sangerhausen (Ger-

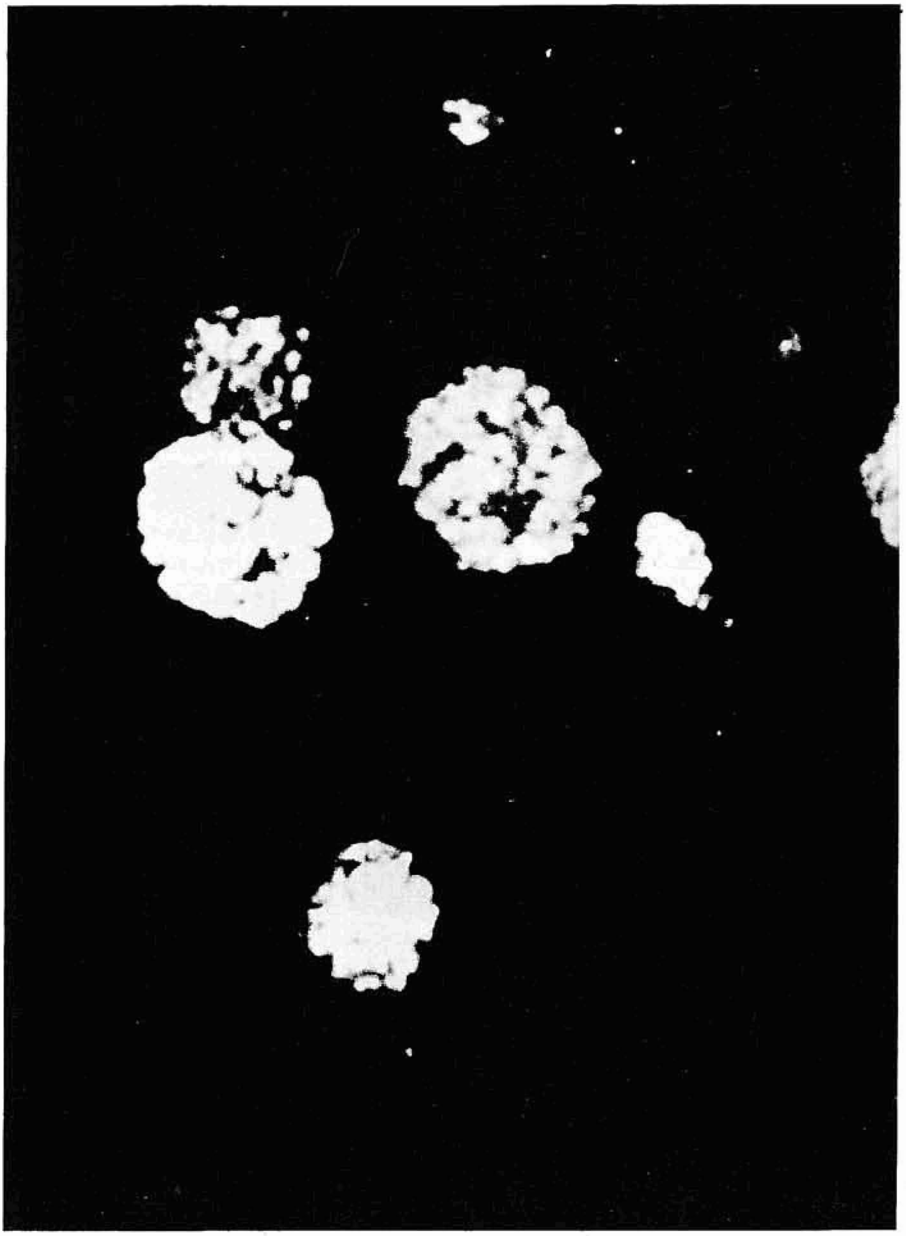


Fig. 3. Microphotograph of chalcocite (grey) beside pyrite (white) framboids from intermediate layer in Kupferschiefer from Polkowice (Point 100/Shaft B1), Fore-Sudetic Monocline (Poland)

The size of the aggregates is 8–10 µm containing grains with a size of about 1 µm; the mineral composition has been identified by microprobe (H. P. Koch, 1989)

Mikrofotografia chalkozynu (szare) obok pirytowych fromboidów (białe) w łupku miedzionośnym z Polkowic (stanowisko 100/szyb B1), monoklina przedsudecka (Polska)

Agregaty o wymiarach 8–10 µm zawierają ziarna o średnicy 1 µm; skład mineralny określony w mikroobszarze (H. P. Koch,1989) many) and Polkowice (Poland) lead us to detect very small framboids (≤ 10 μ size) of chalcocite, bornite and chalcopyrite in these materials (H. P. Koch, 1989, c.f. Fig. 3). Z. Sawłowicz (1993) reported the occurrence and formation of copper and copper-iron sulphide framboids in the deposits of the Fore-Sudetic Monocline. After the detection of framboids of pyrite in the suspended matter of the anoxic water column in the Framvaren Fjord in Norway (J. M. Skei, 1988) the old controversy about the nature of framboids in this case could be solved in favour of bacterial sulphide production in anoxic seawater. This allows us to assume that the framboids of copper minerals in Kupferschiefer samples are also products of bacterial sulphide precipitation. They indicate higher than seawater Cu concentrations in the anoxic waters of their source. The major fraction of the sulphides of Zn, Pb, Cu and Fe occurs in coarser than framboidal grains. They have to be explained as products of remobilization and recrystallization of originally bacteriogenic sulphides. The latter being identified by their extremely light sulphur isotopic composition. Recrystallization has abundantly occurred at temperatures lower than 75°C because we could identify bornite from Sangerhausen and Groningen as being low-temperature species with excess sulphur as defined by R. Brett and R. A. Yund (1964).

A model of sulphide precipitation in anoxic seawater can be used to form ideas about the mineralization of the Kupferschiefer. Such a model requires estimates about the rate of sediment accumulation and assumptions about the rate of water exchange between the oxic and anoxic part of a stagnant seawater column of Black Sea type. Dissolved sulphide precipitates those metal ions in which oxic seawater concentrations exceed the solubility of their sulphides. These sulphides are diluted in the sediment by detrital minerals. For a continuous process of sulphide precipitation a permanent oscillation of the O_2/H_2S interface in the stagnant seawater column is required. In our model we have assumed an amplitude of oscillation of 30 m per year. This is a large amplitude compared with a value of 2 m per year for the present Black Sea (G. Östlund, 1974). If the detrital accumulation is as low as in the present North Atlantic (1 cm/1000 years) the maximum metal concentration precipitated as sulphide will be 1200 ppm Zn, 800 ppm Cu, 8 ppm Ag and 2 ppm Pb in the model sapropelic sediment. Metal concentrations in oxic seawater used for this balance are values reported by K. W. Bruland (1983). Our model can explain the accumulations of Cu, Zn and Cd in the sapropelic sediment of the Framvaren Fjord and the Cariaco Trench observed by L. Jacobs *et al.* (1985, 1987). But it cannot explain the economic mineralizations of the Kupferschiefer bed. As a consequence one has to postulate distinctly higher than normal seawater concentrations of Cu, Pb, Zn, Ag etc. in the fluids which caused the different Kupferschiefer mineralizations. Non-seawater Cu/Zn and Pb/Zn ratios are required in the source fluid.

Black shales and sapropelic sediments rarely exceed concentrations of 50 ppm Pb, 150 ppm Cu and 500 ppm Zn (J. D. Vine, E. B. Tourtelot, 1970; H. -J. Brumsack, 1988). In relation to these background levels we have classified concentrations exceeding 5000 ppm Zn, Pb or Cu as appreciable mineralizations. Figure 4 demonstrates that values exceeding 5000 ppm Zn or Pb occur over a relatively large area and values of more than 5000 ppm Cu are restricted to a small area of Kupferschiefer coverage. For the evaluation of Figure 4 it must be conceded that sampling of the total Kupferschiefer area is still incomplete. The area highly mineralized in copper is underlain by thick deposits of Rotliegendes sandstones and conglomerates with good permeability. But several regions highly mineralized in lead

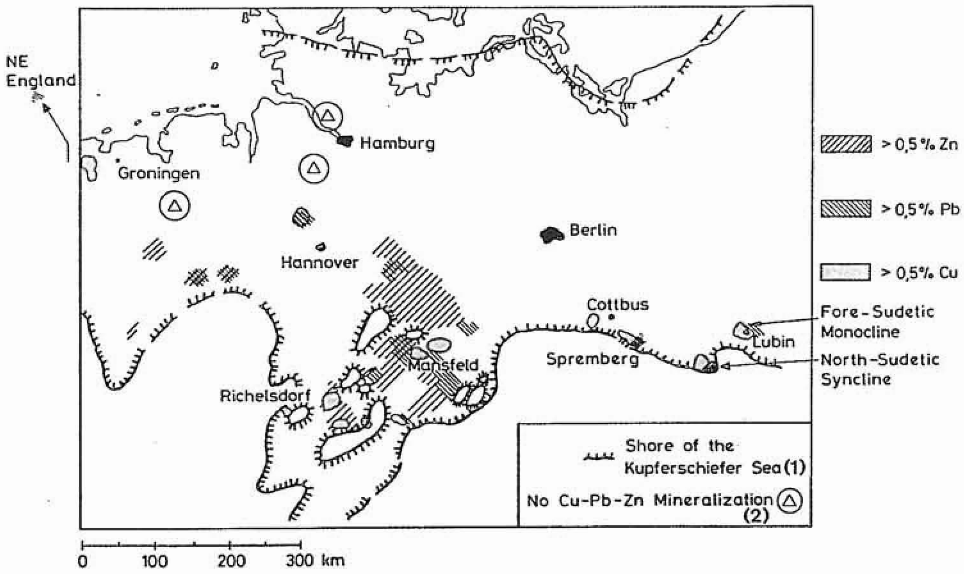


Fig. 4. Map of Kupferschiefer deposition in Central Europe and areal distribution of Kupferschiefer mineralization exceeding 0.5% Cu, Pb or Zn; the latter is based on information from G. Richter (1941), K. H. Eisenhuth, E. Kautzsch (1954), E. Messer (1955), D. M. Hirst, K. C. Dunham (1963), K. H. Wedepohl (1964 and unpublished), G. Knitzschke (1966), R. Erzberger *et al.* (1968), C. Harańczyk (1970, 1986) and S. Speczik *et al.* (1986)

Mapa sedymentacji łupku miedzionośnego na obszarze Europy środkowej oraz obszary zawierające mineralizację w łupku miedzionośnym o zawartości ponad 0.5% Cu, Pb lub Zn; występowanie mineralizacji według G. Richtera (1941), K. H. Eisenhutha, E. Kautzscha (1954), E. Messera (1955), D. M. Hirsta, K. C. Dunhama (1963), K. H. Wedepohla (1964 i prace niepublikowane), G. Knitzschkego (1966), R. Erzbergera i in. (1968), C. Harańczyka (1970, 1986) i S. Speczika i in. (1986); 1 — pierwotny zasięg morza łupku miedzionośnego; 2 — bez mineralizacji Cu-Pb-Zn

and/or zinc and areas with distinctly higher than background copper concentrations occur on top of almost impermeable greywackes and cherts of Devonian to Carboniferous age.

Mining of the Kupferschiefer ores in the Richelsdorf and Mansfeld – Sangerhausen areas of Germany was discontinued because of a restricted mineralization of the hanging and footwall beside the Kupferschiefer bed itself. The economic conditions are much better in the Fore-Sudetic Monocline (Lubin – Sieroszowice mining area) of Poland where a thicker Kupferschiefer plus footwall and hanging wall are highly mineralized. The mineralization of the Weissliegendes sandstone in the footwall locally occurs in rhythmic bands of disseminated digenite and chalcocite grains very light in sulphur isotopes ($\delta^{34}S$ –39 to –44‰). The white sandstones host Cu and Cu-Fe sulphides to a depth of 1 to 20 m. W. Mayer and A. Piestrzyński (1990) and Z. Sawłowicz and K. H. Wedepohl (1992) explained the sulphide bands as a precipitate of hydrogen sulphide generated within the Kupferschiefer and diffused into the porous volume of the sandstone which was soaked with water and dissolved copper. The latter was supplied from the underlying red sandstone. The almost equidistant sulphide bands were formed from top to bottom as soon as a certain supersaturation of copper sulphide was attained in the stream of sulphide diffusion (Z. Sawłowicz, K. H. Wedepohl, 1992). This model of diagenetic mineralization allows the supply of bacteriogenic sulphide from the still unconsolidated Kupferschiefer environment and copper from the thick red-bed footwall.

The relatively small Cu-rich prospects are usually bordered by a secondarily oxidized and unmineralized equivalent of the Kupferschiefer, which is called "Rote Fäule" (for details see C. Freese, W. Jung, 1965; R. Erzberger, 1965; J. Rentzsch, 1965). A belt with high Zn mineralization of more than 100 km length trends NE/SW from the Flechting Rise through the eastern slope of the Harz Mts. to the northern part of the Thuringian Mts. (J. Rentzsch, G. Knitzschke, 1968). Its trend is parallel to that of the large Rotliegendes troughs. W. Jung and G. Knitzschke (*fide* R. Erzberger *et al.*, 1968) present information on a lateral zoning of mineral parageneses in the SE foreland of the Harz Mts. with the following sequence: hematite ("Rote Fäule"), covellite-idaite, chalcocite, bornite-chalcocite, galena-sphalerite-chalcopyrite, galena-sphalerite, pyrite. This lateral zoning agrees only partly with a gradient of decreasing oxygen fugacity. The scale of regional metal zoning in the Mansfeld – Sangerhausen district and in the Fore-Sudetic Monocline can be tens of kilometres (for the latter area see map in E. C. Jowett *et al.*, 1987*b*; H. Kucha, 1990).

The vertical zoning of metals in Kupferschiefer profiles from England to Poland has been reported by D. M. Hirst, K. C. Dunham (1963), G. Richter (1941), K. H. Eisenhuth, E. Kautzsch (1954), K. H. Wedepohl (1964), G. Marowsky (1969), W. Mayer, A. Piestrzyński (1985) and H. Kucha (1990). In areas with high Cu mineralization this element is mainly accumulated at the base of the Kupferschiefer bed (often including the top of the footwall-rock). The major Pb-Zn mineralization usually occurs in the higher layers of the profile. The commonly (but not always) observed vertical zonation from chalcocite or bornite to chalcopyrite, and from chalcopyrite through galena to sphalerite follows an increasing solubility of these sulphides in H_2S containing fluids with seawater NaCl concentration (H. C. Helgeson, 1969).

SOURCE AND ACCUMULATION OF METALS

The total amount of certain elements in the sulphide mineralization (Fe, Zn, Pb, Cu and Ag) in the organic fraction (V, Mo, Ni, Co and Cr) and in the carbonate minerals (Mn) of the Kupferschiefer bed has been roughly estimated with the following results: 10^{10} t Fe > 10^9 t Zn, Pb, Mn > $5 \cdot 10^8$ t V > 10^8 t Ni, Mo, Cu > $3 \cdot 10^7$ t Co > 10^5 t Ag. An equal mass of an oxidized pelitic sediment would contain: 10^{10} t Fe > $4 \cdot 10^8$ t Mn > $4 \cdot 10^7$ t Zn, V > 10^7 t Ni, Cu > $8 \cdot 10^6$ t Pb, Co > $4 \cdot 10^5$ t Mo, Ag. The difference between the two sets of data is 10^9 t Pb, Zn; $5 \cdot 10^8$ t Mn, V; 10^8 t Ni, Cu, Mo. At least this mass of metals is required for the mineralization of the Kupferschiefer sapropelic sediment.

Seawater of the Zechstein transgression and porous fluids with a salinity high enough to dissolve Cu, Zn and Pb sulphides in the ppb range leached the footwalls of Rotliegendes age very efficiently for the extraction of metals. The penetration of the footwall sandstones and conglomerates of Rotliegendes age was much larger than that of Carboniferous greywackes and cherts because of the higher permeability of the former rocks. Weathering of mica and feldspar probably contributed the largest fraction of Zn and Pb from the decomposed sandstones. Oxidation of sulphides of Fe, Cu, Zn and Pb in the hot climate transformed these minerals into leachable compounds. J. Rentzsch *et al.* (1976) report average concentrations of 29 ppm Cu, 61 ppm Zn and 22 ppm Pb in 1750 samples of sandstones, siltstones and conglomerates of Permian age. If for example Pb is completely leached from sediments of this composition a mass of $4 \cdot 10^{13}$ t sandstones and conglomerates is required to supply the 10^{9} t Pb which is stored in the Kupferschiefer bed. The layer of Rotliegendes sediments to be completely leached must have had a thickness of about 30 m. This is a realistic assumption confirmed by observation. Galena from Kupferschiefer deposits in Germany inherited an isotopic composition from a source which contained a U/Pb ratio close to that of the upper continental crust (K. H. Wedepohl *et al,* 1978; J. Hammer *et al.*, 1987). Arkoses and sandstones of Rotliegendes age contain erosion products of Variscan magmatic and sedimentary rocks with the required composition. R. A. Zieliński *et al.* (1983) reported that the mobilization of V, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, U etc. from detrital minerals of red beds could also be a significant source of these metals for circulating fluids. Leaching of Fe and Mn oxides requires reducing fluids which also mobilize Cu, Cr, Mo, Zn, Co and Pb being incorporated in the iron and manganese oxides (W. L. Newman, 1962; M. Hartmann, 1963; A. Buckley, 1989). Reducing fluids, which originated from the organic fraction of the Kupferschiefer environment, have decolorized the upper layer of the penetrated sandstone (Weissliegendes).

Anoxic bottom water formed from saline stratification in near-shore basins of the marine Zechstein transgression. Organic production in the surface water was high enough for its degraded matter to feed bacterial sulphate reduction and sulphide production in the anoxic bottom water. The saline H_2S containing bottom water partly soaked the porous footwall sediment and dissolved metals in it. At increasing sulphide concentrations, metal sulphides were precipitated in sequence of their sulphide solubility. With an excess of metal ions over sulphide ions the precipitation sequence was consequently controlled by the rate of bacterial sulphide production. The solubility increases in the following sequence: $Ag_2S < Cu_2S < PbS < ZnS$. The vertical and lateral zonation of sulphides in the Kupferschiefer and its footwall is consequently a function of these solubilities and the size of the system of dissolution and precipitation. Increasing $\delta^{34}S$ indicates a closing of the system (M. Hartmann, H. Nielsen, 1969; G. Marowsky, 1969; Z. Sawłowicz, 1989).

Reworking of already precipitated sulphides may be caused by the oscillation of the O_2/H_2S interface in the shallow waters of the basins. Such remobilization of sulphides or a mechanical erosion and redeposition of sulphide-bearing sediment has been described from the Rudna lagoon (Fore-Sudetic Monocline, Poland) by C. Harańczyk (1986) and from the Richelsdorf deposit (Germany) by E. Messer (1955), respectively.

The formation of "Rote Fäule" was due to the penetration of the already deposited Kupferschiefer by oxic water with partial oxidation of its organic materials and of pyrite (Z. Sawłowicz, 1989; J. Hammer *et al.*, 1990). The oxic waters supplied metals from the footwall into the adjacent sediment for a late diagenetic sulphide precipitation. The copper accumulation in the neighbourhood of "Rote Fäule" partly attained economic grades, which mainly occur in the upper layers of the Kupferschiefer bed and its hanging wall up to the Zechstein Limestone layer (G. Gunzert, 1953; J. Rentzsch, 1965; S. Speczik *et al.*, 1986). This late diagenetic mobilization of sulphides bordering "Rote Fäule" areas probably ceased after the time of the Zechstein Limestone deposition. An increase of isotopically light oxygen (beyond seawater levels) in carbonates and silicates of Lower Zechstein sediments close to "Rote Fäule" areas indicates some proportion of meteoric waters in the late diagenetic oxidizing fluids (J. Hammer *et al.*, 1990; A. Bechtel, S. Hoernes, 1993).

Any model of the formation of the Kupferschiefer bed and its syngenetic to diagenetic mineralization including that of the footwall (Weissliegendes, Zechstein conglomerate) has to explain a large variety of observations of which the majority is condensed in the following list:

1. Major fraction of sulphide sulphur of bacteriogenic origin, pyrite not equilibrated with Cu-Pb-Zn-sulphides.
2. Framboidal chalcocite, bornite, chalcopyrite as primary precipitates of sulphide.
3. Lateral and vertical zonation of Zn, Pb, Cu accumulation (including area of "Rote Fäule" formation).
4. Isotopic composition of Pb.
5. Major Zn, Pb, Cu mineralization in Kupferschiefer covering Permian sandstones with high permeability, occasionally covering Carboniferous greywackes and cherts with low permeability.
6. Mineralization over large distances (>1000 km).
7. Palaeogeographical control of mineralization at modest coastal distance.
8. Abnormal mobilization and accumulation of Pb, Zn > Mn, V > Ni, Cu, Mo.

Investigations have also to consider the Kupferschiefer composition outside the mining localities. Several investigations specialized on a minor number of items listed have not been reported in this paper. In the past two decades a number of authors have suggested an epigenetic formation of the Kupferschiefer mineralization by brines during a Mesozoic event. Readers interested in this suggestion are referred to E. C. Jowett *et al.* (1987*b*); H. Kucha (1990) and papers listed by these authors.

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REFERENCES

ANDERSON L. G., DYRSSEN D., HALL P. O. J. (1988) — On the sulphur chemistry of a super-anoxic fjord, Framvaren, South Norway. Marine Chem., **23**, p. 283–293.

BECHTEL A., HOERNES S. (1993) — Stable isotopic variations of clay minerals: A key to the understanding of Kupferschiefer-type mineralization, Germany. Geochim. Cosmochim. Acta, **57**, p. 1799–1816.

BERNER R. A. (1984) — Sedimentary pyrite formation: An update. Geochim, Cosmochim. Acta, **48**, p. 605–615.

BRETT R., YUND R. A. (1964) — Sulfur-rich bornites. Amer. Miner., **49**, p. 1084–1098.

BRULAND K. W. (1983) — Trace elements in sea-water. In: Chemical Oceanaography (ed. J. P. Riley, K. Chester), **845**, p. 157–220.

BRUMSACK H. -J. (1980) — Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36 and 41). Chem. Geol., **31**, p. 1–25.

BRUMSACK H. -J. (1986) — Trace metal accumulation in black shales from the Cenomanian/Turonian boundary event. In: Global Bio-Events. Lecture Notes in Earth Sciences (ed. O. Walliser), **8**, p. 337–343.

BRUMSACK H. -J. (1988) — Rezente, C_{org}-reiche Sedimente als Schlüssel zum Verständnis fossiler Schwarzschliefer. Thesis for Habilitation. Göttingen.

BUCKLEY A. (1989) — An electron microprobe investigation of the chemistry of ferromanganese coatings on freshwater sediments. Geochim. Cosmochim. Acta, **53**, p. 115–124.

DEPOWSKI S. (1978) — Lithofacies-paleogeographical atlas of the Permian of platform areas in Poland. Wyd. Geol. Warszawa.

DONEGAN D., SCHRADER H. (1982) — Biogenic and abiogenic components of laminated hemipelagic sediments in the central Gulf of California. Marine Geol., **48**, p. 215–237.

EISENHUTH K. H., KAUTZSCH E. (1954) — Handbuch für den Kupferschieferbergbau. Fachbuchverlag. Leipzig.

ERZBERGER R. (1965) — Zur Paläogeographie und Verbreitung der Rotfärbung in der Werra-Serie (Zechstein 1) Südbrandenburgs. Freib. Forsch., **C193**, p. 25–39.

ERZBERGER R., FRANZ R., JUNG W., KNITZSCHKE G., LANGER M., LUGE J., RENTZSCH H., RENTZSCH J. (1968) — Lithologie, Paläogeographie und Metallführung des Kupferschiefers in der Deutschen Demokratischen Republik. Geologie, **17**, p. 776–791, H. 6/7.

FREESE C., JUNG W. (1965) — Über die Rotfärbung der Basalschichten des Zechsteins (Rote Fäule) und ihre Beziehungen zum Nebengestein im südöstlichen Harzvorland. Freib. Forsch., **C193**, p. 9–23.

GUNZERT G. (1953) — Über die Bedeutung nachträglicher Erzverschiebungen in der Kupferschieferlagerstätte des Richelsdorfer Gebirges. Notizbl. Hess. Landesamt Bodenforsch., **81**, p. 258–283.

HAMMER J., HENGST M., PILOT J., RÖSLER H. J. (1987) — Pb-Isotopenverhältnisse des Kupferschiefers der Sangerhäuser Mulde: Neue Untersuchungsergebnisse. Chem. Erde, **46**, p. 193–211.

HAMMER J., JUNGE F., RÖSLER H. J., NIESE S., GLEISBERG B., STIEHL G. (1990) — Element and isotope geochemical investigations of the Kupferschiefer in the vicinity of "Rote Fäule" indicating copper mineralization (Sangerhausen Basin, GDR). Chem. Geol., **85**, p. 345–360.

HARAŃCZYK C. (1970) — Zechstein lead-bearing shales in the Fore-Sudetian Monocline in Poland. Econ. Geol., **65**, p. 481–495, no. 4.

HARAŃCZYK C. (1986) — Zechstein copper-bearing shales in Poland. Lagoonal environments and the sapropel model of genesis. In: Geology and Metallogeny of Copper Deposits (ed. G. H. Friedrich *et al.*), p. 461–476. Springer-Verlag. Berlin, Heidelberg.

HARDER H. (1974) — Abundance of boron in common sediments and sedimentary rock types. Section 5-K in: Handbook of Geochemistry, **2.** Springer-Verlag. Berlin, Heidelberg, New York.

HARTMANN M. (1963) — Einige geochemische Untersuchungen an Sandsteinen aus Perm und Trias. Geochim. Cosmochim. Acta, **27**, p. 459–499.

HARTMANN M., NIELSEN H. (1969) — δ^{34}S-Werte in rezenten Meeressedimenten und ihre Deutung am Beispiel einiger Sedimentprofile aus der westlichen Ostsee. Geol. Rundsch., **58**, p. 621–655.

HELGESON H. C. (1969) — Thermodynamics of hydrothermal systems at elevated temperatures and pressures. Am. J. Sc., **267**.

HIRST D. M., DUNHAM K. C. (1963) — Chemistry and petrography of the marl slate of S. E. Durham, England. Econ. Geol., **58**, p. 912–940.

JACOBS L., EMERSON S., SKEI J. (1985) — Partitioning and transport of metals across the O_2/H_2S interface in a permanently anoxic basin: Framvaren Fjord, Norway. Geochim. Cosmochim. Acta, **49**, p. 1433–1444.

JACOBS L., EMERSON S., HUESTED S. S. (1987) — Trace metal geochemistry in the Cariaco Trench. Deep Sea Res., **34**, p. 965–981.

JACOBSON R. L., USDOWSKI H. E. (1976) — Partitioning of strontium between calcite, dolomite and liquids: An experimental study under higher temperature diagenetic conditions, and a model for the prediction of mineral pairs for geothermometry. Contr. Miner. Petrol., **59**, p. 171–185.

JOWETT E. C., PEARCE G. W., RYDZEWSKI A. (1987*a*) — 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., RYDZEWSKI A., JOWETT R. J. (1987*b*) — The Kupferschiefer Cu-Ag ore deposits in Poland: a re-appraisal of the evidence of their origin and presentation of a new genetic model. Can. J. Earth Sc., **24**, p. 2016–2037, no. 10.

JUNG W. (1968) — Zechstein. In: Grundriß der Geologie der DDR, **1**, p. 219–237.

KNITZSCHKE G. (1966) — Zur Erzmineralisation, Petrographie, Hauptmetall- und Spurenelementführung des Kupferschiefers im SE-Harz-vorland. Freib. Forsch., **C207**, p. 1–147.

KOCH H. P. (1989) — Mikrosondenuntersuchungen an Sulfiden aus Kupferschiefer Westeuropas. Dipl. Thesis, Göttingen.

KUCHA H. (1990) — Geochemistry of the Kupferschiefer, Poland. Geol. Rundsch., **79**, p. 387–399.

LÉVÊQUE J., HAACK U. (1993) — Pb isotopes of hydrothermal ores in the Harz. Miner. Deposita, **30**, p. 197–210.

MAROWSKY G. (1969) — Schwefel-, Kohlenstoff- und Sauerstoff-Isotopenuntersuchungen am Kupferschiefer als Beitrag zur genetischen Deutung. Contr. Miner. Petrol., **22**, p. 290–334.

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**.

MAYER W., PIESTRZYŃSKI A. (1990) — Sulphide banding in the mineralized Weissliegendes sandstones from the Lubin copper District, SW Poland. Miner. Pol., **21**, p. 15–22, no.1–2.

MENNING M. (1986) — Zur Dauer des Zechsteins aus magnetostratigraphischer Sicht. Z. Geol. Wiss., **14**, p. 395–404.

MESSER E. (1955) — Kupferschiefer, Sanderz und Kobaltrücken im Richelsdorfer Gebrige (Hessen). Hess. Lagerstättenarch., **3**, p. 1–125.

NAZARKIN L. A. (1960) — The role of the sedimentation rate in the accumulations of absolute masses of organic matter in a sediment. Dokl. Acad. Sci. USSR. Earth Sc., **130**, p. 15.

NEWMAN W. L. (1962) — Distribution of elements in sedimentary rocks of the Colorado Plateau — A preliminary report. U. S. Geol. Surv. Bull., **1107F**.

NIELSEN H. (1978) — Sulfur istopes in nature. Section 16-B in: Handbook of Geochemistry, **2**. Springer-Verlag. Berlin, Heidelberg.

NIŚKIEWICZ J. (1980) — Matasomatic phenomena in the Zechstein copper ore deposits of Lower Silesia (in Polish with English summary). Geol. Sudetica, **15**, p. 76–80.

ODIN G. S. (1982) — Numerical dating in stratigraphy. Wiley, Chicester. New York, Brisbane, Toronto, Singapore.

ÖSTLUND G. (1974) — Expedition "Odysseus 65": Radiocarbon age of Black Sea deepwater. In: The Black Sea — Geology, Chemistry and Biology (ed. E. T. Degens, D. A. Ross). Am. Ass. Petrol. Geol. Mem., **20**, p. 127–132.

PAUL J. (1982) — Zur Rand- und Schwellen-Fazies des Kupferschiefers. Z. Dtsch. Geol. Ges., **133**, p. 571–605.

RENTZSCH J. (1965) — Fazielle Gesetzmäßigkeiten beim Auftreten der Roten Fäule. Freib. Forsch., **C193**, p. 99–106.

RENTZSCH J., KNITZSCHKE G. (1968) — Die Erzmineralparagenesen des Kupferschiefers und ihre regionale Verbreitung. Freib. Forsch., **C231**, p. 189–211.

RENTZSCH J., SCHIRMER B., RÖLLIG G., TISCHENDORF G. (1976) — On the metal source of non-ferrous mineralizations in the Zechstein basement (Kupferschiefer type). In: The current metallogenic problems of Central Europe (ed. J. Fedak), p. 171–188. Wyd. Geol. Warszawa.

RICHTER G. (1941) — Geologische Gesetzmäßigkeiten in der Metallführung des Kupferschiefers. Arch. Lagerstättenforsch., Neue Folge Heft, **73**, p. 7–61.

SAWŁOWICZ Z. (1989) — On the origin of copper mineralization in the Kupferschiefer: a sulfur isotope study. Terra Nova, **1**, p. 339–343.

SAWŁOWICZ Z. (1993) — Primary sulphide mineralization in Cu-Fe-S zones of Kupferschiefer, Fore-Sudetic Monocline, Poland. Trans. Inst. Min. Metall. (Sect. B Applied Earth Sc.), **101**, p. 1–8.

SAWŁOWICZ Z., WEDEPOHL K. H. (1992) — The origin of rhythmic sulphide bands from the Permian sandstones (Weissliegendes) in the footwall of the Fore-Sudetic "Kupferschiefer" (Poland). Miner. Deposita, **27**, p. 242–248, no. 3.

SCOTESE C. R., BAMBACH R. K., BARTON C., VAN DER VOO R., ZIEGLER A. M. (1979) — Paleozoic base maps. J. Geol., **87**, p. 217–277.

SKEI J. M. (1988) — Formation of framboidal iron sulfide in the water of a permanently anoxic fjord — Framvaren, South Norway. Marine Chem., **23**, p. 345–352.

SPECZIK S., SKOWRONEK C., FRIEDRICH G., DIEDEL R., SCHUMACHER C., SCHMIDT F. -P. (1986) — The environment of generation of some base metal Zechstein occurrences in Central Europe. Acta Geol. Pol., **36**, p. 1–35, no. 1–3.

STACEY J. S., KRAMERS J. D. (1975) — Approximation of terrestrial lead isotope evolution by a two-stage model. Earth Planet. Sc. Lett., **26**, p. 207–221.

TONNDORF H. (1994) — Metallogenie des Urans im ostdeutschen Zechstein. Abhandl. Sächsische Akad. Wiss. Leipzig Mat. Natur. Kl., **58**, p. 1–132, no. 3.

VEIZER J. (1978) — Abundance of Sr in common sediments and sedimentary rock types. Section 38-K in: Handbook of Geochemistry, **2**.

VINE J. D., TOURTELOT E. B. (1970) — Geochemistry of black shale deposits — A summary. Econ. Geol., **65**, p. 253–272.

WEDEPOHL K. H. (1964) — Untersuchungen am Kupferschiefer in Nordwestdeutschland. Ein Beitrag zur Deutung der Genese bituminöser Sedimente. Geochim. Cosmochim. Acta, **28**, p. 305–364.

WEDEPOHL K. H., DELEVAUX M. H., DOE B. R. (1978) — The potential source of lead in the Permian Kupferschiefer bed of Europe and some selected Paleozoic mineral deposits in the Federal Republic of Germany. Contr. Miner. Petrol., **65**, p. 273–281.

ZIEGLER P. A. (1982) — Geological atlas of Western and Central Europe. Shell Internationale Petroleum Maatschappij B.V.

ZIELIŃSKI R. A., BLOCH S., WALKER T. R. (1983) — The mobility and distribution of heavy metals during the formation of first cycle red beds. Econ. Geol., **78**, p. 1574–1589.

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SKŁAD I GENEZA ŁUPKÓW MIEDZIONOŚNYCH

Streszczenie

Próbki łupku miedzionośnego, pobrane z odsłonięć powierzchniowych, z kopalń oraz z otworów wiertniczych na obszarze Anglii, Holandii, Niemiec i Polski, zostały poddane badaniom mineralogicznym, chemicznym i izotopowym (C, O, S, Pb). Datowanie izotopowe (Pb) oraz paleomagnetyczne wskazuje na wiek mineralizacji zbliżony do granicy perm–trias. Szybkość sedymentacji laminowanego łupku sapropelowego była niewielka, zbliżona do współczesnej depozycji osadów w północnej części Oceanu Atlantyckiego. Framboidalne struktury chalkozynu, bornitu, chalkopirytu i pirytu są prawdopodobnie produktem pierwotnej precypitacji w beztlenowym, redukcyjnym środowisku, obejmującym wodę morską i osad. Lekka izotopowo siarka pochodzenia bakteriogenicznego występuje w siarczkach pierwotnych i rekrystalizowanych. Piryt nie jest w równowadze izotopowej z siarczkami Zn, Pb i Cu ze względu na odmienne źródło siarki. Pionowa i pozioma strefowość rozmieszczenia Ag, Cu, Pb i Zn, odpowiadająca malejącej rozpuszczalności siarczków tych metali, jest kontrolowana przez powolną produkcję siarki biogenicznej. Podczas transgresji cechsztyńskiej procesy ługowania piaskowców dolnego permu dostarczyły prawdopodobnie głównej części metali do beztlenowych wód basenów przybrzeżnych. Silnie okruszcowany łupek miedzionośny może lokalnie występować ponad skałami karbonu o bardzo niskiej przepuszczalności. Większość obserwacji, wykonanych na dużym obszarze, wskazuje na syngenetyczno-diagenetyczny model mineralizacji.