

## The origin of rhythmic sulphide bands from the Permian sandstones (Weissliegendes) in the footwall of the Fore-Sudetic “Kupferschiefer” (Poland)\*

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**Abstract.** Rhythmic copper sulphide bands occur in the Weissliegendes sandstones, in the footwall of the Kupferschiefer in the mining district of SW Poland. The  $\delta^{34}\text{S}$  values of sulphides vary from  $-39$  to  $-44\%$  (6–7‰ lighter than Kupferschiefer sulphides). The copper sulphides are represented mainly by digenite and chalcocite. According to microprobe results their Pb, Ni, Zn and Ag contents are similar to those in the Kupferschiefer. The bands are assumed to be formed by diffusion of bacterially produced hydrogen sulphide from the Kupferschiefer into the porous volume of the white sandstones containing dissolved copper. The sulphides were precipitated in almost equidistant bands, from top to bottom, probably according to the Ostwald-Prager supersaturation theory. The increase of isotopically heavier sulphur towards the lower levels in the sandstone might be explained by closing of the bacterial sulphate reduction system.

Several stratiform base metal sulphide deposits are characterized by large numbers of conformable, monomineralic sulphide bands. The sets of such rhythmically repeated copper sulphide bands occur locally also in the upper part of the Permian white sandstones (Weissliegendes) in the mining area of copper deposits in the Fore-Sudetic monocline (Poland).

White sandstones, usually several metres thick but varying from one to a few tens of metres, form the uppermost part of the Lower Permian Rotliegende underlying the Kupferschiefer. The upper part of the Weissliegendes has been redeposited in shallow-marine low-energetic waters during the Zechstein transgression (Peryt 1976; Nemeč and Porebski 1977). The white sandstones host disseminated, spotty and cemented Cu and Cu-Fe sulphide mineralization to a depth of from 1 to 20 m (Banas et al. 1982), locally being the most important copper ore. The importance of the rhythmic sulphide bands among other types of ore mineralization in sandstones varies from place to place. The bands are found in different

parts of all mines (Lubin, Polkowice, Rudna, Sieroszowice) in the mining district, with the exception of areas where the Kupferschiefer is not present. An earlier study (Mayer and Piestrzynski 1990) and this present one show that the appearance of the bands in different underground galleries is generally similar as is their microscopic size and intergrowth. Eighteen samples (out of 35) in five profiles represent the typical examples of the sulphide bands from the Weissliegendes. Their sampling localities and positions in vertical sections are given in the caption of Fig. 3 and in Table 1.

The origin of the rhythmic sulphide bands in the Weissliegendes is usually described as diagenetic. However, no attempt has been made to explain in detail the mechanism of their formation and only general suggestions are reported in the literature. The common discordancy between such sulphide bands and the neighbouring primary sedimentary structures of sandstones (Jerzykiewicz et al. 1976), and the lack of primary sources of hydrogen sulphide within the white sandstones (as mentioned by Mayer and Piestrzynski 1982) exclude a syngenetic formation of the sulphide bands.

Kucha and Pawlikowski (1986) assumed that the formation of sulphide bands requires diffusion of sulphide ions from the Kupferschiefer and/or an “upper cold brine” (UCB) from the evaporate sequence and supply (diffusion) of copper from a “lower hot brine” (LHB) from the red-bed sequence below. They also suggested that “each chalcocite lamina may represent the LHB pulse”.

Haranczyk (1989) supposed that the sulphide bands are a result of a fluctuating water table which moved down in the interstitial space of the sandstone.

Mayer and Piestrzynski (1990) regarded the sulphide bands as “a result of the diffusion of hydrogen sulphide generated within the Kupferschiefer and metal ions migrating from the opposite direction, i.e. from the underlying red sandstone of the Lower Permian”.

Geochemical and sulphur isotope data presented here are used for another explanation of the formation of the rhythmic sulphide bands in the Weissliegendes.

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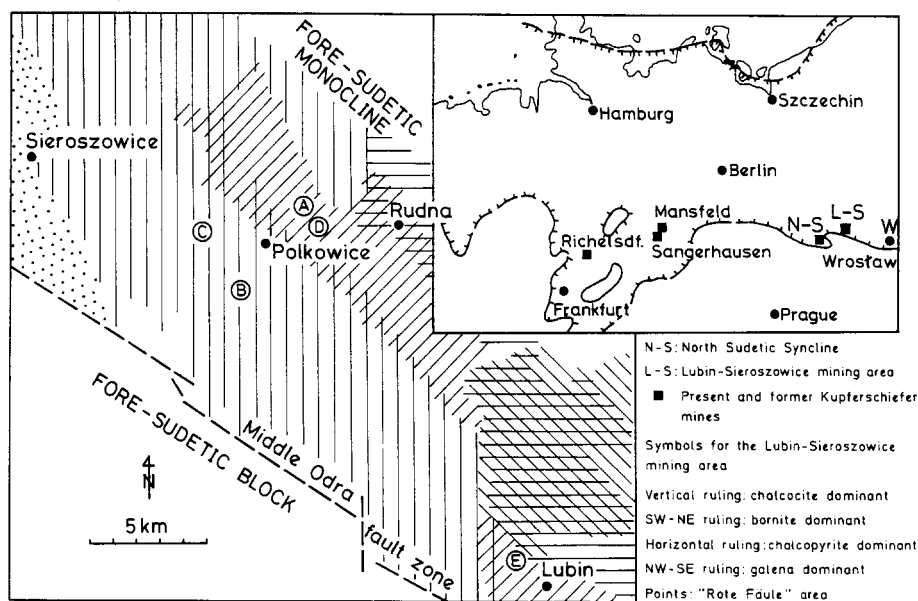


Fig. 1. Position of the Fore-Sudetic Monocline in Poland

Table 1. Description of samples from the sulphide bands in the Weissliegendes (Fore-Sudetic Monocline), analysed for sulphur isotopic composition

Section	Locality	Subsequent band <sup>a</sup>	Distance between the shale and the upper band in metres	Distance between bands in a set in centimetres	$\delta^{34}\text{S}$ in permil (CDT)
A	Rudna Mine Main Field Gallery U-6	6	0.7	0.6–1.0	–42.2
		7			–43.4
		8			–43.5
		9			–44.1
B	Polkowice M. Main F. Gall. G-27	7	1.3	0.5–1.5	–43.1
		8			–43.2
C	Polkowice M. West F. Gall. E-13	6	1.1	1.0–1.5	–41.2
		7			–41.2
		8			–42.0
D	Rudna M. Main F. Gall. K-11	1	1.0	0.7–1.5	–39.4
		2			–40.2
		3			–42.0
		4			–41.1
E	Lubin M. East F. Gall. C-6	1	1.4	0.5–1.3	–39.8
		2			–41.8
		3			–40.1
		4			–41.0
		5			–42.3

<sup>a</sup> From the base of a set

## Methods

Microprobe analyses were carried out with an ARL SEMQ 2, using 25 kV and 20 nA. Natural minerals were used as standards, and data reduction was done by the program MAGIC IV.

The individual sulphide bands were mechanically separated from each other. After crude crushing the concentrates were successively enriched by handpicking, removing of carbonates, isodynamic magnetic separation and heavy liquid separation. The concentrates contained from 50 to 90% copper sulphides. Sulphur dioxide for isotopic measurement was obtained by using a modified technique of Ricke (1964).

Sulphur isotope measurements were made on a Finnigan MAT 251 mass-spectrometer. The precision was  $\pm 0.1\%$ . The isotopic composition of sulphur is reported as permil deviation from the CDT-standard.

## Results

### Position and shape of the sulphide bands

The form and the position of the sulphide bands at the upper part of the Weissliegendes was described in detail by Jerzykiewicz et al. (1976) and recently by Mayer and Piestrzynski (1990). Rhythmic conformable sulphide bands (from a few up to several tens) form sets, 0.1–2 m thick (Figs. 2 and 4). The bands continue over a distance of 10–20 m at least. They trend horizontally or are slightly inclined, usually parallel to the base of the Kupferschiefer. The distribution of the sulphidic bands is often independent of the primary sedimentary structures in the sandstones (Jerzykiewicz et al. 1976). The rhythmic bands are not observed in areas where copper-bearing shale is missing. The distance between the top of the set and the top of the sandstone is usually about 0.5–1.5 m. The thickness of a band can vary from about 0.5 to 2 cm, but is generally uniform in every set. The lower surfaces of the bands are generally sharp. The lowest one or two bands usually differ from the upper ones. They are often more diffuse (Fig. 2a). At some sites more distinct and less diffuse bands occur, with higher contents of sulphides along the sharp lower boundary (Fig. 2b). Field observations show that rhythmic sulphide bands are the

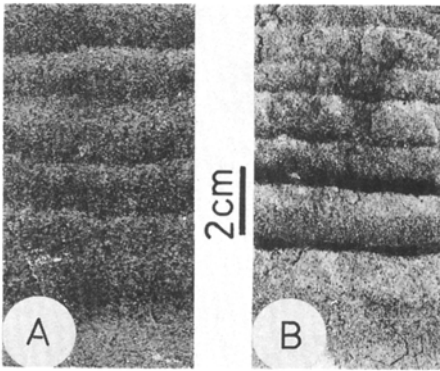


Fig. 2 A–B. Sets of copper sulphide bands in the Permian Weissliedenges from the Fore-Sudetic monocline. A Note the diffused boundaries of the lowermost two bands (Polkowice Mine, East Field). B Note the sharp and more distinct lower boundaries of the two lowermost bands (Rudna Mine, Main Field)

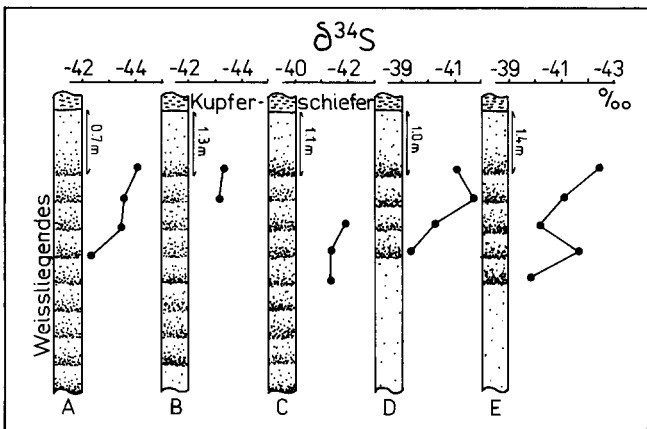


Fig. 3 A–E.  $\delta^{34}\text{S}$  values of copper sulphides from the different profiles of the Weissliedenges from the Fore-Sudetic Monocline (A, C Rudna Mine, Main Field, B Polkowice Mine, Main Field, D Rudna Mine, West Field, E Lubin Min, Maine Field) (not on scale)

earliest copper sulphide mineralizations in the Weissliedenges.

#### Chemical composition of the sulphide bands

The sulphide bands consist of copper sulphides, mainly digenite (collective term for digenite  $\text{Cu}_{1.8}\text{S}$  and anilite  $\text{Cu}_{1.75}\text{S}$ ) and chalcocite (for chalcocite  $\text{Cu}_2\text{S}$  and djurleite  $\text{Cu}_{1.97}\text{S}$ ). The mineralogy of sulphides in the bands in the sandstone does not depend on the mineralogy of sulphides (Cu or Cu-Fe) in the overlying shale. The proportion of chalcocite to digenite varies from set to set. Locally covellite  $\text{CuS}$  and “blaubleibender” covellite are present. The latter is an association of yarrowite  $\text{Cu}_{1.12}\text{S}$  and sponkiopite  $\text{Cu}_{1.4}\text{S}$  (see Goble 1980). The sulphide grains often consist of more than one phase. Digenitization of chalcocite occurs in some samples. Intergrowths of digenite and covellite are common. The parageneses of copper sulphides are generally the same in one set of bands, but can differ between sets from different locations. In some cases the large grains consist of minute grains smaller than  $1\ \mu\text{m}$ . Sulphides replace earlier clay

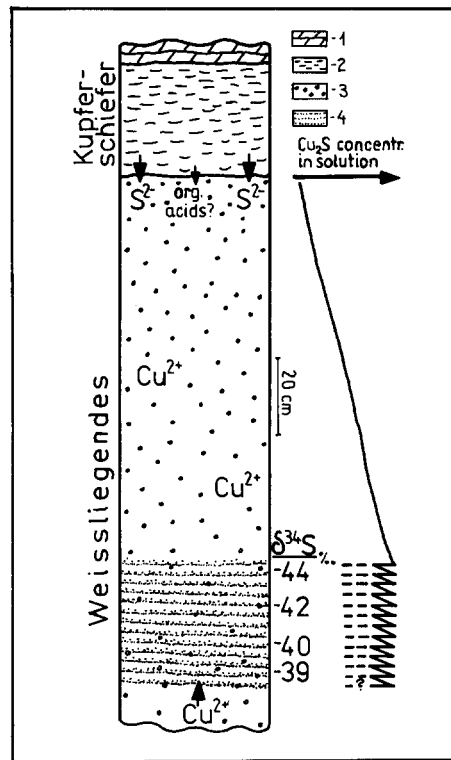


Fig. 4. Idealized model of the formation of rhythmic sulphide bands in the Weissliedenges. 1 – dolomites Ca1, 2 – Kupferschiefer, 3 – Weissliedenges sandstone, 4 – copper sulphide bands

minerals, silica and sometimes carbonates in the interstitial cement matrix of the sandstones (Jerzykiewicz et al. 1976; Mayer and Piestrzynski in press). Small relics of clay minerals and quartz are abundant in sulphide grains. Digenitization of chalcocite grains seems to obliterate such relics in some sites. A corrosion of quartz grains, common in later forms of the sulphide mineralization (Banas et al. 1982), is rarely observed in the sandstone of the rhythmic bands. Droplet-like forms of copper sulphides rarely overlap the bands. Other sulphides are very rare in these bands. Harancyk (1989) reported sulphide bands consisting of chalcopyrite, bornite or marcasite. Kucha and Pawlikowski (1986) have observed chalcocite bands traversing through bands in a transition from bornite-chalcopyrite to hematite. Individual copper sulphide grains from the bands reveal a wide range of Cu/S ratios. They vary from 1.26 to 2.00, although most of them fall into the range from 1.65 to 1.85, generally typical for digenite-type sulphides.

Chemical compositions of copper sulphides representative of the sulphide bands under investigation are presented in Table 2. Comparison between sulphides from rhythmic bands of Weissliedenges and from Kupferschiefer (dispersed mineralization and large diagenetic grains, Sawlowicz 1990) shows that the former sulphides contain usually small amounts of iron (except Sample D1234), comparable with those from large grains in the Kupferschiefer bed. The concentrations of nickel and lead are comparable in sulphide bands and Kupferschiefer copper sulphides. Zinc is lower and silver higher in the sulphide bands relative to the Kupferschiefer sul-

**Table 2.** Geochemical characteristics of the copper sulphides from the sulphide bands in the Weissliegende (Fore-Sudetic Monocline), according to microprobe analyses

Sample	No. of grains for analysis	Fe	Cu	S	Pb	Bi	As	Ni	Zn	Ag	Cu/S Atomic ratio			
		Arithm. averages and standard deviations (SD) in wt.pt.												
A1245	15	0.04	78.5	23.1	0.14	0.18	<0.02	0.04	0.18	0.26	1.68			
		SD 0.04	3.2	2.7	0.08	–	0.06	0.01	0.04	0.06				
D1234 <sup>L</sup>	26	1.20	76.4	21.7	0.08	0.09	0.02	0.05	0.13	0.67	1.77			
		SD 1.86	2.7	0.9	0.07	0.07	0.03	0.01	0.07	0.30				
D1234 <sup>U</sup>	13	0.11	77.7	21.3	0.05	0.09	0.03	0.05	0.16	0.51	1.83			
		SD 0.23	0.9	0.4	0.05	0.07	0.03	0.01	0.08	0.16				
Kupferschiefer <sup>a</sup>	63	Large secondary-formed grains			0.12	78.2	21.1	0.05	–	<0.02	0.08	0.30	0.30	1.89
		Spherules from early precipitates												
Kupferschiefer <sup>a</sup>	133	0.25	75.2	20.2	0.10	–	<0.02	0.08	0.30	0.19	1.82			

<sup>a</sup> After Sawlowicz (1990), Sample A1245- section A, bands 1, 2, 4, 5, Rudna Mine, Main Field, Sample D1234- section D, bands 1, 2, 3, 4, Rudna Mine, Main Field, L- lower and U- upper parts of the individual bands

phides. This means that chemical differences between copper sulphides in the bands in the Weissliegende and in the related Kupferschiefer are not large.

In Sample D1234 different contents of iron (and silver) were observed in the upper and lower part of individual bands (Table 2). The content of iron in a separate grain is uniform which might suggest that no direct replacement of iron-bearing minerals preexisting in the sandstones took place. In the case of a replacement of iron sulphide by copper sulphide, the distribution of iron in copper sulphide is usually not uniform (Sawlowicz in press). In the upper part of individual bands minor amounts of small bornite grains are present besides abundant copper sulphides.

### Sulphur isotopes

$\delta^{34}\text{S}$ -values of sulphides range from  $-44.1$  to  $-39.4\%$  (Table 1, Fig. 3). These are the lightest known in the total sulphide mineralization of the Kupferschiefer deposit (compared with Marowsky 1969 and Sawlowicz 1989). There is a general trend to sulphur values becoming heavier towards the bottom of a set of bands. Such a trend was observed by Haranczyk (1989 and written communication 1989) for one large set (15 bands) of sulphide bands. The bands are on average 6–7‰ lighter than the average values of dispersed copper sulphides in the related Kupferschiefer (Sawlowicz 1989) and much lighter (up to 33‰) than copper sulphides from other forms of a late mineralization in the Weissliegende (Sawlowicz, unpublished data).

No relationship between the sulphur isotopic composition and the chemical composition of copper sulphides from the sulphide bands has been found.

### Discussion of genesis

Experiments have demonstrated that conformable, monomineralic sulphide bands can be produced by diffu-

sion of sulphide ions into an environment where metals are adsorbed on clays, or occur in the form of carbonates or in the form of dissolved species (Temple and Le Roux 1964; Weiss and Amstutz 1966; Lambert and Bubela 1970; Bubela 1981). The process of their formation and especially of their periodic repetition is still not completely understood however.

A well-known diffusion phenomenon described by RE Liesegang (1897) should be recalled here. In his original experiment Liesegang placed a drop of silver nitrate solution on a slab of potassium dichromate-impregnated gel and then observed the formation of concentric bands, or rings of silver dichromate precipitate separated by zones without visible precipitation. A number of theories have been proposed to explain Liesegang banding. Amongst them, the so-called Ostwald-Prager supersaturation theory (Ostwald 1897; Prager 1956) seems to be the most plausible and the best documented one. A quantitative interpretation for the diffusion phenomenon involved in the formation of periodic precipitation zones has been given by Wagner (1950). According to the supersaturation theory, as ions of a certain species diffuse into the gel containing ions of a reactant species, an increasing concentration of the former is built up along the diffusion path. When this concentration reaches a certain degree of supersaturation, crystallization occurs and a zone of precipitate forms causing depletion of ions in the adjacent zones. The border of a precipitation zone is caused by the necessity of a considerable supersaturation for a noticeable rate of formation of new nuclei (Wagner 1950). This supersaturation has not been reached in the zone immediately below the precipitation because of the time required for diffusion. The overall diffusion process continues and the diffusion front passes the zone of initial precipitation and nucleation. The whole process is repeated until one of the ions is consumed. As a result, a set of bands of precipitate separated by bands devoid of precipitate is formed. According to Stern (1954) the concentration of ionic species introduced from outside to the system must be higher than that of the reactant ions inside the system.

Although most of the investigations on Liesegang rings have been done in gels, some of them were done also in other media: e.g. Morse (1930) has observed periodicity for cupric sulphide and many other substances in aqueous solution, Bubela and McDonald (1969) have found similar results for agar, silica gel and glass beads as the supporting media. It was found that neither gel nor other colloid is necessary for periodic precipitation (Morse 1930; Stern 1954). The experiments have also shown that at least one of the ions must diffuse from outside into the environment of periodic precipitation. The other ion can be present in this environment or may be introduced from outside.

The following model, based on the Ostwald-Prager theory, for the origin of the copper sulphide rhythmic bands in the Weissliegende is suggested (Fig. 4). Separate sources of copper (in the porous volume of the sandstone) and sulphide (from the Kupferschiefer) are proposed. A surplus of hydrogen sulphide from bacterial sulphate reduction (BSR) (Marowsky 1969; Sawlowicz 1989), taking place during sedimentation and early diagenesis of the Kupferschiefer, diffused continuously into the white sandstone containing dissolved copper. A few tens of centimeters off the Kupferschiefer bed the pore solutions got saturated and probably supersaturated with respect to copper sulphide. The supersaturation led to the nucleation and growth of copper sulphide grains and the first and uppermost band (with the lightest sulphur) was formed. Continuous diffusion of  $H_2S$  (and Cu ions) into this zone resulted in depletion of the adjacent zone. The  $S^{2-}$  front passed the volume of precipitation and travelled further down. When the supersaturation with respect to copper sulphides was again built up, the next band was formed. The following copper sulphide bands were formed successively towards the bottom until sulphur was exhausted to cause nucleation. According to Stern (1954) and by analogy with Berner's (1969) model regarding the Liesegang iron sulphide banding we may expect moderate concentrations of copper compared with the activity of dissolved sulphide available. The fact that on both sides the boundaries of the last band are not sharp might result from a vanishing concentration of hydrogen sulphide which did not produce supersaturation in a sharp front at increasing distance from the source.

In the case of the sulphide bands we are dealing not only with a primary precipitation but also with a potential replacement of earlier carbonates. These two processes on the scale of one band can be explained by essentially the same model (Berner 1980). Some larger grains might form by agglomeration of minute grains precipitating from supersaturated solution, fixing some rock-forming minerals between micro-grains. Such a mechanism could explain the abundant relics of carbonates, quartz and clay minerals in the sulphides. It is not impossible that replacement of rock-forming minerals also took place during recrystallization and perhaps micro-scale remobilization of the earlier formed copper sulphides.

The minor element contents in copper sulphides from the bands in the Weissliegende similar to the large grains in the Kupferschiefer might suggest similarities in composition of ore-mineralizing solutions and/or a mecha-

nism of precipitation in both environments. Where the iron was present in higher amounts, a different product of its precipitation is observed in different parts of an individual band. Due to a lower solubility of Cu-Fe sulphides compared with Cu sulphides the former could be precipitated as dispersed grains in the upper part of a band at the beginning of the precipitation process. Precipitation of the remaining large volumes of copper sulphides in the lower part of the band could cause incorporation of some iron in copper sulphides which would explain the high content of iron in such sulphides (Table 2).

#### Source of sulphide

The  $\delta^{34}S$  values of  $-44$  to  $-39\%$  imply that the copper sulphides from the Weissliegende are enriched in  $^{32}S$  by more than 50% compared to contemporaneous Permian seawater sulphate ( $+10\%$ , Thode and Monster 1965; Claypool et al. 1980) or Permian evaporites. Such light values have also been found in Recent sediments (Hartmann and Nielsen 1969; Anderson et al. 1988). A sulphur isotope fractionation factor between sulphate and sulphide of 50 is related to a temperature of about  $135^\circ C$  (Sakai 1977). This indicates temperatures of about  $100^\circ C$  in the case of some observed fractionations if they were caused by an equilibrium process. Such an equilibrium process must be excluded because sulphate cannot be reduced inorganically at  $100^\circ C$ . Therefore kinetic processes like bacterial sulphate reduction can exclusively explain the observed fractionation. Authors like Püttmann and Merz (1989) have overlooked these stringent conditions. The process of bacterial sulphate reduction (BSR) by *Desulfovibrio desulphuricans* has been discussed in detail by Nielsen (1978) and also by Marowsky (1969) and Schwarcz and Burnie (1973). Such a process of BSR took place in the Kupferschiefer during its sedimentation and early diagenesis producing  $\delta^{34}S$  values reaching  $-35$  to  $-40\%$  (Sawlowicz 1989). In Bubela and McDonald's (1969) experiments an initial zone of precipitation moved towards the sulphide source of microbial activity. Thus, diffused upper boundaries of copper sulphide bands confirm the direction of transport of  $H_2S$  from the Kupferschiefer towards the bands. Also the relatively narrow range of isotopic values in a set of sulphide bands suggests a rather uniform sulphide supply and points to the overlying shale as its only possible source.

Simple calculations have been made to check whether the organic matter in the Kupferschiefer was a limiting factor for the production of additional bacterial  $H_2S$  to be bound in the sulphide bands in the Weissliegende. In our example the content of sulphur and organic carbon in the Kupferschiefer (30 cm thick) is 2 wt% and 5 wt% respectively, and the content of copper and sulphur in a 30-cm-thick zone of sulphide bands is 2 wt% Cu and about 0.5 wt% S (as  $Cu_2S$ ). This comparison shows that about a fifth of the potential bulk  $H_2S$  produced in the Kupferschiefer was transferred into the sulphide bands. The balance is based on the simplified BSR reaction ( $2CH_2O + SO_4^{2-} = HS^- + HCO_3^- + H_2O + CO_2$ ). Thus, in the whole process of BSR only about 2 wt% organic

carbon was used up which clearly shows that the amount of  $C_{org}$  was not a limiting factor.

It was shown earlier (Hartmann and Nielsen 1969) that as the bacterial sulphate reduction system in a sediment (as the Kupferschiefer, see Sawlowicz 1989) becomes more closed, the resulting sulphur increases in  $^{34}S$ . In that case the later-formed bands (the lowest) in the Weissliegendes are expected to contain heavier sulphur. This has been observed.

If the hydrogen sulphide diffused from the Kupferschiefer into the Weissliegendes, one may ask why the sulphur isotopic composition in the sulphide bands is about 6–7‰ lighter than in Kupferschiefer (av. –41‰ and –34‰ respectively). Several explanations can be proposed. The production of sulphide for the rhythmic bands is probably connected with the early main stage of BSR in the Kupferschiefer. In that case the diffusing sulphide should be enriched in lighter sulphur during its way downwards through (lower parts of the shale and) the 0.5–1.5 m wide distance in the sandstone, before the first band is precipitated. Some of the downwards-diffusing sulphide could be oxidized to form lighter-than-marine sulphates. These sulphates could in turn be used in BSR producing very light sulphide. It is estimated that about 10% of such sulphide might cause the observed 5‰ decrease in  $\delta^{34}S$  values. An additional BSR process of minor importance could take place in the uppermost parts of the sandstones. A small amount of organic matter has been transported from the Kupferschiefer into the Weissliegendes (Gondek 1979; Szpanier 1979) where it could support BSR. The degree of isotopic fractionation by bacteria in the sandstone could be even higher than in the shale due to the lower rate of sulphate reduction (Sangster 1976; Faure 1986) being caused by lower concentrations of bacterially metabolizable organic compounds (Hoefs 1987). We also have to consider the possibility that copper sulphides in the bands precipitated a little earlier than copper sulphides in the Kupferschiefer. Sawlowicz (1985, 1989) has suggested a delay of Cu sulphide precipitation in the Kupferschiefer due to a possible intermediate formation of copper-organic complexes. Under the conditions of a BSR system, an earlier precipitation of copper from the solution (not through intermediate organic complexes) in the Weissliegendes could lead to the formation of the lightest copper sulphides in bands.

#### Source of copper

The Rotliegend red-bed sediments underlying the Kupferschiefer seem to be the most favourable source rocks of the metals concentrated in the Kupferschiefer-type deposits (Wedepohl 1964; Rentzsch et al. 1976, Lur'ye 1977). Schmidt and Friedrich (1988) suggested that copper solutions were pre-concentrated in the upper parts of Lower Permian sandstones at the edges of the Zechstein basin. The white sandstones reworked by the Zechstein sea (Jerzykiewicz et al. 1976; Nemeč and Porebski 1977; Glennie and Buller 1983) could have been "soaked" with Cu-bearing fluids and thus could have served as a source of copper during sedimentation and

early diagenesis of the Kupferschiefer (Schmidt and Friedrich 1988; Wedepohl in press). In that case  $H_2S$  from the black shale generator would have diffused into the relatively homogeneous pore space system. The precipitation of copper sulphides in the upper bands probably controlled the upwards diffusion of copper ions from the lower parts of the sandstone due to a concentration gradient.

A significant contribution of metals through brines rising up from the deeper-seated reservoirs in the Rotliegendes should be considered with reluctance. Such brines are expected, being chloride-rich (Rose 1976). Experiments of Koehn and Mainzhausen (1937) suggest that rhythmic precipitation is influenced by the presence of the chloride ion. At higher concentrations the simple geometry of rhythms disappears.

It is interesting to note that in Bubela and McDonald's (1969) experiments free metal and sulphide ions were still present in the reaction medium, although no further precipitation occurred after the stabilization of the bands. Part of such solutions could participate in the later phases of copper sulphide mineralization in the Weissliegendes.

#### Conclusions

The rhythmic copper sulphide bands in the Weissliegendes were formed by the diffusion of biogenic hydrogen sulphide from the Kupferschiefer into the white sandstones soaked with copper solutions. The sulphides precipitated in bands, from the top to the bottom, very probably according to the Ostwald-Prager supersaturation theory. Copper diffused further from the source to the site of precipitation than required by saturation. The zone from saturation to supersaturation could feed the precipitation in a band.

The very light sulphur has resulted mainly from early steps of the bacterial sulphate reduction in the shale but could be modified by different processes of oxidation and additional BSR. The trend towards heavier sulphur values downwards within a set of bands might be explained by closing of the BSR system.

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