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ORIGINAL PAPER

The composition of brines in the early diagenetic mineralization of the Permian Kupferschiefer in Germany

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Abstract The Kupferschiefer is an approximately 0.5 m thick black marly shale of Lower Zechstein age in Germany. If one includes some of its footwall and hanging wall, it contains 300 Mt Cu, 800 Mt Zn and 300 Mt Pb. The regional pattern of metal distribution demonstrates its relationship to Variscan and Permian tectonic structures. Faults and the topographic relief of the basement apparently controlled the uprise and lateral migration of reducing and slightly acid hot brines from deeper crustal levels to supply the metals for the mineralization of the Proto-Kupferschiefer. Deep fluids are mainly richer in Zn than Pb and richer in Pb than Cu. Mixing of such slightly acid fluids with slightly alkaline formation waters (seawater) caused a gradient in pH from about three to eight and in sulfide concentration. Most of the sulfide came from dissolved pyrite which was very light in sulfur isotopes. This gradient controlled the sequential precipitation of bornite, chalcopyrite, (chalcocite), galena and sphalerite, which is observed in a lateral and vertical zoning of these sulfides. The fluids experienced a fractionation of the metals during migration over meter to kilometer distances from the tectonically controlled vents within the unconsolidated Proto-Kupferschiefer. Close to the vents the sulfide deposits attained concentrations up to 2% Zn + Pb + Cu. The migration of the metals over large distances took place in unconsolidated sediment. Thus the major mineralization of the Kupferschiefer has to be classed as an early diagenetic process.

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Introduction

The Kupferschiefer bed in England, Holland, North and Central Germany and Poland is a well known stratigraphic marker horizon representing the lowermost unit of the marine Upper Permian which is called Zechstein. It occurs mainly as a black laminated marly shale which is about half a meter thick. The lamination is caused by alternating layers, one dark consisting of clay minerals with organic carbon and one light consisting of carbonates. The maximum transgression of the Zechstein sea into the peneplain formed on the eroded Variscan Mountains was slightly larger than that of the short Kupferschiefer period. Details of the geography, stratigraphy, lithology and biostratigraphy of the Kupferschiefer deposit have been summarized by Paul (2006).

Because of a very restricted vertical water circulation in the marine Kupferschiefer basin, comparable with the present Black Sea, the lower part of the water column was anoxic. In the central basin the bottom waters containing hydrogen sulfide were probably 200 m thick (Paul 2006). In the almost stagnant deep water, sulfate was reduced by bacteria living on organic compounds from the upper water column. This process formed isotopically very light sulfide not known from inorganic reactions (Marowsky 1969; Bechtel et al. 2001). The sulfide reacted with iron oxides and was accumulated in the sediment as pyrite.

The very low solubility of copper, lead and zinc sulfides in anoxic seawater and their occurrence as crystals less than 50 μm in size in abundant exposures of the Kupferschiefer bed stimulated an early hypothesis of a syngenetic Cu, Pb and Zn mineralization (Pompecky 1914; Richter (Bernburg) 1941; Kautzsch 1942; Wedepohl 1964). However, mass balance calculations based on Cu, Pb and Zn sulfides precipitated from 300–100 m stagnant seawater, which was yearly exchanged, and a rate of clay accumulation as in the present Black Sea failed to explain concentrations greater than 0.1% Cu and 0.2% Zn, respectively (Wedepohl 1980, Table 11). The extremely low lead concentration in seawater in the range from 0.002 to 0.01 ppb (ppb = 10^{-7}%) (Flegal and Patterson 1983) excludes the possibility of lead concentrations as high as 0.01% Pb in Kupferschiefer samples to be syngenetically deposited from stagnant seawater. The minimal contributions from these sources suggested an early diagenetic instead of a syngenetic model of the Kupferschiefer mineralization. We will report about the role of brines, which are chlorine rich thermal fluids at temperatures in the order of 100°C in the ore deposition.

Almost 800 years of mining Kupferschiefer for copper and silver demonstrates the former importance of this ore deposit (Hartwig et al. 1999). Because of its large grade and thickness, the copper ore deposit in the Fore Sudetic Monocline of Poland is still economic and will be for several decades (Cathles et al. 1993).

The sulfide mineralization of Kupferschiefer and the ore bearing zone of the Zechstein basal sequence will be discussed by us on the basis of lateral and vertical zoning of high and medium Cu, Zn and Pb concentrations in these rocks. The lateral zoning can be easily observed in maps of North and Central Germany presenting the coverage of Zechstein basal rocks containing 0.2% Cu, 0.2–1% Cu and > 1% Cu (Fig. 1). Figures 2 and 3 present the respective concentrations of Zn and Pb. The signatures on the maps indicate high (dark grey), medium (light grey) and low metal concentrations (white). The selection of signatures depend on analytical data for local samples out of the bulk of 10,000 samples. These samples were collected in 1,082 underground and surface exposures. The former included a large number of drill cores. Minimum concentrations were 0.1% Cu, Zn or Pb, respectively.

Regional zoning of high and medium concentrations of Cu, Pb and Zn in Kupferschiefer

The lowest Zechstein bed in Germany covers an area of 160,000 km^2. The ore bearing layer contains 2.5 × 10^5 Mt of rocks. They consist of 30% sandstone, 65% Kupferschiefer and 5% limestone. The ore is estimated to contain 300 Mt copper, 800 Mt zinc and 300 Mt lead according to detailed analytical investigations of a great number of drill cores (Rentzsch and Franzke 1994). From these data it is possible to calculate an average concentration of 0.19% Cu, 0.48% Zn and 0.19% Pb in the bed which contains about 4.5% organic carbon. These values exceed by far typical abundances of the respective metals in syngenetically mineralized black shales as those of Cretaceous age from the Atlantic Ocean. Brumsack (1980) reports 0.016% Cu, 0.08% Zn, 0.002% Pb and more than 1% C as average from four legs of DSDP. The syngenetic Proto-Kupferschiefer if comparable in metal concentrations to these Atlantic sapropels contained 40 Mt Cu, 200 Mt Zn and 5 Mt Pb.

The maps on the lateral distribution of Cu, Zn and Pb in the rocks of the Zechstein base in Central Europe prepared by Rentzsch and Franzke (1997) showing the distribution of the metals and tectonic lineaments are reproduced in Figs. 1–3. Dashed lines separate the Moldanubian, Saxothuringian, Mid-German Crystalline Rise, Northern Phyllite Belt and Rhenohercynian as structural subdivisions of the Variscan Orogen. The latter are with the exception of the NE part taken from Franke (2000). The position of the NE part of the dashed lines is taken from Rentzsch and Franzke (1997). The metal concentrations in these maps are given in 2, 2–10 and > 10 kg/m^2. Assuming an average thickness of the Kupferschiefer bed of 40 cm and a density of the rocks of 2.5 g/ccm, a concentration of 2 kg/m^2 almost equals 0.2% of the metal. There exist areas with a thicker bed suggesting an average of about 60 cm. We prefer the value of 40 cm for easier conversion of the data.

The former mining areas on copper at the Zechstein base occur exclusively above the Mid-German Crystalline Rise, the Northern and the Southern Phyllite Belt of the Variscan Orogen (the Southern Phyllite Belt is not marked on our maps). Rentzsch (1974, 1981) has called this region (plus the respective one in Poland) the "Central European Copper Belt" when comparing it with the Rhodesian Copper Belt. We realize that the metal accumulations at the Zechstein base above the Rhenohercynian are larger than above the Saxothuringian. This observation includes the Polish deposits (Speczik 1985).

High concentrations of copper in the ore layer exceeding 1% (Fig. 1) occur in the western part of the SW–NE trending copper belt in relatively small areas. Metal transport from below was controlled by the intersection of the Mid-German Crystalline Rise

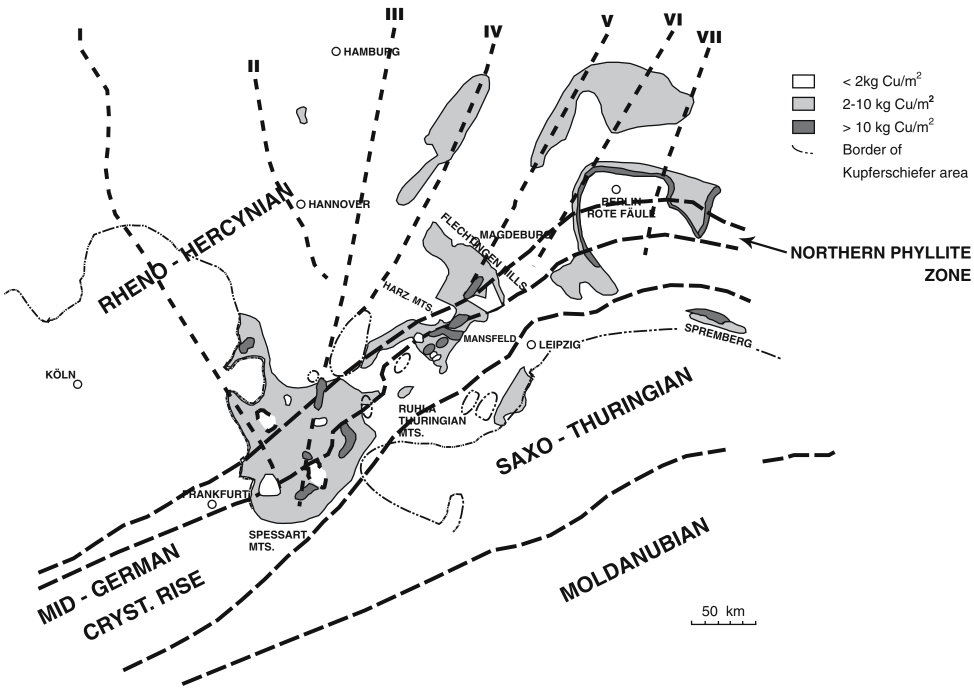

Fig. 1 Regional distribution of high, medium and low concentrations of copper according to Rentzsch and Franzke (1997). A total of 2 kg Cu/m^2 almost equals 0.2% Cu. Borders between structural belts of the Variscan Orogen mainly according to Franke (2000) are marked by *dashed lines*. Tectonic lineaments are numbered: *I* Ems-Altenbüren, *II* Steinhude, *III* Hessia, *IV* Arendsee, *V* Rheinsberg (Eastern Harz), *VI* Liebenwalde, *VII* Schwedt–Stettin according to Rentzsch and Franzke 1997)

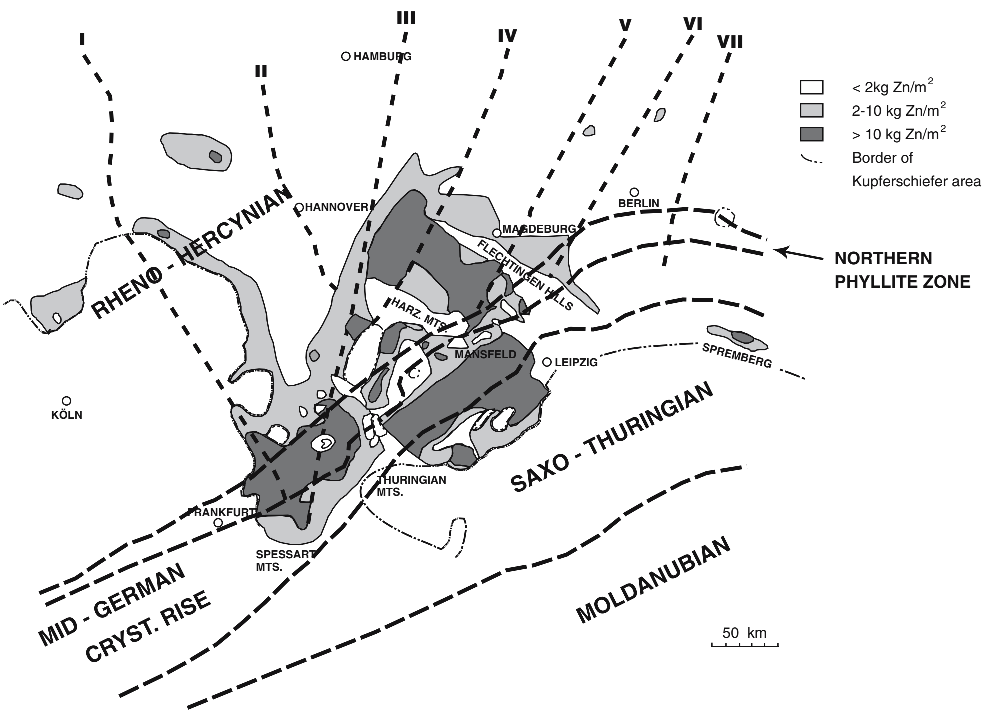

Fig. 2 Regional distribution of high, medium and low concentrations of zinc according to Rentzsch and Franzke (1997). A total of 2 kg Zn/m^2 almost equals 0.2% Zn. Structural belts and lineaments as in Fig. 1

with NNW–SSE and SSW–NNE striking fracture zones (Rentzsch and Franzke 1997). The copper accumulation in the Richelsdorf area is about 1 Mt, Spessart–Rhoen–Ruhla rise about 1 Mt, NNE–SSW striking Oberkatz Rift 0.5 Mt, and Mansfeld–Sangerhausen deposit plus the Bernburg–Aderstedt area 10 Mt. To the east of the River Elbe, the Mid-German Crystalline Rise and the belt of copper accumulation changes from a SW–NE into a NW–SE trend. The Spremberg deposit with 1.5 Mt Cu is located at the intersection of the southern Lower Lusatia Depression with the SSW–NNE trending Mulkwitz Rift. In the extension to the ESE the North Sudetic Syncline and the very large accumulation of the Fore-Sudetic Syncline in Poland contain about 350 Mt Cu (Cathles et al. 1993).

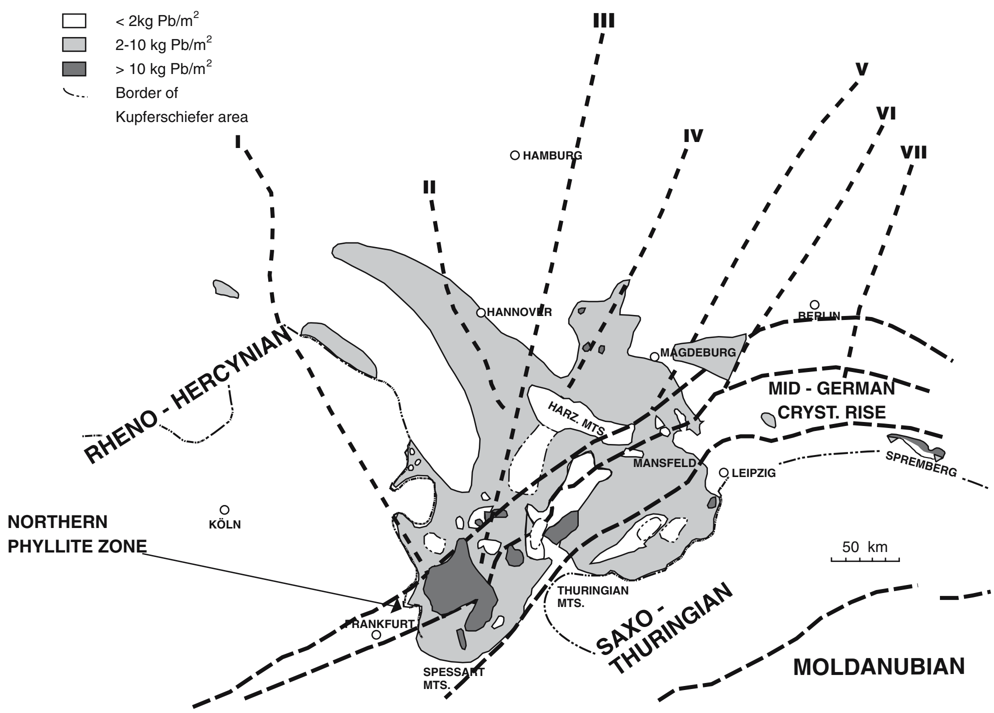

Fig. 3 Regional distribution of high, medium and low concentrations of lead according to Rentzsch and Franzke (1997). A total of 2 kg Pb/m^2 almost equals 0.2% Pb. Structural belts and lineaments as in Fig. 1

Rocks of the Zechstein base with Zn concentrations above 1% Zn (Fig. 2) cover much larger areas (some 4,500–5,800 km^2 in size) than those with high Cu concentrations. They occur above the Werra–Fulda Depression, above the Thuringian part of the Saale Depression, between the Hessian and the Rheinsberg Lineaments and above parts of the Muehlhausen and Ilfeld Depressions. The coverage of rocks with lead concentrations of more than 1% Pb (Fig. 3) is intermediate between high-Cu and high-Zn rocks.

The relatively large light grey areas of medium concentrations of metals ranging from 0.2 to 1% Cu (Fig. 1), 0.2 to 1% Zn (Fig. 2) and 0.2 to 1% Pb (Fig. 3) cover almost 20% of the Rhenohercynian, Phyllite Belt and Mid-German Crystalline Rise on the maps. Medium-Cu areas trend from SW to NE, Medium-Zn accumulations also follow the SW to NE trend and branch into a more northern direction. A belt with medium-Zn rocks occurs in SSE–NNW trend between the Ems-Altenbüren and Steinhude Lineaments. The large coverage of high and medium-Pb rocks overlaps with high- and medium-Zn Kupferschiefer with the exception of a SE to NW trending belt near the Steinhude lineament. Close to the vents of fluids located on the tectonic structures the sulfides attained up to 2% Zn + Pb + Cu. The maps clearly demonstrate the existence of different patterns of lateral metal distribution. The NW–SE direction of tectonic elements governs the accumulation of Cu, Zn and Pb mainly. Very important for Pb and Zn accumulation is also the SSW–NNE direction. We assume that these patterns reflect positions of vents for flows of the metal containing thermal fluids within layers of the unconsolidated carbon rich clays, which later formed the Kupferschiefer bed. After uprise on fractures the slightly acid fluids were trapped by reactions with slightly alkaline formation waters causing an increase in pH. The circulation of fluids on fractures beneath the Zechstein level depended on gradients in temperature and pressure and on the topography of the area. Because of their erosion immediately after the uplift, the rock masses of the Mid-German Crystalline Rise were slightly warmer than those of the neighbouring regions. These late orogenic conditions were recorded in zircons of granitic rocks of the Ruhla Massif in Thuringia, which was part of the Mid-German Crystalline Rise (Zeh et al. 2003).

Lead loss from the rims of zircons reflects the disintegration of mountain ridges and their erosion during the upper Carboniferous and Lower Permian (300–280 Ma ago). Fission track ages of zircons confirm that this part of the Mid-German Crystalline Rise was still rising 264 Ma ago. The almost equal thickness of the Kupferschiefer bed at about 0.5 m indicates that the early Upper Permian transgressed over a large peneplain about 258 Ma ago (Menning 2000). Depressions were previously filled with Lower Permian sandy sediments. The SW–NE and NW–SE trending ridges which were remains of the Variscan Orogeny separated basins with a few hundred meters water depth as essential for the early Zechstein deposition. Because of the latitudinal position of the Permian Central Europe at about 20–30° North (Scotese et al. 1979) the climate was arid. The final Variscan magmatism produced rhyolitic, andesitic and basaltic melts of early Lower Permian age.

Before the transgression of the Zechstein Sea from the North large quantities of weathering products were formed because of the favorable climate. These compounds were partly dissolved in seawater and acted as nutrients for the abundant organisms in the surface layers of the sea (for details see Paul 2006).

They led to contents of organic carbon as high as 4.5% on average in the Kupferschiefer. Bacterial life in the lower water column reduced seawater sulfate to sulfide, which reacted with iron oxides to form framboidal pyrite in the sediment. The concentration of sulfide sulfur in the Kupferschiefer bed ranged between 1.5 and 2% S. This lower Zechstein is characterized by a C/S ratio of 2.6 which compares with a C/S ratio of 4.3 in the laminated organic carbon rich sediments in the central Black Sea (Lyons and Berner 1992). The pyrite formation in the latter environment was apparently limited by the availability of reactive iron. A C/S ratio of 2.6 in Kupferschiefer is close to the general marine C/S ratio of 2.8 mentioned by Lyons and Berner (1992).

Detailed information on the origin of the sulfides in the Kupferschiefer bed can be derived from the isotopic composition of sulfur. Marowsky (1969) reported an average δ^{34}S–35‰ for pyrite in more than hundred samples of this bed mostly from NW Germany. The fraction of Cu, Zn and Pb sulfides in his samples was a little heavier (δ^{34}S –32.5‰). It is obvious that (1) the light sulfide was formed from bacterial sulfate reduction and (2) both sulfide fractions with Cu, Zn and Pb sulfides heavier than pyrite did not equilibrate (Ohmoto and Rye 1979). Pyrite in the English Marl Slate ranges in δ^{34}S from –30‰ to –37‰ (Sweeney et al.1987). Sawlowicz (1989) observed an average δ^{34}S –36.3‰ in nine samples of copper sulfides (plus some pyrite) in Kupferschiefer of the Fore-Sudetic Monocline in Poland. Bechtel et al. (2001) report an average δ^{34}S –36.4‰ for the upper two-thirds of the bed in the Sangerhausen Basin containing 0.12–3.8‰ Cu. Their δ^{34}S increased to –8.4/–21.7‰ in the lower third of the bed with 9.3% Cu. This increase indicates a secondary influx of heavy sulfide in thermal fluids from below. Reactions of these fluids with carbonates caused an increase of pH above three where pyrite became unstable and was replaced by chalcopyrite and bornite at pH 3–5 (Helgeson 1979) and by chalcocite, galena and sphalerite at a slightly higher pH.

The Kupferschiefer bed consists of three lithologic microcycles each beginning with a larger proportion of clay and ending with a larger proportion of carbonate. This subdivision occurs everywhere in the basin (Rentzsch 1965). The proportion of carbonates in the bed containing more dolomite than calcite ranges between 35 and 40%. It mainly formed the light layer of the lamination. The average concentration of about 300 ppm Sr in these carbonates is lower than in a $CaCO_3$ precipitate from seawater (Lorens and Bender 1980). This observation indicates that the majority of carbonates in Kupferschiefer was formed from secondary solutions.

The most abundant silicate is illitic mica occurring in a proportion of about 30%. Thermal solutions responsible for the secondary Cu, Zn and Pb mineralization caused an internal oxygen isotope fractionation in the illite fraction. Bechtel and Hoernes (1993) calculated a temperature of 130°C for mica from Kupferschiefer at Richelsdorf (Hessia). The average Kupferschiefer bed contains a little more than 15% quartz and 10% albite plus chlorite (Wedepohl 1964).

We have to explain that Kupferschiefer together with some of its footwall and hanging wall can grade locally into a littoral sandy facies containing coarse quartz from sandbars. Because of their permeability these sandy rocks could be penetrated by oxidizing fluids as seawater, etc. They channelled these fluids and oxidized ferrous iron minerals as pyrite, etc. to form red stains, streaks, ribbons and veinlets of hematite. These barren rocks are called ''Rote Faeule'' according to an old miners' term (Rentzsch 1964, 1991; Dette 1965; Schmidt 1987; Oszczepalski 1989). They occur relatively close to localities where early diagenetic ore is dissolved by oxidizing fluids and reprecipitated within a redox gradient. Vertical and lateral zones with the sequence of Cu, Pb and Zn sulfides reflect this gradient and the flow pattern in the basal Zechstein. ''Rote Faeule'' occurs in relatively small areas of some thousand square meters to square kilometers at Richelsdorf and Mansfeld–Sangerhausen but covers a large area of about 10,000 km^2 in Brandenburg, Lower Lusatia and Lower Silesia, the latter in Poland. The mentioned footwall and hanging wall of Kupferschiefer can range from Rotliegend sandstone to Werra anhydrite.

There exist several publications on the geologic age of the mineralization of the Kupferschiefer. The estimates from the direction of the remanent magnetization of iron minerals in ''Rote Faeule'' (Jowett et al. 1987) and from K/Ar dating of the small grain size of mica (Bechtel et al. 1996) are not precise enough to get the age of the mineralization of the thin bed. Recently, Pätzold (2005) plotted an isochron based on nine data in a $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ diagram. They came from analytical investigations of a set of drill core samples from Sangerhausen–Lengefeld with layers containing 0.8–0.93% Cu. These high-Cu layers also contained the largest Re and Os concentrations. He got an isochron of 257 ± 1.5 Ma. This age is expected to be that of the early diagenetic mineralization. It is almost identical with the beginning of the Zechstein deposition at 258 Ma as reported by Menning (2000).

Local vertical and lateral zoning of high and medium Cu, Zn and Pb concentrations in Kupferschiefer

We will evaluate exposures of vertical and lateral zoning of Cu, Zn and Pb in the ore-bearing layers for general conclusions on the sequence of ore deposition from mineralizing hot fluids. In Fig. 4 we present three

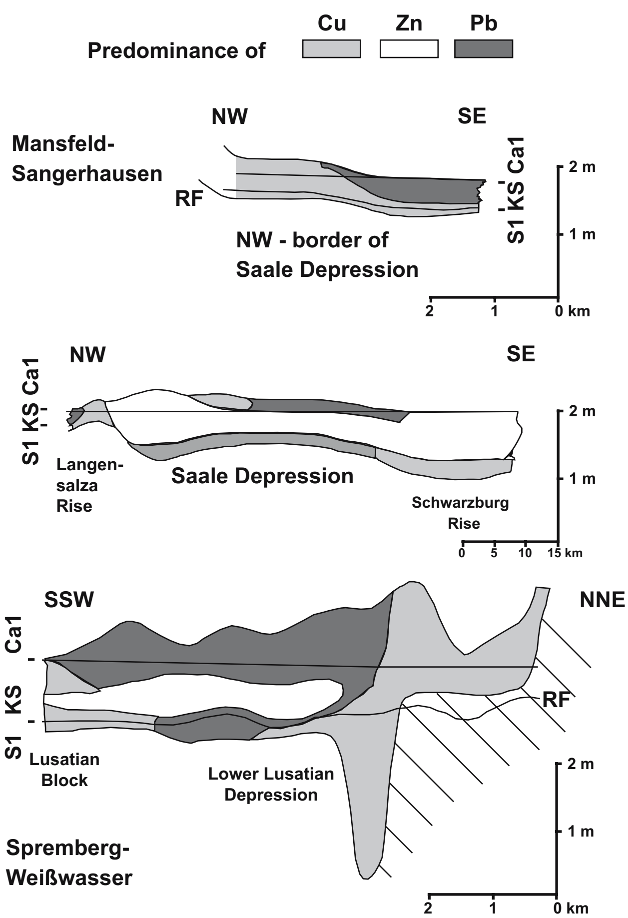

Fig. 4 Lateral and vertical zoning of the predominance of Cu, Pb and Zn in the Kupferschiefer bed (KS), its footwall (S1 sandstone) and its hanging wall (Cal Zechstein limestone). **a** Mansfeld-Sangerhausen, **b** Thuringian Basin and **c** Spremberg Weisswasser according to Rentzsch and Franzke (1994)

profiles from Sangerhausen, the Saale Depression and Spremberg reported by Rentzsch and Franzke (1994), which demonstrate the local predominance of one over the other metals if one moves 4, 70 or 7 km from NW to SE (in case of Spremberg from SSW to NNE), respectively.

At Sangerhausen, copper occurring as chalcocite is the major metal in a 2 km broad zone SE of the barren "Rote Faeule" (RF) area. Moving into SE direction Cu is replaced by Pb. In a profile at the Muenzer–Shaft (Wedepohl 1964, based on data from Eisenhuth and Kautzsch 1954), Cu concentrations are about 10% close to the contact of Zechstein sandstone with Kupferschiefer. High-Cu grades into high-Pb (1.5%) and high-Zn (4%) about 30 cm above the contact. The mineralizing fluids probably rised in the permeable sandy "Rote Faeule" equivalent of Kupferschiefer and passed into the neighboring carbonaceous clay where it increased the pH to >3 and replaced pyrite by chalcocite. Fluids almost depleted in Cu from this reaction migrated in the Kupferschiefer bed into higher levels and more distant zones to precipitate galena and sphalerite.

Above the large Saale Depression (100 × 70 km in size) both Zn and Pb predominate over Cu and the mass of Zn is larger than that of Pb. In the SE (Schwarzburg Ridge) the lower layer consists of chalcopyrite superimposed by smaller abundances of sphalerite/galena. The major proportion of the Kupferschiefer bed in the Saale Depression contains 2% Zn in the NW and 1% Zn in the SE. High-Pb (1%) occurs in the lower level at the center of the depression and low-Pb in higher levels SE. The metal accumulation in this large basin probably reflects the average composition of hot brines mineralizing the Kupferschiefer bed with zinc in higher concentrations than lead and lead higher than copper. The hot fluids listed in Table 2 (except Fluid 9) contain on average 0.3 ppm Cu, 3 ppm Zn and 1.2 ppm Pb. Metal concentrations decrease in the same sequence as in Kupferschiefer of the Thuringian Basin.

At Spremberg, we again observe a metal accumulation controlled by fluids channelled through a neighbouring "Rote Faeule" equivalent of Kupferschiefer plus footwall and hanging wall with a favorable permeability for fluids. This is the large Brandenburg Lower Lusatia complex in the NNE of the Spremberg ore deposit. Here, zoning is comparable to Sangerhausen and Richelsdorf with high-Cu in a 3 km broad belt close to the "Rote Faeule". This belt contains 1–2% Cu with bornite and chalcocite predominating over chalcopyrite. Chalcocite occurs closest to the "Rote Faeule". Galena- and sphalerite-rich Kupferschiefer with 0.1–2% Pb or Zn represents the 4 km

Table 1 Concentrations in percent of selected elements in Kupferschiefer, Black Sea sediments, Permian and Variscan basement and continental crust

	B	C	S	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Mo	Ag	Pb	Reference
Kupferschiefer	0.015	5.0	1.75	13.3	0.31	0.13	0.014	0.22	3.0	0.010	0.027	0.18	0.48	0.014	0.02	0.025	0.01	0.19	Rentzsch and Franzke (1994); Wedepohl (1964)
Sapropelic sediments Black Sea (22)		3.9	1.1	9.2	0.32	0.016	0.012	0.089	3.9	0.0027	0.012	0.007	0.0082	0.0021	0.045	0.0045	0.000011	0.0016	Brumsack (1989)
Lower Permian sediment rocks												0.0023	0.0047					0.0019	Rentzsch and Franzke (1994)
Lower Permian volcanic rocks												0.0018	0.0094					0.0024	Rentzsch and Franzke (1994)
Variscan basement		0.22	0.083	3.3	0.40	0.0091	0.014	0.081	3.8	0.0016	0.017		0.0080					0.0017	Schulz-Dobrick and Wedepohl (1983)
Continental crust	0.0011	0.2	0.07	3.85	0.40	0.0098	0.013	0.072	4.3	0.0024	0.0056	0.0025	0.0065	0.0002	0.033	0.0001	0.000007	0.0015	Wedepohl (1995)

broad zone outside the high-Cu belt. The lateral and vertical metal zoning controlled by a ‘‘Rote Faeule’’ complex also occurs at Richelsdorf–Ronshausen in Hessia.

In case of the ore deposits of Spremberg, Sangerhausen and Richelsdorf, we have observed that thermal solutions which apparently went up in a sandy ‘‘Rote Faeule’’ contact to Kupferschiefer precipitated their copper close to this contact. After depletion in Cu the fluids migrated through organic carbon rich layers of unconsolidated clay for distances in the 100 m to km range while they precipitated galena and sphalerite from sulfide of dissolved pyrite at increasing pH. Such lateral migration over long distances was only possible before the Kupferschiefer bed was completely consolidated. It is a strong proof in favor of an early diagenetic mineralization of the Kupferschiefer bed.

Composition and origin of the thermal fluids

In the previous sections we have presented evidence for an early diagenetic accumulation of Cu, Zn and Pb in the Proto-Kupferschiefer from thermal fluids uprising from some depth. These were channelled through clay layers with some porosity from organic carbon. They precipitated the metal sulfides on reaction with alkaline formation waters. Fluids from below were kept on circulation by hydrostatic pressure from the difference in altitude between ridges and basins.

Because we do not know the composition of these fluids from direct sampling we are left to deduce their general behavior from data on thermal brines in the oceanic and continental crust. During recent decades the Deep Sea Drilling Project and other shipboard research has gained considerable experience on processes in ocean ridges (German and von Damm 2003). High temperature fluids in the ocean crust are obviously acidic, reducing metal-rich NaCl solutions low in Ca and Mg. Ca was lost into the precipitation of anhydrite above 130°C and Mg went into silicates as smectite and chlorite in water-rock interactions.

Oceanic vent fluids were heated by magmatic intrusions and by conduction from deeper layers.

The temperature of the Central European continental crust increases with a gradient of about 30°/km. Deep faults in the upper crust are required for water circulation. Fracturing is almost restricted to the upper 10 km because of a change of rock behavior from brittle to ductile. The continental deep drilling project (KTB) (Emmermann 1998) at Windisch–Eschenbach in Bavaria has obtained hot saline fluids at depths from several thousand meters to a maximum depth of 9.1 km. At this depth the temperature was 270°C. On

Table 2 Composition of thermal fluids from the continental and oceanic crust in relation to seawater (*ppb)

	T (°C)	pH (25°C)	CO_2 (ppm)	Na (%)	Mg (ppm)	SO_4 (ppm)	H_2S (ppm)	CI (%)	K (%)	Ca (%)	Mn (ppm)	Fe (ppm)	Cu (ppm)	Zn (ppm)	Ag (As) (ppm)	I (ppm)	Pb (ppm)	Reference
Atlantis II Red Sea[a]	56	5.3		8.8	800	950		16.3	0.3	0.54	82–134	81–83	0.5–1.5	0.5–7.1	0.04		0.3–0.63	White in Weissberg et al. (1979)
Cheleken II/III Caspian Sea[b]	70–105	5.2–6	22	7.1	3,000	150–310	7.2	15.7	0.05	2.0	47	4.2–14	0.9–1.4	0.2–3.1	(0.03–0.5)	25–32	3.6–9.2	Lebedev and Nikita (1968)
Arima Springs Japan[c]	13–95	6.1	450	0.6	17	4	Very low	1.19	0.11	0.12	17	58	0.1	0.2		< 0.01	0.4	Nakamura and Maeda (1961)
Tamagawa Springs Japan[d]	98	2.4		0.01	80	1,300	20	0.32	0.006	0.02	4.2	105	0.01	2.8	(3)		1.0	Ozawa et al. in Weissberg et al. (1979)
Continentral Deep Drill (KTB) Bavaria[e]	118			0.55	7	390	Low	3.95	0.02	1.47	0.7	3.8	n.d.	0.2			n.d.	Emmermann (1998)
Ocean ridges sediment covered[f]	100–315	5.1–5.9		0.7–1.3	Very low	Very low	35–190	1.5–2.4	0.05–0.19	0.11–0.32	0.55–13	0–10	0.0013–0.07	0.0065–2.6	< 0.0001–0.025		< 0.004–0.13	German and von Damm (2003)
Escanaba vent Gordon E. Pacific[g]	212	5.4	550	1.3	270	170	35	2.27	0.14	0.13	1.5	2.8	0.2	0.7		13	0.3	von Damm et al. (2005)
Matsao E205 Taiwan[h]	245	2.4	2	0.55	130	350	Very low	1.34	0.09	0.15	42	220	0.05	13	(3.6)		0.6–0.9	Ellis in Weissberg et al. (1979)
Salton Sea 1/IID California[i]	240 – 360	5.2	> 150	5.0	50	5	16	15.5	1.8	2.8	1,400	2,290	8	540	1.4 (12)	18	102	Muffler and White in Skinner (1979)
Seawater		7.8	140	1.08	1,300	2,700		1.9	0.039	0.041	0.03*	0.05*	0.25*	0.39*	0.003*	0.06	0.002*	Turekian (1969), Bruland (1983)

[a] Fluid related to basalt, sediments, (evaporites?)

[b] Fluid related to Neogene red beds

[c] Fluid related to altered rhyolite

[d] From magmatic fumaroles

[e] Fluid from 4 km depth in gneiss and amphibolite

[f] Fluid from alteration of basalt and sediment cover

[g] Vent fluid from alteration of basalt covered with 400 m turbidite

[h] From 1,500 m deep hole in andesite

[i] Fluid from 2,470 m deep hole in Tertiary shales, siltstones (evaporites?)

its way, the drill passed at least nine faults. Major fractures occurred between 6.8 and 7.2 km depth. At a depth between 2 and 3 km, fluids in caverns were dominated by Ca^{2+} and contained dissolved methane and nitrogen. Emmermann (1998) reported that, in a pumping experiment at 4 km depth,750 tons of saline solutions containig 1.4% NaC1 and 3.1% $CaCl_2$ at a temperature of 118°C were obtained within 120 days. The detailed composition of this fluid with 4 ppm Fe, 0.7 ppm Mn and 0.2 ppm Zn is listed in Table 1.

The continental hot fluids derived most of their water and NaCl from the compaction of marine sediments. At about 3 km depth, less than 20% of their original porosity is left (Hanor 1979). The majority of fluids listed in Table 2 is reducing and slightly acid. Cu, Zn and Pb were extracted through the reduction of iron and manganese oxides, etc. The slightly acid fluids were neutralized on hitting the carbonates in the Kupferschiefer bed. At increased pH they precipitated their Mn, Fe, Cu, Zn, Pb, etc.

Table 1 gives the average composition of Kupferschiefer and of the rocks in the continental crust of pre-Zechstein age. The black shale of Lower Zechstein age contains distinctly higher concentrations of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag and Pb than sapropelic sediments from the present Black Sea as reported by Brumsack (1989). The factors of accumulation in the former relative to the latter sediment range from 2.5 (Mn, Ni) to 7 and 8 (As, V). Their source is probably the reduction of Mn and Fe oxides by brines in the upper continental crust. Each of the elements Cu, Zn and Pb occurs in comparable concentrations in the Lower Permian, Variscan and bulk continental rocks. Based on the data from Table 1, we expect that Fe, Mn, Zn, Pb and Cu will be transported in almost this order of abundance in reducing uprising brines.

In many brines listed in Table 2 sulfate is distinctly lower than in seawater because of precipitation as anhydrite (ocean crust) or reduction and precipitation as sulfide. Water rock interaction lowers the concentration of Mg in hot fluids (Table 2). Because of this low concentration of Mg and higher abundance of Ca in continental brines, we expect calcitization and not dolomitization during secondary mineralization of the Kupferschiefer bed.

The fluids from worldwide sampling listed in Table 2 are selected as containing more than 0.1 ppm Cu, Zn and Pb (ppm = 10^{-4} weight %). The majority of these fluids either came from the continental crust (2, 5, 9) or has reacted with typical crustal rocks such as rhyolite (3), turbidite (7) and andesite (8). These hot fluids (except Fluid 9) contain on average 28 ppm Mn, 60 ppm Fe, 0.3 ppm Cu, 3 ppm Zn and 1.2 ppm Pb. Fluid 9 from the 2.5 km deep wells at Salton Sea in California is extreme in temperature (240–360°C) and metal concentrations (2300 ppm Fe, 540 ppm Zn, 102 ppm Pb and 8 ppm Cu). All these brines are low in Mg and the majority low in K.

If the brines which have mineralized the Kupferschiefer bed contained about 1 ppm Cu, 3 ppm Zn and 1 ppm Pb, a mass of water in the order of 3×10^8 Mt was required to deposit the estimated 300 Mt Cu, 800 Mt Zn and 300 Mt Pb in the ores. Such a large amount of water needs 10% of open space on faults, cleavages, porosity, etc. in the brittle upper crust (containing 4×10^9 Mt rocks) too much to be seriously considered. Consequently, we expect metal concentrations above 1–3 ppm in the thermal fluids which have mineralized the Kupferschiefer.

The thermal fluids migrated upwards using deep faults as those observed in the hole of the deep drilling of KTB in Bavaria. Such pattern of the deep faults was caused by the stress regime at late Variscan and early Permian time. This pattern changed from NE–SW and SE–NW to NNE–SSW and NNW–SSW. Certain lineaments exposed mainly in the Rhenohercynian Belt are numbered from I to VII and marked in Figs. 1–3 by dotted lines. Their names are listed in the caption of Fig. 1. Lineaments I and II converge in the area of the Hessian Depression where this convergence favored a high accumulation of Cu, Zn and Pb.

Conclusions

The early diagenetic accumulation of 300 Mt Cu, 800 Mt Zn and 300 Mt Pb from thermal fluids in the Kupferschiefer was preceded by a syngenetic deposition of an estimated mass of 40 Mt Cu, 200 Mt Zn and 5 Mt Pb from anoxic seawater. The thermal fluids were slightly acid and reducing and migrated upwards from several km depth on NNE–SSW and NNW–SSE trending faults into the pumping system of different hydrostatic pressures. These differences occurred between Variscan ridges residual from erosion and Permian basins. Fluids contained metals in concentrations higher than a few ppm with Zn > Cu and Cu ~ Pb almost according to crustal abundances. In the fluids of Table 2, Zn is roughly correlated to Fe indicating the reduction of iron oxides in the source. From tectonic vents mostly in the area of the eroded Mid-German Crystalline Rise and the Northern Phyllite Zone thermal solutions migrated laterally within porous layers of the unconsolidated Proto-Kupferschiefer. Seawater and carbonates caused a pH of about eight in the porous fluids of the Proto-Kupferschiefer. Their mixture with slightly acid thermal solutions formed a gradient of acidity and sulfide concentrations from the vents into the sediment. In this gradient carbonates and pyrites were dissolved and the sequence bornite, chalcopyrite,(chalcocite), galena and sphalerite was precipitated from the metal ions advected by the thermal fluids. Dependent on this fractionation of Cu, Pb and Zn the separation of the different sulfides occurred over cm to km lateral distance in the Kupferschiefer bed.

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