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THE *KUPFERSCHIEFER* IN COMPARISON WITH THE DEPOSITS OF THE ZAMBIAN COPPERBELT

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1. INTRODUCTION

For a long time, the *Kupferschiefer* has been known as a prototype of a syngenetic sedimentary sulfide mineralization. In most cases, very simple monogenetic models were formerly given for the explanation of the genetic processes which formed these economically important copper deposits. These copper deposits are the largest in Europe. According to Wedepohl (1971) their extension is in the range of about 0.2 % of the total *Kupferschiefer* coverage ($\sim 6 \times 10^5$ km^2). The areas with increased lead and zinc contents are much larger. Over an area of 28 000 km^2 in the southern part of the *Kupferschiefer* area in the GDR, we found a relation Cu : Pb : Zn = 1 : 1.6 : 3.4 in the sediments at the base of the marine Upper Permian (*Zechstein*). This *Kupferschiefer* mineralization contains in the whole area from southeastern England to the western part of the Soviet Union more than 10^9 t of copper, lead, and zinc.

Within the last twenty years, the discovery of new copper rich areas on the southern margin of the *Zechstein* area in Poland and the eastern part of the GDR has greatly stimulated research about the *Kupferschiefer* mineralization. On the basis of a complex interpretation of the results of a large prospecting and exploration drilling program, we now have a much more concrete picture about the problems of the syngenetic, diagenetic, and katagenetic processes which occurred during sedimentation and lithification of the *Kupferschiefer*. In the southern part of the *Kupferschiefer* area in the GDR, the metal and ore mineral distribution in the sediments at the base of the *Zechstein* has been completely mapped. Attention was especially paid to the problem of the immediate neighbourhood of barren red-colored rocks (so-called *Rote Fäule*) and copper ores of economic grade. Geochemical and metallogenetic investigations of the sediments and volcanics of the lower Permian and Silesian red beds that lie under the *Kupferschiefer* gave a better knowledge about the source of metals. These investigations resulted in a much more complicated model of the development of this stratiform sulfide mineralization than was seen before.

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2. GEOLOGY

The *Kupferschiefer* is situated at the base of the marine sediments of the Upper Permian (*Zechstein*) and lies directly upon the clastic continental red bed sediments of the lower Permian. For this reason, it is the oldest sediment of the platform sequence in the variscan folded part of northern Middle Europe. The sedimentation area of the marine sediments of the *Zechstein* sea is located directly south of the East European Platform and in its northern and north-eastern part, it extends over the East European Platform. This area reaches from south-eastern England, the Netherlands, the FRG, and the GDR to Poland and the western part of the Soviet Union. In the northern part of the GDR we find the *Kupferschiefer* upon continental sediments of the lower Permian and Silesian and also upon unfolded old paleozoic sediments with platform character. At the southern border of the *Zechstein* area it is partly overlapping the variscan or pre-Cambrian folded basement. Increased copper, lead, and zinc contents in the sediments at the base of the *Zechstein,* especially in the *Kupferschiefer* were proved only over molasse intra-deeps of the variscan orogen. All copper deposits are restricted to an area above the border between the Rhenohercynian and Saxothuringian zones of the variscan orogen (Richelsdorf-FRG; Mansfeld-Sangerhausen, Lower Lusatia-GDR; North-Sudetic syncline, Pre-Sudetic Syncline-Poland).

The marine sediments of the *Zechstein* are divided into four (Richter-Bernburg, 1955) or five cycles (Reichenbach, 1963) with evaporitic sedimentation. The *Kupferschiefer* and its equivalent sediments of the littoral zone are at the base of the first cycle (Z 1). Each cycle starts with such a pelitic sediment (Z 2, *Stinkschiefer*; Z 3, *Grauer Salzton*; Z 4, *Roter Salzton*; Z 5, *Aleurite*). With the exception of the *Kupferschiefer,* there are no increased metal contents in these pelitic rocks. The *Stinkschiefer* at the base of the second cycle (Stassfurt-cycle) is the mother rock of the *Zechstein* oil and gas deposits.

3. LITHOLOGY AND PALEOGEOGRAPHY OF THE SEDIMENTS OF THE BASAL « ZECHSTEIN » (Z 1)

3.1. Clastic and other Rocks under the « Kupferschiefer »

At the southern margin of the *Zechstein* basin or over tectonic uplifts of the variscan folded basement, there are in some cases crystalline and slightly metamorphosed rocks of the folded basement or late variscan volcanites of the molasse stage directly under the *Kupferschiefer* or the *Zechstein* Limestone. Very often there are intercalations of sedimentary breccias between the *Kupferschiefer* and these rocks. Around the margin of the basin we find a seam of conglomerate rocks which grade into sandstones, sandy aleuritic rocks, and aleurites toward the center of the basin. These clastic rocks consist mostly of redeposited material of the lower Permian. The uppermost meters of the continental red beds of the lower Permian are very often bleached by the *Zechstein* sea. Sometimes redeposited

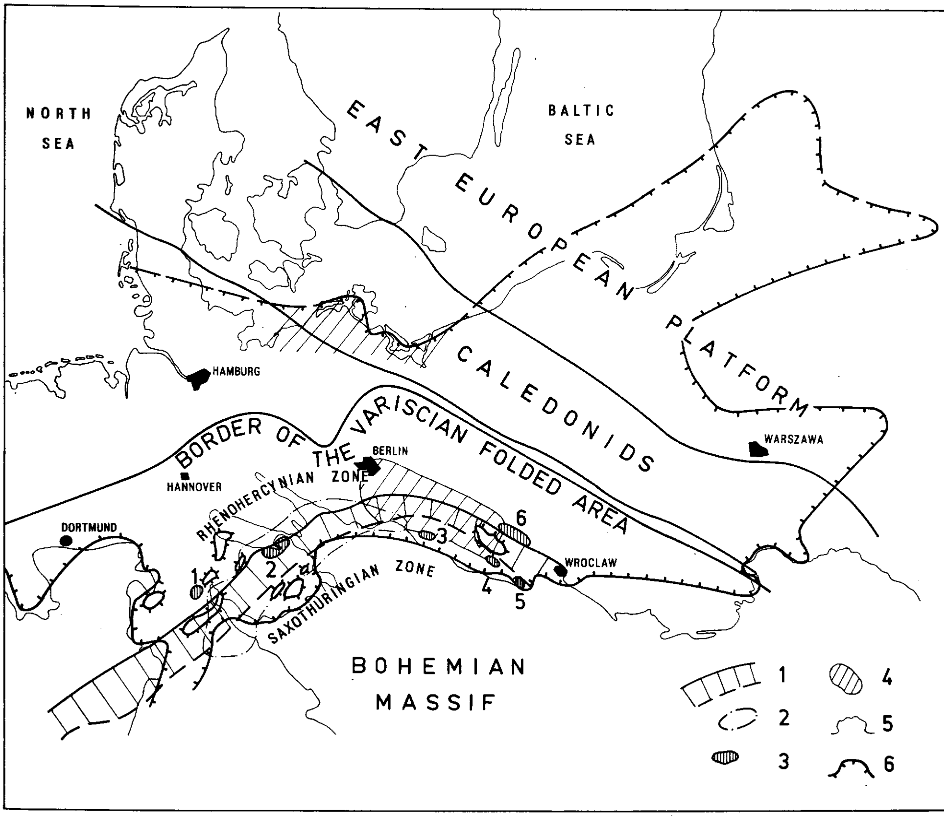

FIG. 1. — *The* Kupferschiefer *area in Central and East Europe. 1, crystalline zone of the Saxothuringian zone; 2, area of the Saale-trough at the end of the Silesian; 3, copper deposits (1, Richelsdorf; 2, Mansfeld-Sangerhausen; 3, Lower Lusatia; 4+5, North Sudetic Syncline; 6, Pre-Sudetic Syncline); 4, large areas with* Rote Fäule *facies; 5, precenozoic outcrop of the variscan folded basement; 6, area of the* Kupferschiefer.

sediments are of a primary grey color. The carbonate content of the matrix of the clastic rocks increases toward the *Kupferschiefer.*

In very shallow lagoonal environments or over the mentioned uplifts of the basement, there are thin layers of a carbonate rock (basal limestone) under the *Kupferschiefer.* In this carbonate rock the content of clastic components decreases toward the *Kupferschiefer.* In the area of copper deposits and barren red colored rocks at the base of the *Zechstein,* the sandstones are very often deposited as shallow marine sandbars of different sizes (Kurze, 1961; Prior, 1971; Haranczyk, 1972). In former times, these sandbars were thought to be eolian and, in the deposit of Mansfeld, they were called dunes (Meinecke, 1910; Gillitzer, 1936). The average composition of the main constituents of the clastic and carbonate rocks is given in table 1. The analyses were made only of the uppermost decimeters which are sulfide-bearing. The average carbonate content of the sandstones in the Pre-Sudetic Syncline is 8 % (Haranczyk, 1972).

TABLE 1

Rock	Silic. %	Calc. %	Dol. %	Total carb. %	Analysed thickn. cm	No. of analyses
Conglomerate	67.3	8.3	11.1	19.4	24.5	20
Sandstone	74.4	9.7	7.4	17.1	24.3	24
Sandy aleurite	62.0	6.1	15.2	22.5	26.2	36
Carbonate rock	17.6	12.8	59.8	72.6	26.4	22

The silicates consist of rock fragments, quartz, and feldspars. In addition to the mentioned main constituents, the rocks contain sulfates, organic carbon, sulfides, and accessory minerals. The carbonate (and sulfate) matrix is replacing in part the clastic components like rock fragments, feldspars, and even quartz. Authigenic minerals are mainly quartz and albite.

The sulfide-bearing clastic rocks are called *sand ore*. The sulfides replace the carbonate (and sulfate) matrix and such parts of the clastic components that were replaced earlier by carbonates and sulfates (Ludwig and Rentzsch, 1967). In the sulfide-bearing clastic rocks there are many sulfide (and arsenide) metacrysts. Haranczyk (1972) holds the opinion that there are two types of sulfide mineralization in the clastic rocks. The first type is said to be early diagenetic and the second to belong to a later infiltration stage of downward moving solutions which originated in the sediments of the *Kupferschiefer.*

3.2. « Kupferschiefer » (« Kupfermergel » in the North Sudetic Syncline in Poland)

The term *Kupferschiefer* (or *Kupfermergel*) is a synonym for the lithostratigraphic unit which was deposited in the *Zechstein* sea between the above mentioned clastic or carbonate rocks and the overlying *Zechstein* limestone. There is no real possibility to divide between the *Kupferschiefer* and the *Kupfermergel* facies. The composition of this lithostratigraphic unit changes dependent on the paleogeographic position from sulfide-bearing, coaly bituminous claystones to clay-bearing carbonate rocks (Table 2, fig. 2). This is valid for single samples of these rocks and also for complete profiles of the *Kupferschiefer*. The average composition of these profiles was calculated under consideration of the contents and thicknesses of the single samples. Typical features of these rocks are the organic substance and the changing contents of sulfides. The nomenclature of the rocks is modified after Füchtbauer (1959) and Haranczyk (1964).

The layers which are poor in carbonates consist of a black foliated shale; the carbonate rich layers consist of a platy shale. The lower contact against the clastic rocks is very clear. The upper contact against the rocks of the *Zechstein* limestone is sometimes hardly visible. The most characteristic feature is the end of the lamination of the rocks at the upper contact of the *Kupferschiefer.*

The thickness of the *Kupferschiefer* horizon varies between a few centimeters and about 2 meters. The average thickness ranges between 30 cm and 60 cm. The *Kupferschiefer* consists of three lithologic rhythms. Each rhythm starts with a

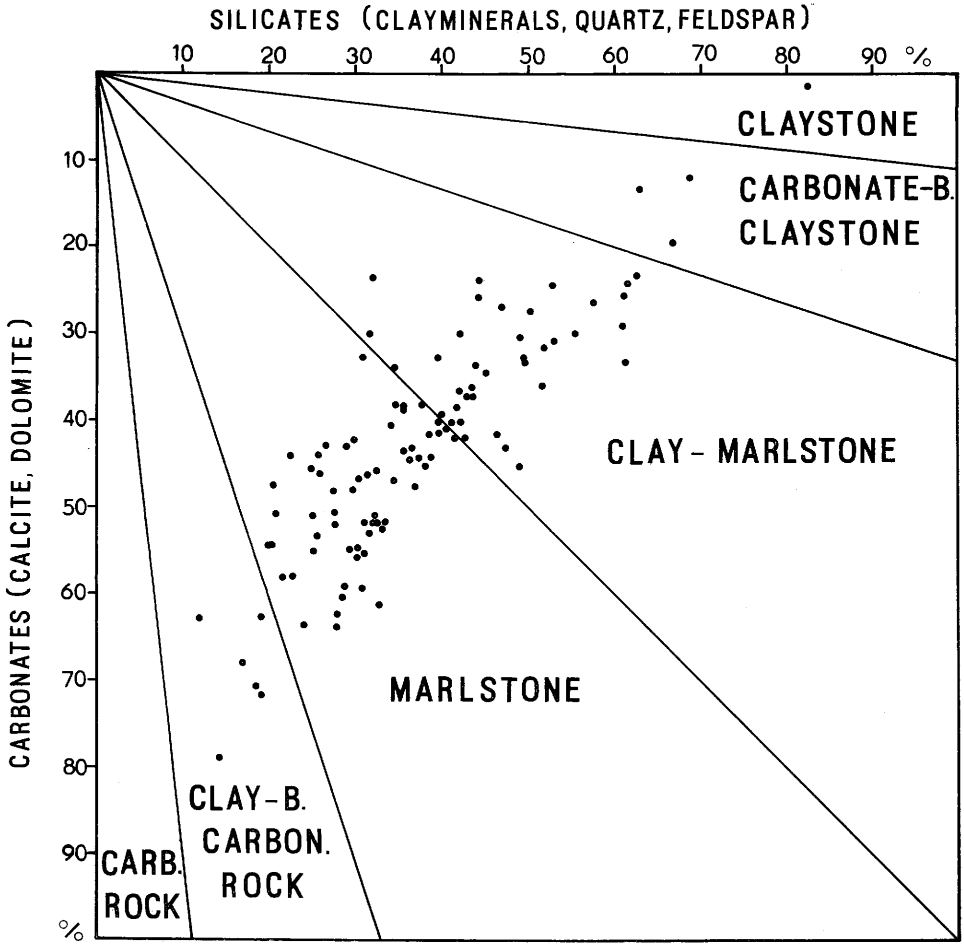

FIG. 2. — *Rock types of the* Kupferschiefer *(each point represents a complete profile).*

high clay and detritus content. The carbonate content increases in the upward direction (Siegert, Tzschorn and Winkler, 1963; Luge, 1965; Rentzsch, 1965*b*). This lithostratigraphic subdivision does not correlate exactly with the old subdivision of the *Kupferschiefer* in the area of Mansfeld (Feine Lette, Grobe Lette, Kammschale, Schieferkopf, Schwarze Berge). This old subdivision was made partly on the basis of diagenetic partings.

The quartz content of the *Kupferschiefer* ranges from 4 % (clay-bearing carbonate rocks) to 18 % (clay-marlstones), which means that 20-36 % of the silicates are represented by quartz. The main clay mineral is illite (18-27 % at Mansfeld after Ludwig, 1959). Chlorite is also very frequent, but kaolinite is rarely found (Wedepohl, 1964). In illite-bearing rocks there is a relation $Al_2O_3 : SiO_2 = 1 : 2.5$ (Haranczyk, 1964). In a lagoonal environment in the Pre-Sudetic Syncline, the same author found a lead-bearing *Kupferschiefer* with mixed layer clay minerals

TABLE 2. — *Composition of the rocks of the* Kupferschiefer (own data and WEDEPOHL, 1964)

Rock	Thickness cm	Silic. %	Calc. %	Dolom. %	Total carbon. %	C_{org} %	No. of profiles	No. of analyses
Claystone	8.0	82.5	0.0	1.5	1.5	9.0	1	1
Carbonate-bear. claystone	25.0	67.3	12.4	4.7	17.1	6.3	3	3
Clay-marlstone	38.6	47.0	12.7	20.9	33.6	5.0	36	246
Marlstone	73.9	30.9	25.3	23.5	48.8	3.8	61	618
Clay-bearing carbonate-rock	95.4	17.1	23.6	44.9	68.5	2.7	6	61

of the montmorillonite-illite group. The sedimentation of the *Kupferschiefer* is strongly dependent on the paleogeographical situation of the *Zechstein* sea. Rentzsch, Tischendorf, Ungethuem and Pilot (1973) prove a negative correlation between the thickness of the *Kupferschiefer* and its contents of silicates and organic carbon (fig. 3). A positive correlation is observed between the thickness and the carbonate content. Carbonate rich *Kupferschiefer* with a thickness of more than 0.4 m is deposited in shallow water areas while *Kupferschiefer* rich in silicates and organic carbon with a thickness less than 0.4 m is generally deposited in deeper parts of the basin. In marginal lagoons with a high salinity, gypsum precipitated instead of the carbonates in the *Kupferschiefer*. In near shore areas or over tectonic uplifts of the basement, calcite predominates among the carbonates of the *Kupferschiefer*. In the center of marginal basins or lagoons, dolomite is the main carbonate mineral. In the central parts of the *Zechstein* basin the relation calcite/colomite changes. The *Kupferschiefer* contains many microfossils (foraminifera, ostracods, etc.) in areas where it is deposited under very shallow water conditions.

The organic substance consists of saprovitrinite and exinite (Kaemmel, 1965). Its composition ranges from 85 % kerogen and 15 % soluble bitumen to 97 % kerogen and 3 % soluble bitumen (Palmberg, 1964). A small part of the organic substance originates from plants and fishes. The carbonification of the organic substance of the *Kupferschiefer* is higher in the copper deposits than in the areas with lead-zinc mineralization.

The sulfide mineralization of the *Kupferschiefer* and its adjacent rocks in their present form is fixed in the diagenetic and katagenetic stage of lithification. All the textures of the ore minerals are not really syngenetic sedimentary, they are of diagenetic or later origin. Pyrite is, in part, the oldest diagenetic sulfide mineral (*mineralized bacteria*, etc.). All the other ore minerals are younger than the diagenetic recrystallization of the carbonates and are replacing the carbonates and the early diagenetic pyrite (Schouten, 1937; Neuhaus, 1941; Kaemmel, 1965; Rentzsch and Knitzschke, 1968). Haranczyk (1972) distinguishes between a primary syndiagenetic ore mineralization and a secondary diagenetic mineralization. This is possible in the case of the pyrite, however, the formation of the copper, lead, and zinc sulfides during the stages of lithification is one single process which cannot be divided.

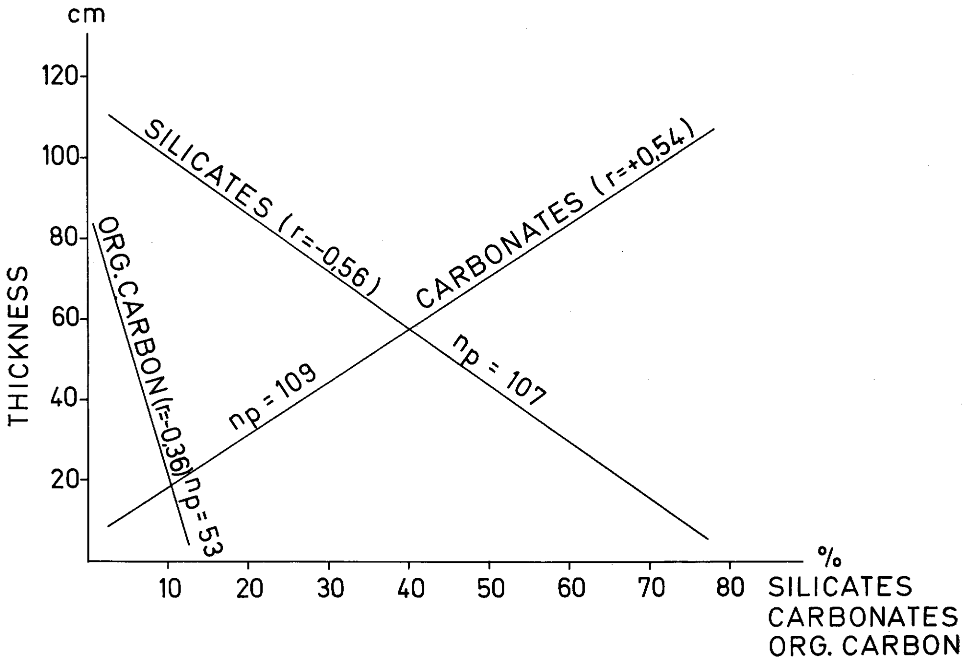

FIG. 3. — *Correlation thickness* Kupferschiefer/*silicate content, thickness* Kupferschiefer/ *carbonate content, thickness* Kupferschiefer/C_{org} *content. After Rentzsch, Tischendorf, Ungethuem and Pilot (1973). np = number of profiles.*

3.3. "Zechstein Limestone" (Hangingwall-rock of the "Kupferschiefer")

The *Zechstein Limestone* represents the maximum extension of the *Zechstein* sea. Its thickness varies from 3 to 6 m in the center of marginal basins or in central parts of the *Zechstein* basin and from 6 to 152 m in the marginal parts of the basin or over tectonic uplifts of the folded basement. Areas with a thickness larger than 10 m are very restricted. At some places along the southern margin of the *Zechstein* basin there are reefs. However, these reefs do not always represent only the *Zechstein Limestone.* In such cases, they include parts of the *Werra Anhydrite.* In marginal basins and lagoons dolomite predominates. Calcite rich carbonate rocks are deposited in shallow water areas with low salinity. In the central part of the basin dolomitic limestones are deposited. A high anhydrite content of the dolomitic carbonate rocks is characteristic for shallow water areas upon sandbars, tectonic uplifts of the basement, or in closed lagoons as an indication of increased salinity. A lithostratigraphic subdivision of the basin type *Zechstein Limestone* is given by Jankowski and Jung (1962). It is possible to compare the basin profiles with the marginal ones (Jung, 1968).

Normally, the rocks of the *Zechstein Limestone* have a light grey color. Dependent on the content of the organic carbon, the color changes to dark grey. The problem of the locally occurring rocks with red stains and streaks will be discussed later. The composition of the rocks is studied on a regional scale only in the lowermost decimeters of the *Zechstein Limestone* (Table 3).

TABLE 3. — *Composition of the rocks of the basal parts of* Zechstein Limestone (data from WEDEPOHL, 1964 and from the author)

Rock	Silic. %	Calc. %	Dol. %	Total carbon. %	C_{org} %	No. of profiles	No. of analyses
Carbonate- bear. claystone	61.8	7.9	9.9	17.8	([a])	1	2
Clay-marlstone	48.2	12.6	23.1	35.7	0.7	14	27
Marlstone	31.0	37.7	21.9	59.6	0.3	29	61
Clay-bearing carbonate rock	17.7	26.6	47.2	73.8	1.0	8	23
Carbonate rock	5.9	25.2	63.6	88.8	([a])	4	9

(*a*) Not analyzed.

The composition of these rocks varies very little from those of the *Kupferschiefer.* Only the C_{org} and sulfide contents are lower, and the texture is different.

The silicates consist of the same components as in the *Kupferschiefer.* The quartz content ranges from 4 to 21 %, which means 28 to 48 % of the silicates are formed by quartz. Sandstone layers with a thickness up to 0.5 m are locally deposited in the *Zechstein Limestone.* The sulfate content of the *Zechstein Limestone* is mentioned above. Fluorite and celestite occur rarely. The sulfide mineralization most often occurs in the form of pyrite concretions, which are replaced by copper, lead, or zinc sulfides or in katagenetic fissures. Only in the marly layers are there the same ore textures as in the *Kupferschiefer.*

3.4. Rote Fäule

One of the most important features of the basal sediments of *Zechstein* is the occurence of barren red colored rocks. They were first observed in the mining area of Mansfeld in a layer near to the base of *Zechstein Limestone* called *Fäule.* For this reason, this facies type in the basal sediments of the *Zechstein* are called *Rote Fäule* facies. In the North Sudetic Syncline, the red stained rocks occur in a sequence of basal limestone, marls, and limestone layers immediately under the copper-bearing rocks (Eisentraut, 1939; Konstantynowicz, 1964). These red stained marls do not represent a lithostratigraphic unit. The upper border of the red colored rocks goes up and down in the lithologic sequence between the sandstone, basal limestone, and the copper-bearing marl (Konstantynowicz, 1964; Krason, 1964). Red colored rocks also lie directly under the copper-bearing sandstone, *Kupferschiefer,* and basal parts of the *Zechstein Limestone* in Lower Lusatia (Franz, 1965; Rentzsch and Langer, 1963). Freese and Jung (1965) describe four cycles of red colored rocks in the area of Mansfeld-Sangerhausen in the sequence between sandstone, *Kupferschiefer, Zechstein Limestone*, and the basal part of *Werra Anhydrite*. The copper ores of economic grade lie directly upon the first cycle of red colored rocks (sandstone, *Kupferschiefer*, and the basal part of *Zechstein Limestone*). The angle of the diagonal crossing of the facies border between the dark sapropelitic rocks of the *Kupferschiefer* and the so-called *Rote Fäule* facies is always less than 1° in Mansfeld-Sangerhausen and Lower Lusatia.

Areas with barren red colored rocks at the basal parts of the *Zechstein* were discovered in, or immediately beneath, the copper deposits near the southern margin of the *Kupferschiefer* area (Richelsdorf, Mansfeld-Sangerhausen, South Brandenburg-Lower Lusatia-Dolny Slask). In Mansfeld-Sangerhausen, a single area has a size from some thousand m^2 to some km^2. The immense area between South Brandenburg and Dolny Slask encloses more than 10 000 km^2. The northern margin of the *Kupferschiefer* area is accompanied by a large area with *Rote Fäule* facies, but it shows no copper enrichment of economic grade at the border against the sapropelitic rocks. The red colored rocks are not restricted to the shoreline of the *Zechstein* sea. The only exceptions are the areas at the northern margin and in the North Sudetic Syncline. All transversal layered sandbars at the base of the *Zechstein* are situated in, or in the neighbourhood of, red colored rocks. In some parts of the *Rote Fäule* facies, a high content of detritus (grain size 100-600 μm) is observed in the *Kupferschiefer* and in the *Zechstein Limestone* (Rentzsch, 1965*a*; Rydzewski, 1965). The calcite content in the *Kupferschiefer* increases in the direction of the *Rote Fäule* facies. Glauconite is observed at the border between sapropelitic and red colored rocks (Rydzewski, 1965). In South Brandenburg there are slumpings in the red colored *Zechstein Limestone* (Erzberger, 1965). The red colored rocks are partly more fossiliferous than the grey ones. The C_{org} content of the *Kupferschiefer* decreases toward the *Rote Fäule* facies and, therefore, its color changes from black to light grey at the margin and sometimes to red in the center of the areas with red colored rocks. Freese and Jung (1965) distinguish two types of red colored rocks. In the first type the red stains and streaks are stratabound whereas, in the second type, the red colors are limited on the surrounding of diagenetic or katagenetic fissures and veinlets. In the first type they observed red points, stains, clouds, streaks, and ribbons.

4. ORE MINERALIZATION OF THE ROCKS AT THE BASE OF THE "ZECHSTEIN"

4.1. Ore Minerals

The stratiform sulfide mineralization of the basal rocks of the *Zechstein* consists commonly of α-chalcocite, bornite, chalcopyrite, tennantite, galena, sphalerite, pyrite, and marcasite. Digenite, covellite, native silver, stromeyerite, acanthite are rare or extensively distributed (Schneiderhöhn, 1921; Hoffmann, 1924; Schouten, 1937). Knauer (1960) observed idaite and Langer (1963) bravoite. Rentzsch and Knitzschke (1968) described extensively distributed arsenopyrite and some occurrences of enargite, linneite, millerite, and pyrrhotite. By use of a microanalyser, Haranczyk (1972) proved djurleite, vaesite, rammelsbergite, nicollite, smalthite, maucherite, skutterudite, safflorite, cobaltian loellingite, and cobaltite. Enargite, bravoite, vaesite, and the nickel-cobalt arsenides are restricted to the bottom sandstones. The author observed very scarce molybdenite at the top of the sandstones. From the contact sandstone-*Kupferschiefer*, Haranczyk described delafossite, cuprite, tenorite, cerussite, smithonite, and goethite. Knauer (1960) found traces of anglesite.

The red color of the rocks in the *Rote Fäule* facies is produced by hematite or hydrohematite. In these rocks there are rare occurrences of magnetite.

In some epigenetic veins (so-called *Mansfelder Rücken*) cutting the sediments of the *Zechstein* base in the mining areas of Richelsdorf, Mansfeld-Sangerhausen, and in the Pre-Sudetic Syncline (Kautzsch, 1953; Messer, 1955; Schueller, 1959, and Haranczyk, 1972), there are, together with quartz, barite, anhydrite, fluorite, strontianite, and calcite, the following ore minerals: nicollite, rammelsbergite, pararammelsbergite, maucherite, safflorite, skutterudite, chloanthite, native bismuth, native silver, acanthite, stromeyerite, jalpaite, betechtinite, wittichenite, molybdenite, pitchblende, clausthalite, α-chalcocite, bornite, covellite, chalcopyrite, tennantite, tetraetrite, arsenopyrite, vaesite, cattierite, bravoite, millerite, pyrite, marcasite, galena, sphalerite, and goethite.

4.2. Associations of the Ore Minerals

Ten associations of ore minerals are observed by Rentzsch and Knitzschke (1968) in the sulfide-bearing rocks at the *Zechstein* base. They distinguish a hematite type, a covellite-idaite type, a chalcocite type, a bornite-chalcocite type, a bornite type, a bornite-chalcopyrite type, a chalcopyrite-pyrite type, a galena-sphalerite-chalcopyrite type, a galena-sphalerite type, and a pyrite type.

The hematite type is the typical association of the barren *Rote Fäule* facies. Hematite occurs in dispersions and pseudomorphic after pyrite. Locally there are pseudomorphs of magnetite after pyrite. The covellite-idaite type is only of local importance. There is no copper deposit without a chalcocite or bornite-bearing sulfide association. Associations with chalcopyrite as the main copper mineral are only exceptionally of economic grade (border of the *Rote Fäule* facies). The most frequent associations are those with dominant galena and/or sphalerite and the pyrite type. The sulfides have a very small grain size. One part of the mineralization is submicroscopic (Haranczyk, 1972), a large part occurs in small lenses from 20 μm to 100 μm diameter (*Speise*), another part in the form of larger aggregates or horizontal nebulite veins (*Erzlineale*), etc.

5. GEOCHEMISTRY OF THE MINERALIZED ROCKS AT THE "ZECHSTEIN" BASE

5.1. Geochemistry of the Ore Elements Copper, Lead, Zinc, and Silver

The contents of the elements copper, lead, zinc, and silver in the investigated lithologic sequence vary extremely. On a local scale, the silicate and C_{org} rich rock types have higher contents of these elements than the carbonate rich, but on a regional scale, the metal contents of the clastic rocks, the rock types of the *Kupferschiefer* and the basal part of the *Zechstein Limestone* are independent of rock composition (Table 4). The given data is not representative of a single area, it characterizes the rock types only on a regional scale. The enrichment factors defined as the ratios content *Kupferschiefer*/average content black shale (Table 5) (Vine and Tourtelot, 1970) vary between 0 and ~15 000 for copper, between 0 and ~5 000 for lead, and between 0 and ~500 for zinc. A very detailed study was published by Knitzschke (1966) about the mineralization of the *Kupferschiefer* of Mansfeld-Sangerhausen. He found a rather good correlation between lead and zinc in the investigated rocks. This correlation is of local character. A good correlation exists between copper and silver (Knitzschke, 1966; Rentzsch, Tischendorf, Ungethuem, and Pilot, 1973). The copper-silver correlation obviously represent the differences in the metal supply in the different parts of the *Kupferschiefer* area (fig. 4). Copper, lead, zinc, and silver are concentrated in the mentioned

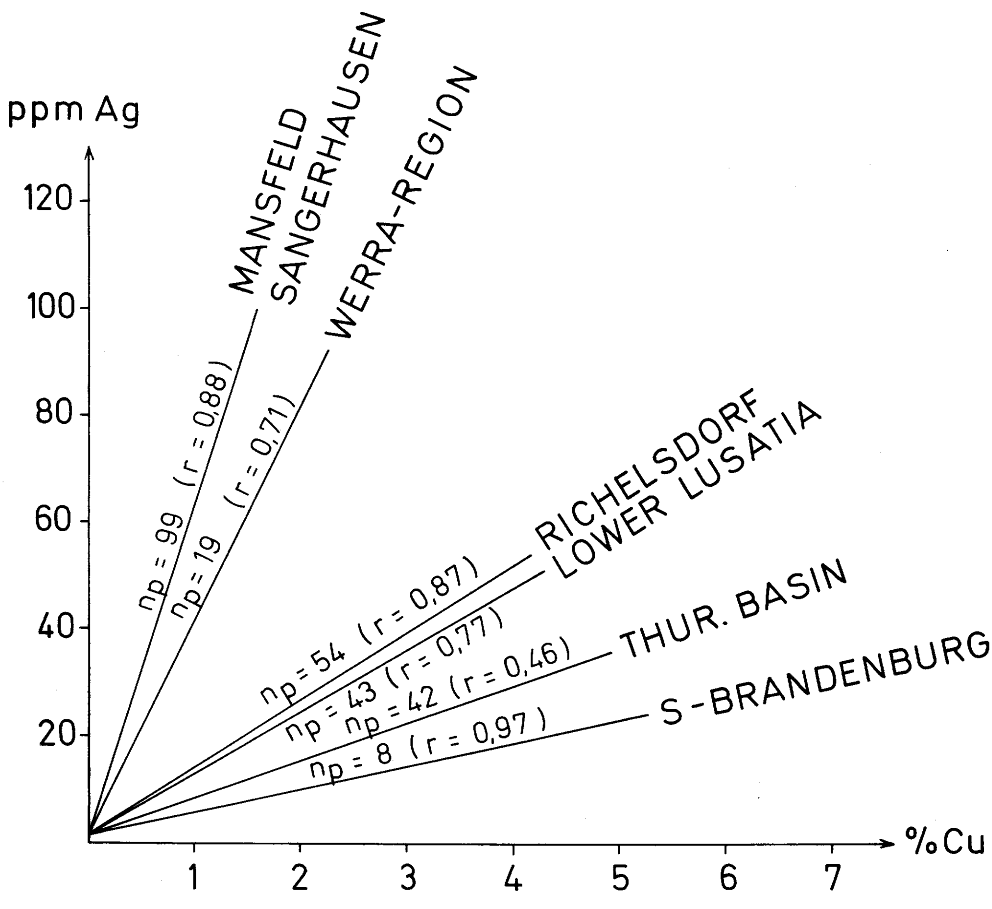

FIG. 4. — *Correlation between* Cu *and* Ag *in different* Kupferschiefer *areas. After Rentzsch, Tischendorf, Ungethuem and Pilot (1973). np = number of profiles.*

sulfides. Silver occurs also as native metal. In the sulfides, it is mainly concentrated in chalcocite and bornite and, in a smaller amount, also in galena (Knitzschke, 1966, Haranczyk, 1972).

5.2. Geochemistry of some Trace Elements

64 elements were identified in the *Kupferschiefer*. Besides Cu, Pb, Zn, and Ag, the following are produced from the Mansfeld-Sangerhausen ores: V, Pt, and allied elements, Se and Au. In former times, there was also a production of Mo, Ni, Re, Ge, and Cd. The elements V, Mo, Ni, Co, etc. show a clear correlation with rock composition and C_{org} content of the *Kupferschiefer* (fig. 5). Wedepohl (1964) and Haranczyk (1972) found that V and Mo are concentrated in the organic substance. An adsorptive fixation to clay minerals is also possible. Traces of molybdenite were only identified in the bottom sandstones. Nickel and cobalt are partly fixed in the organic substance, partly in the sulfides and the arsenides. The contents of the elements V, Mo, Ni, and partly Co are in the normal range of metal enriched black shale (Table 5). Se is fixed in the organic substance of the *Kupferschiefer*. There exists a good correlation between C_{org} and Se (Jung, Knitzschke,

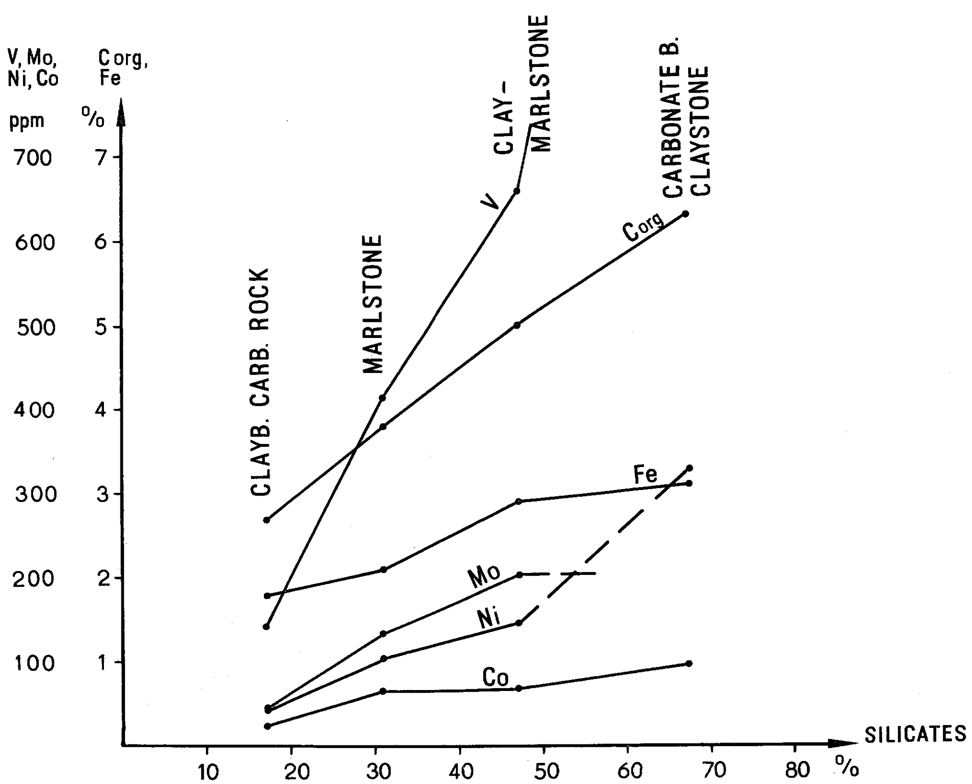

FIG. 5. — *Correlation between the rock types of the* Kupferschiefer *and the* C_{org}, Fe, V, Mo, Ni, *and* Co *content.*

and Gerlach, 1973). As is fixed in the sulfides arsenopyrite, enargite, and tennantite both in the *Kupferschiefer* and the *sand ore*. In the *sand ore* of the Pre-Sudetic Syncline, it is also concentrated in the arsenides (Haranczyk, 1972). The average As content of the *Kupferschiefer* ranges between 50 ppm and several hundred ppm and, in the *sand ore,* it is concentrated up to 5 000 ppm. According to Wedepohl (1964, 1971) and Haranczyk (1972), Mn is concentrated in the carbonates (up to 0.6 % Mn in the *Kupferschiefer,* up to 0.8 % in the carbonate rocks).

TABLE 4. — *Metal contents of the basal parts of the* Zechstein

Rock	Fe %	Cu %	Pb %	Zn %	Ag ppm	V ppm	Mo ppm	Ni ppm	Co ppm	
Carbonate-bear. claystone	2.2	0.18	0.01	0.03	([a])	79	([a])	30	5	*Zechstein Limestone*
Clay-marlstone	2.3	0.04	0.17	0.15	([a])	91	8	38	13	
Marlstone	1.8	0.09	0.16	0.10	([a])	54	6	45	12	
Clay-bear. carbonate rock	1.4	0.01	0.19	0.10	([a])	([a])	([a])	22	18	
Carbonate rock	1.1	0.01	0.07	0.05	([a])	([a])	([a])	7	4	
Claystone	6.5	1.70	0.15	0.00	([a])	2 000	550	430	160	*Kupfer-schiefer*
Carbonate-bear. claystone	3.1	0.02	0.75	1.76	([a])	1 640	204	328	95	
Clay-marlstone	2.9	0.53	0.31	0.66	6	559	203	146	66	
Marlstone	2.1	0.44	0.52	0.77	7	413	134	104	64	
Clay-bearing carbonate rock	1.8	0.03	0.23	0.83	2	142	43	40	24	
Conglomerate	3.1	0.30	0.18	0.14	3	46	15	34	54	*Sand ore*
Sandstone	1.9	0.36	0.15	0.15	6	51	39	45	55	
Sandy aleurite	4.2	0.35	0.11	0.29	3	138	36	66	82	
Carbonate rock	2.9	0.03	0.07	0.11	0,5	27	3	25	13	

([a]) Not analyzed.

TABLE 5. — *Metal content of average black shale* (VINE and TOURTELOT, 1970)

C_{org}	3.2 %	Ag	< 0.0001 %
Fe	2.0 %	V	0.015 %
Mn	0.015 %	Mo	0.001 %
Cu	0.007 %	Ni	0.005 %
Pb	0.002 %	Co	0.001 %
Zn	< 0.03 %		

5.3. Geochemistry of Iron

Until now, the geochemistry of iron in the rocks of the *Zechstein* base has not been studied. According to Wedepohl (1971), the iron content of the different rock types of the *Kupferschiefer* and the basal part of the *Zechstein Limestone* is the same as that of nonbituminous marls and shales. For this reason, the iron content is of detrital origin and/or was bound to the clay minerals. Now the iron of the sapropelitic *Kupferschiefer* is located in the carbonates ($\sim$15 % of the total Fe), the oxides ($\sim$1 % of the total), and the silicates (40-50 % of the total). The rest, i.e. about 35-45 %, is now located in pyrite (pyrrhotite), bornite, chalcopyrite, etc. According to Haranczyk (1972), 80 % of the iron in the *Kupferschiefer* of the deposit in the Pre-Sudetic syncline is concentrated in the sulfides.

In the basal parts of the *Zechstein Limestone* the carbonates contain 20-35 % of the total iron, the oxides 2-4 %, the silicates 40-50 %, and the sulfides 10-40 %. The iron content of the sulfide-bearing rocks at the base of the *Zechstein* (*sand ore* = 2.34 %; *Kupferschiefer* = 2.24 %; *Zechstein Limestone* = 1.97 %) is higher than in the barren red colored rocks (sandstone = 1.84 %; *Kupferschiefer* = 1.98 %; *Zechstein Limestone* = 1.71 %). In the *Kupferschiefer* of the marginal parts of the *Rote Fäule* facies, 27 % of the total iron is located in carbonates, 3.5 % in oxides, 10-30 % in sulfides, and 30-50 % in silicates. It is evident that the content of hematite in the rocks of the *Rote Fäule* facies is very low. The ratio Fe^{2+}/Fe^{3+} in the marginal parts of the *Rote Fäule* facies is 7 to 14.5 (basal part of the *Zechstein Limestone*) and 28.2 (*Kupferschiefer*). In the sulfide-bearing rocks in the neighbourhood of the *Rote Fäule* facies the ratio Fe^{2+}/Fe^{3+} is 23 to 58 (basal part of the *Zechstein Limestone*) and 92.5 (*Kupferschiefer*). A minimum iron content is fixed in the copper rich chalcocite and covellite + idaite associations with 0.95 % of iron in the *Kupferschiefer*.

5.4. Geochemistry of C_{org}

The average C_{org} contents of the rock types in the reducing environment at the base of the *Zechstein* are given in tables 2 and 3. The average C_{org} content of the rocks of the *Rote Fäule* facies is 1.7 % in the *Kupferschiefer* and 0.1 % in the basal part of the *Zechstein Limestone*. This means that the C_{org} content of the rocks decreases in the direction to the *Rote Fäule* facies. The carbonification of the organic substance increases in the same direction (Palmberg, 1964) (fig. 6). Whereas the carbonification of the organic substance in the lead-zinc-bearing rocks of the *Kupferschiefer* is nearly the same over the whole thickness of the rock (H/C = 0.75-1.3), the carbonification of the organic substance in the copper-bearing rocks in the neighbourhood of the *Rote Fäule* facies decreases from the bottom to the top of the *Kupferschiefer*. In this direction, the relation H/C of the kerogen ranges from 0.43-1.2.

Commonly, there is no linear correlation between Cu and C_{org}. This correlation exists only in such areas where the saturation of S^{2-} by copper is perfect (Haranczyk, 1972). Also, the correlation between Cu + Pb + Zn and C_{org} is only a local one. In the Pre-Sudetic Syncline there exists a common correlation between C_{org} and S^{2-}. The correlation between the rock composition of the *Kupferschiefer*, C_{org}, iron, and some trace elements is shown in figure 5.

5.5. Geochemical Facies

The organic substance of the *Kupferschiefer* is of sapropelitic origin. This is shown by the C/N ratio in the organic substance. In the sulfide-bearing rock types,

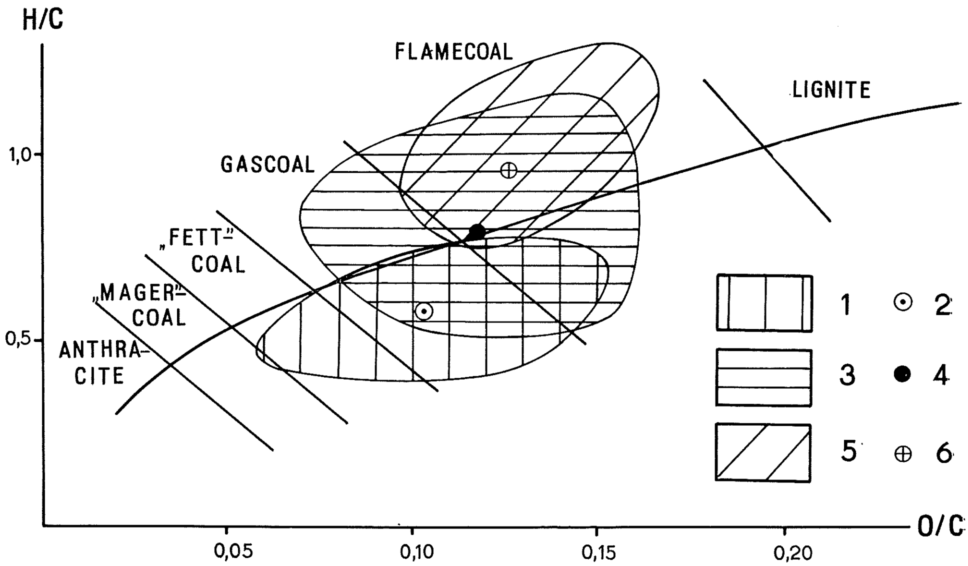

FIG. 6. — *Carbonification of the kerogen of the* Kupferschiefer *in different types of mineralization. Data from Palmberg (1964). 1,* Rote Fäule *facies; 2, average of 1; 3,* Cu *type of mineralization; 4, average of 3; 5,* Pb-Zn *type of mineralization; 6, average of 5.*

this ratio varies from 22 to 47 and, in the *Rote Fäule* facies, from 22 to 29. According to Krejci-Graf and Borchert (1959) the C/N ratio is between 20 to 30 in the sapropelitic facies and between 70 to 350 in the gyttja facies.

Haranczyk (1972) used the ratios S^{2-}/S^{6+} and Cu/S to construct redox maps of the deposit of the Pre-Sudetic Syncline, but the ratio S^{2-}/S^{6+} is possibly not a redox indicator if the grade of evaporation is high. Jung, Knitzschke and Gerlach (1973) try to use the relation Se/S^{2-} as a redox indicator. This is not possible for Se is fixed in the organic substance and not in the sulfides.

6. METAL AND MINERAL DISTRIBUTION AT THE BASE OF THE "ZECHSTEIN"

There exists a clear ore controlling lateral and vertical zonation around the red colored rocks (*Rote Fäule* facies). The normal transgressive zonation is Fe^{3+}—Cu—Zn—Fe^{2+}, which means hematite type—chalcocite type—bornite type—chalcopyrite pyrite type—galena-sphalerite type—pyrite type. This zonation crosses the contacts of the different rock types (figs. 7, 8, 9). For the most part, copper ores of economic grade now occur in the basal part of *Zechstein Limestone*, in the *Kupferschiefer,* and in the *sand ore* (figs. 10, 11, 12). This zonation has been used for a long time for the planning of prospecting and exploration works (Gillitzer, 1936; Richter-Bernburg, 1941; Kautzsch, 1942; Erzberger a. o., 1968). It is, for the most part, not orientated toward the shoreline. The ore enrichments occur offshore, but

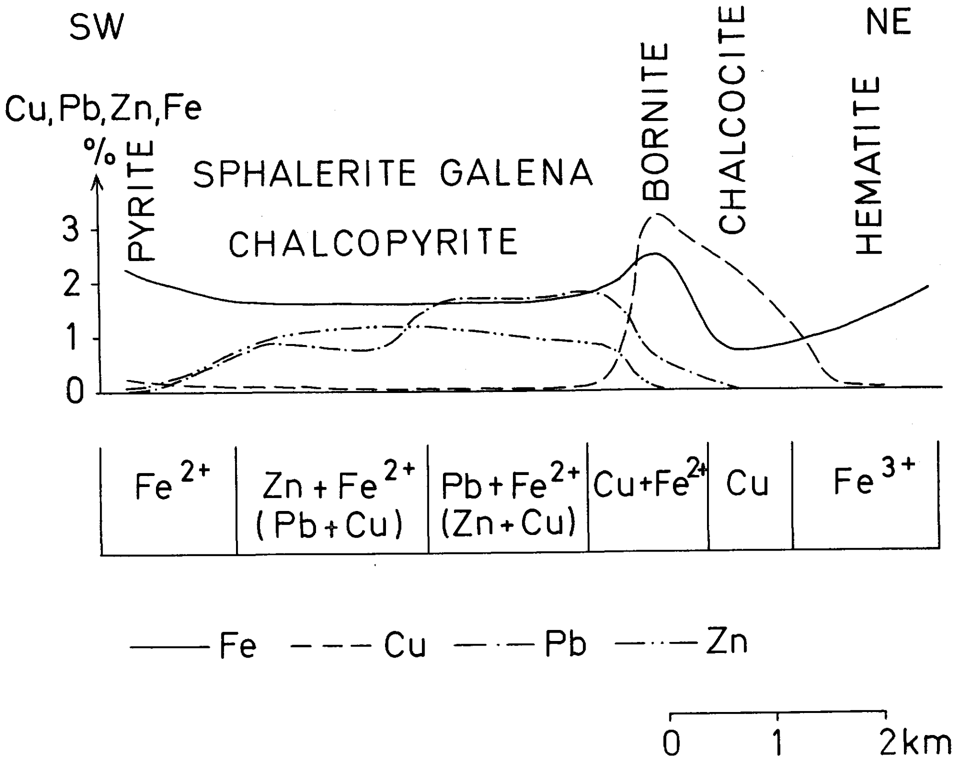

FIG. 7. — *Zonation of the diagenetically influenced mineralization of the* Kupferschiefer. *After Rentzsch, Tischendorf, Ungethuem and Pilot (1973).*

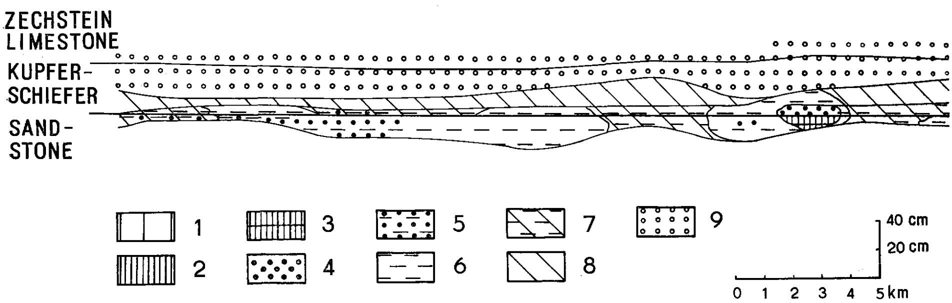

FIG. 8. — *Distribution of the mineral associations in the basin type of the* Kupferschiefer. *After Rentzsch and Knitzschke (1968). 1, hematite type; 2, chalcocite type; 3, bornite chalcocite type; 4, bornite type; 5, bornite chalcopyrite type; 6, chalcopyrite pyrite type; 7, galena sphalerite chalcopyrite type; 8, galena sphalerite type; 9, pyrite type.*

at different distances from the shore around the areas where the *Rote Fäule* facies exists above the margins of the intraorogenic molasse depressions.

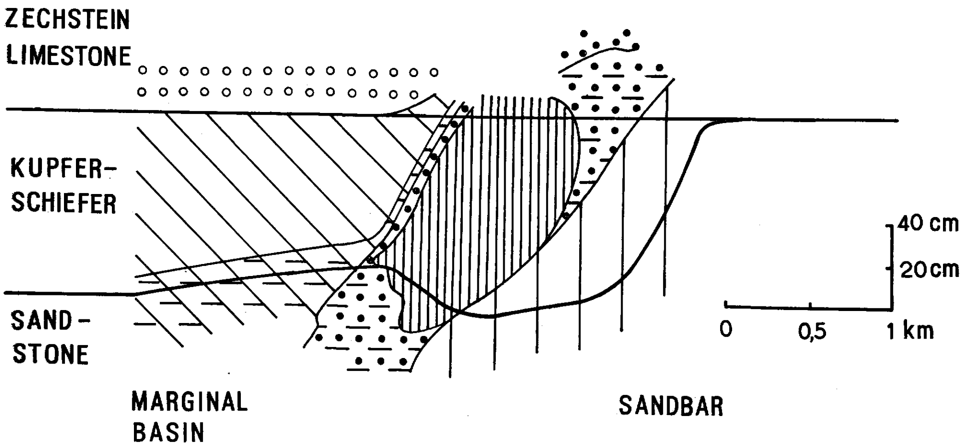

FIG. 9. — *Distribution of the mineral associations of the* Kupferschiefer *at the boundary of an area with the* Rote Fäule *facies after Rentzsch and Knitzschke (1968) (legend, see fig. 7).*

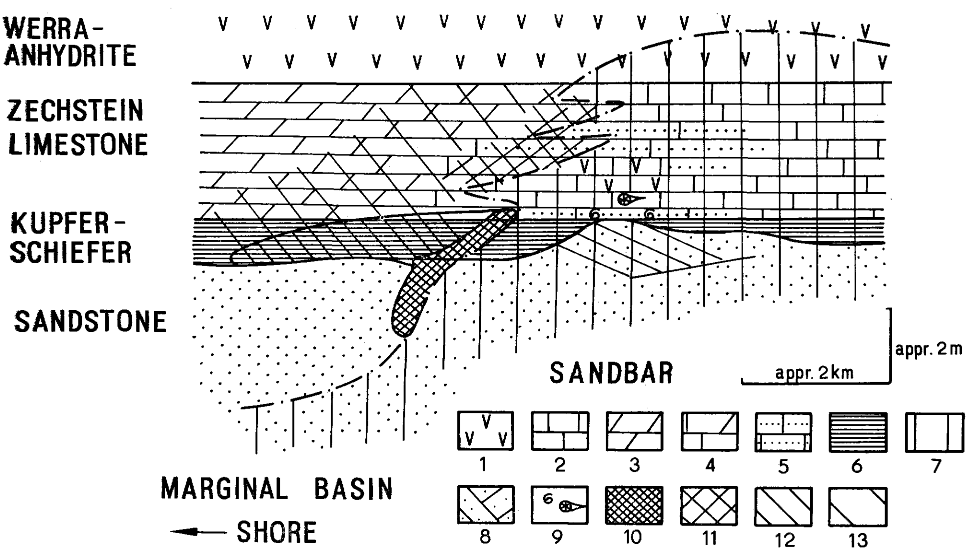

FIG. 10. — *Schematic section of the boundary between reducing environment and* Rote Fäule *facies in the basal part of the* Zechstein. *1, anhydrite; 2, limestone; 3, dolomite; 4, dolomitic limestone; 5, sand layers in limestone; 6,* Kupferschiefer; *7,* Rote Fäule *facies; 8, sandstone, transversal layered; 9, macrofossils; 10,* Cu *ore of economic grade; 11,* Cu *mineralization; 12,* Pb-Zn *ore; 13,* Pb-Zn *mineralization.*

7. GENETIC REMARKS

The discussion about the source of the metals of the *Kupferschiefer* mineralization must take into consideration the following facts:

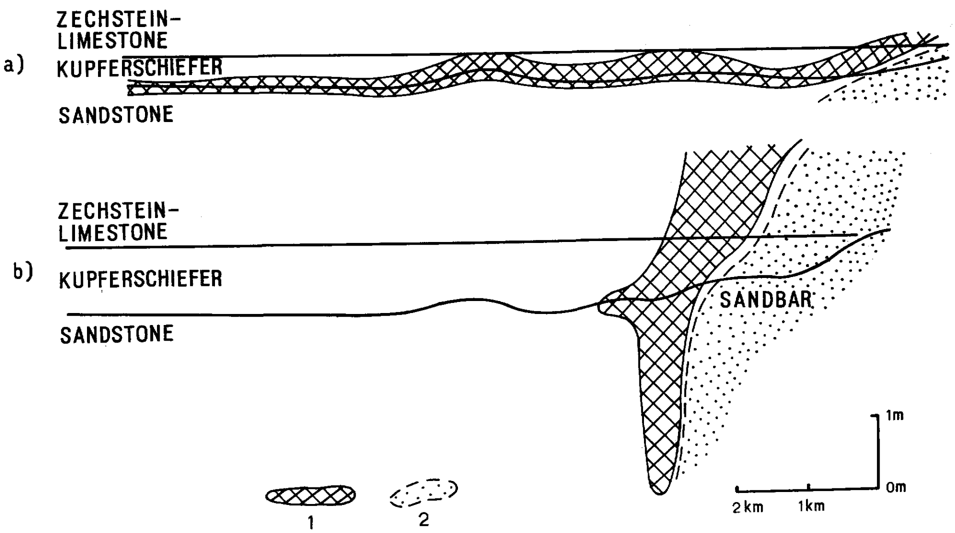

FIG. 11. — Cu *ore bodies at the* Zechstein *base. a) Mansfeld-Sangerhausen; b) Lower Lusatia and Richelsdorf — southern part. 1,* Cu *ore of economic grade; 2,* Rote Fäule *facies.*

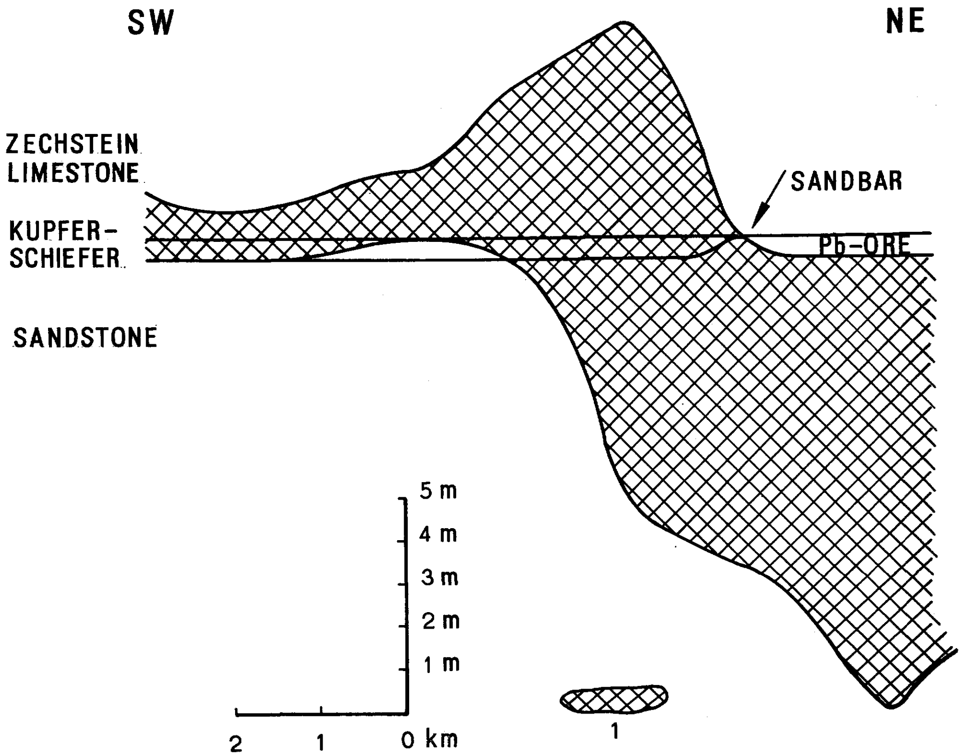

FIG. 12. — Cu *ore bodies at the* Zechstein *base in the Pre-Sudetic Syncline/Poland. After Haranczyk (1972). 1,* Cu *ore of economic grade.*

(*a*) Ore controlling zonation is, for the most part, not orientated toward the shoreline or a river delta.

(*b*) In many places, zonation forms closed rings of mineralization around the *Rote Fäule* facies.

(*c*) All ore enrichments are situated above the margins of the intraorogenic molasse depressions.

(*d*) The late variscan volcanites of the molasse stage show hardly any postmagmatic alterations and mineralizations.

(*e*) The late variscan magmatism (acid granites, rhyolithes, andesites, and basaltic rocks) is specialized with respect to lead.

(*f*) The sediments of the molasse stage and also of the *Kupferschiefer* show the same lead specialization. The relation Cu : Pb : Zn is in the late variscan volcanites 1 : 1.6 : 4.0 ($\sim$3 000 analyses), in the late variscan molasse sediments 1 : 0.8 : 2.1 ($\sim$2 200 analyses), in the rocks of the *Zechstein* base 1 : 1.6 : 3.4 ($\sim$8 000 analyses), and in the folded old paleozoic sediments 1 : 0.35 : 1.7.

(*g*) The lead of the ores comes from different sources (Kautzsch a. o., 1964).

There is a clear connection between the geochemical processes in the molasse stage and in the mineralization at the *Zechstein* base (Rentzsch, Schirmer, Röllig and Tischendorf, 1974). The metals were transported by weathering solutions into the drainless depressions of the intraorogenic deeps. They were concentrated in ground water and in deep-seated waters, because the climate was semi-arid to arid. The metals were located in the hematite (Wedepohl, 1971) and in the clay minerals of the clastic red bed sediments. Their mobilization occurred by reducing gley processes (Perelman, 1972) in deep-seated waters. During the ingression of the *Zechstein* sea the metal-bearing waters of the molasse stage were mixed with sea water. The marginal faults of the molasse depressions played the role of channelways. The centers of metal supply can be located with regard to the ore controlling zonation in areas with an oxidizing environment (Rentzsch, Tischendorf a.o., 1973), i.e. in areas with *Rote Fäule* facies (figs. 7, 9). The precipitation of sulfides was caused by sulfide of bacterial production. The sulfur is of marine origin. The deviation of the ^{34}S values are in the range from -4 % to -44 % (Marowsky, 1969; Roesler, Pilot, Harzer and Krüger, 1968). The zonation of the base metal sulfides is due to the sequence of the solubility products (K_{LCu_2S} 10^{-50}, K_{LPbS} 10^{-28}, K_{LZnS} 10^{-25}, K_{LFeS} 10^{-17}) if there is only a minimum production of sulfide ions. The main sulfide concentration appears directly at the boundary between the oxidizing (*Rote Fäule* facies) and the euxinic reducing environment.

The early diagenetic formation of sulfide minerals depends on the supply of copper, lead, zinc, silver, and cobalt and the activity of sulfide ions, which is imperative for the Eh-pH of the environment (fig. 13). In the ore-bearing sediments there exists a correlation between C_{org} and S^{2-} (Haranczyk, 1972). Consequently, it is not possible that a large part of the organic substance was oxidized during the bacterial reduction of the sulfate ion. In the immediate surrounding of the *Rote Fäule* facies the process of bituminization was stopped by slightly oxidizing waters. The kerogen reached a high grade of carbonification. The H_2 of the organic substance was oxidized (Palmberg, 1964). With the exception of covellite and chalcocite-bearing associations, the formation of the paragenetic types started with early diagenesis. The formation of the copper minerals depends on the Cu/S (Haranczyk,

1792) and Fe/Cu ratios (Rentzsch and Knitzschke, 1968). The rocks with chalcocite and covellite-bearing associations are characterized by an important lack of iron which cannot be explained by the normal iron content of the tock types. The slightly oxidizing solutions which moved from the centers of the *Rote Fäule* areas toward the reducing environment caused, at the boundary, an oxidation of the early diagenetic sulfides and of the organic substance. During this process the boundary between oxidizing and reducing conditions shifted toward the sapropelitic *Kupferschiefer.* This is demonstrated by the pseudomorphs of hematite and magnetite after pyrite and the changing degree of carbonification. This caused an impoverishment of the base metals in the oxidized part and an important enrichment at the boundary of the reducing environment (fig. 7). Chalcocite was formed directly or after covellite. The reaction of copper-bearing solutions with bornite or chalcopyrite was the reason for the impoverishment of iron in the marginal zone of the *Rote Fäule* facies and in the rocks with a covellite or chalcocite mineralization:

$$Cu_5FeS_4 + 11\,Cu^{2+} + 8\,H_2O \leftrightarrow 18\,Cu_2S + 5\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$$

The dissolved iron was fixed in the adjacent bornite type (fig. 7). The flow of this solution during the diagenesis and compaction of the *Kupferschiefer* lasted up to the sedimentation of the basal parts of the *Werra Anhydrite.* This process produced the ore bodies of economic grade in the bottom sandstones of the *Kupferschiefer* and in the *Zechstein Limestone* (Rentzsch and Langer, 1963; Oberg and Serkies, 1968; Rentzsch, Tischendorf, Ungethuem and Pilot, 1973; Haranczyk, 1972). The epigenetic veins do not influence the mineralization of the *Kupferschiefer* on a regional scale. The base metals in them may have been derived from the *Kupferschiefer*, or have been supplied by ascending solutions.

Though the *Kupferschiefer* mineralization is situated at the base of the platform stage, it is the most important product of the late variscan metallogeny.

8. COMPARISON BETWEEN THE MINERALIZATIONS OF THE "KUPFERSCHIEFER" AND THE ZAMBIAN COPPERFELT

In the *Symposium sur le cuivre africain,* Lombard and Nicolini (1960-1962) make a comparison between the stratiform copper deposits of Africa and other stratiform copper deposits. These authors distinguish two types of stratiform copper deposits:

1. Red bed type (Ain Sefra, Morocco, Agadez);
2. Mansfeld type (Mansfeld, Zaire, Zambia, Nyanga)

It is not possible to distinguish between these types, for the deposits of *Kupferschiefer* type are also connected with red beds (lower Permian, *Rote Fäule* facies). There are several similarities between the *Kupferschiefer* type and the deposits of the Copperbelt, but the differences, mainly in the geotectonic position and the lithofacial control, are so evident that it is scarcely possible to define one type of stratiform copper deposit. As a result of detailed studies, Bogdanov (1968) distinguishes between a *Kupferschiefer* type and a copper sandstone type. The main characteristics of these types are :

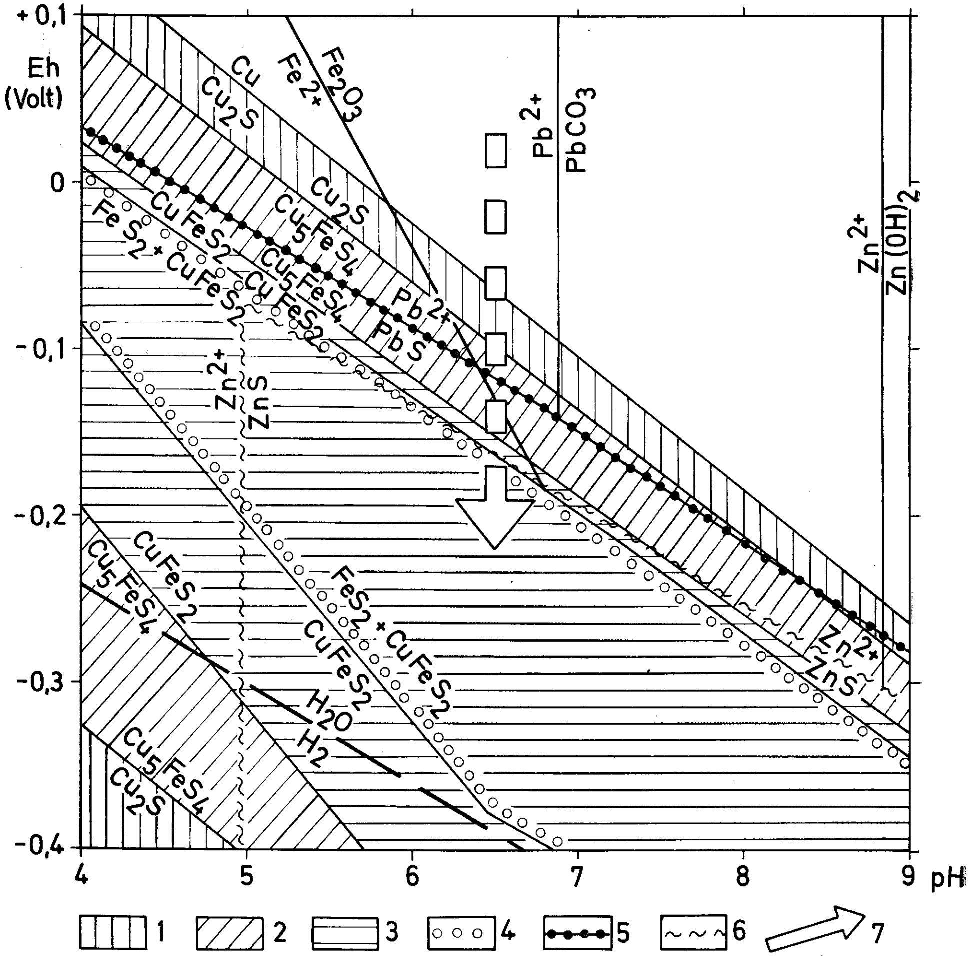

FIG. 13. — *Relations of stability between some compounds of* Cu, Fe, Pb, *and* Zn *for the system* Cu—Fe—Pb—Zn—C—S—H_2O *at 25 °C and 1 atm. After Rentzsch, Tischendorf, Ungethuem and Pilot (1973). Concentrations:* $\Sigma Cu = 10^{-6}$ *mol/l;* $\Sigma Fe = 5 \times 10^{-6}$ *mol/l;* $\Sigma Pb = 10^{-6}$ *mol/l;* $\Sigma Zn = 10^{-6}$ *mol/l;* $\Sigma S = 10^{-6}$ *mol/l;* $\Sigma C = 10^{-3.5}$ *mol/l. 1, chalcocite; 2, bornite; 3, chalcopyrite; 4, pyrite+chalcopyrite; 5, galena; 6, sphalerite; 7, zonal sequence.*

Kupferschiefer type

1. Geotectonic position in marginal depressions of platforms. Formation of the deposits during the first marine transgression (or ingression) over continental red beds.

2. Littoral marine sedimentation of aleurites, marls, and carbonate rocks in shallow water.

3. Ore deposition in marginal lagoons and basins of an inland sea. Stratiform ore bodies.

4. Formation of the present metal accumulations synsedimentary to diagenetic. Only few katagenetic changes.

Copper sandstone type (subtype Djeskazgan)

1. Geotectonic position in depressions of miogeosynclines. Formation of the deposits during the final stages of a regressive cycle.

2. Paralic sedimentation in a lagoonal-deltaic environment. Formation of aleurites, sandstones, conglomerates.

3. Ore deposition in lagoonal and deltaic basins behind sandbars. Ore bodies en echelon.

4. Formation of the present metal accumulations in the diagenetic and katagenetic stage of lithification.

The main similarities between the two types of deposits are:

(*a*) Bacterial reduction of the sulfate ion of the seawater to the sulfide ion.

(*b*) Typical copper-cobalt-nickel association in the ores.

(c) Ore controlling zonation copper-lead-zinc or chalcocite-bornite-chalcopyrite-galena-sphalerite-pyrite.

(*d*) Regional paleogeographic and paleotectonic control of the ore mineralization.

Because of the different geotectonic position of the deposits, it is necessary to distinguish between both types of deposits and to use the classification of Bogdanov (1968). Therefore, the stratiform deposits of the Zambian Copperbelt belong to the copper-sandstone type and not to the *Kupferschiefer* type.

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