An overview of the European Kupferschiefer deposits

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Chapter 18

An Overview of the European Kupferschiefer Deposits*

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Abstract

The Kupferschiefer of northern central Europe is not only one of the largest sediment-hosted accumulations of copper ores worldwide (largest 1% of deposits with >60 Mt contained Cu) but has also one of the longest continuously documented mining histories, starting from at least 1,199 A.D. in the Mansfeld district of Germany. Kupferschiefer ores are currently mined in Poland from several large underground mines with active near-mine exploration and possible downdip extensions at a planning stage. Kupferschiefer mines in the Mansfeld and Sangerhausen districts of Germany had been largely exhausted by 1990 but a new exploration campaign is currently targeting a major deep Kupferschiefer resource near Germany's eastern border with Poland.

The Cu-rich part of the Kupferschiefer mineralization is dominated by chalcocite, chalcopyrite, and bornite and is hosted by several rock types including footwall sandstone and conglomerate, black shale, carbonate rocks in the immediate hanging wall, and anhydrite even higher in the hanging wall. Orebodies can range in thickness from 0.3 m, contained largely within the black shale of the Kupferschiefer sensu stricto, up to more than 50 m, where sublevel stoping, backfilling, and pillar mining reflect the pervasive mineralization. The ore zone can occur at various stratigraphic levels from (1) as low as some 35 m below the Kupferschiefer sensu strict, to (2) within and immediately adjacent to the black shale unit, to (3) several tens of meters above the base of the Zechstein limestone. Economic mineralization also occurs locally where no black shale has been deposited at all, for example, above Weissliegend sand dunes at the basin margin of the Kupferschiefer Sea that were never covered by the black euxinic mud. Ore textures include disseminated ores, disseminated replacement of diagenetic and framboidal pyrite, crosscutting and bedding parallel veinlets, impregnation and replacement ore of carbonate and anhydrite cements, replacement of fossil shells, and even replacement of detrital feldspar and feldspar in lithic clasts.

All copper deposits share a marked metal and ore mineral zonation pattern adjacent to a major secondary redox front, the so-called Rote Fäule. This three-dimensionally, roughly hemispherically zoned mineralization system is transgressive and locally even steeply crosscutting to stratigraphy. It grades from an Fe^{3+} zone (hematite), through a locally developed precious metal (Au, Pt, Pd) zone, an always redox-proximal Cu zone (chalcocite, bornite, chalcopyrite), a locally overlapping Pb and Zn zone, into a distal Fe^{2+} zone of preore, commonly framboidal or early diagenetic pyrite. The oxidized part of the zoned orebodies commonly originates from permeable zones such as fault structures or sand dunes, which might have acted as valves through the relatively impermeable Kupferschiefer.

In general, the Kupferschiefer mining districts occur exclusively within an arcuate belt that is situated above basement rocks of magmatic arc origin, the Mid-European Crystalline High, typically at the intersections with major NW-SE– and NNE-SSW–trending fault structures. Local and regional studies have shown that regional metal distribution, orebody geometry, and metal grades are largely structurally controlled, although divergent opinions were originally expressed as to the timing of metal introduction via these conduits. An absolute age of ca. 255 Ma is generally accepted as the sedimentation age for the "Kupferschiefer" black shale. However, recent paleomagnetic age dating of mineralization at Sangerhausen has revealed late epigenetic mineralization ages of 149 and/or 53 Ma. The results argue for a new metallogenic model, which involves two major epigenetic pulses of metal introduction to the Kupferschiefer ores as impregnations, replacements, and subsequent veins and breccias.

A holistic understanding of the Central European Basin, which hosts the Kupferschiefer ores in its lower part of the stratigraphy, from the basin's origin in the Late Carboniferous to the Tertiary, and particularly the various related extensional and compressive tectonic events helps to put the individual stages of Kupferschiefer mineralization into a European plate tectonic perspective. The time span from Late Jurassic to Mid-Cretaceous was a period of major crustal rearrangement with the break-up of Pangea and the potential for the remobilization of major pulses of metalliferous brines. Both the main quantity of the

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* Plates 1–3 appear at the end of the paper. Digital Appendices are included on the CD-ROM.

Kupferschiefer ores and the giant Mississippi Valley-type (MVT) Pb-Zn ores of Upper Silesia appear to have formed at this stage. The younger, Tertiary, mineralizing event is also noted in both base metal provinces and was probably, again, related to crustal movement that involved metalliferous fluid flow. Additionally, this period was accompanied by magmatic pulses in the wider area of the Kupferschiefer metalliferous belt. Locally, late vein-type Co-Ni-rich mineralization, upgrading preexisting impregnation and replacement ores, gives evidence for this latest hydrothermal event, for example, in the German mining districts of Spessart/Rhön and Richelsdorf.

Introduction

THE ORE DEPOSITS of the European Kupferschiefer are sediment-hosted strata-bound copper deposits, located in Germany and Poland (Fig. 1). The deposits have been mined for many centuries and are currently exploited in deep, modern mines in Poland and actively explored both in Poland and Germany. Historically, the copper-silver ores of the Kupferschiefer have been one of the main metal sources in Germany from medieval times until 1990, when the mines, which had been uneconomic for many decades, finally closed. In Poland, modern exploration and mining started comparatively late, i.e., in the 20th century but continues today with new, even deeper mines in an advanced planning stage. Kupferschiefer ore is by far the most important primary European metal source. Modern exploration, using state-of-the-art geophysical methods, is currently carried out both in Poland and Germany, targeting mineralization at depths greater than 800 m.

The inhomogeneity of the amount and quality of data from the various parts of the metallogenetic belt is also partly reflected in this paper, since research in Poland has remained much more active over the last decades, due to ongoing mining and exploration. This includes strongly opposing genetic models, which include—from very early on—syngenetic and epigenetic models. The number of publications dealing with the various aspects of the Kupferschiefer mineralization mentioned above is vast and cannot be fully included in a brief summary review as the present one. The analytical data base for the much quoted precious and specialty metal concentrations is surprisingly scarce on the German side of the metallogenic belt, due to historical and political reasons. The authors have therefore chosen an approach, in which a comprehensive reference list and selected (previously unpublished) analytical data are included as a digital appendix. This reference list includes a particularly large portion of historical publications in German and Polish, which might be difficult to access and understand for many international readers. It was felt appropriate to point the reader toward these valuable sources of scientific information that are also important documents for

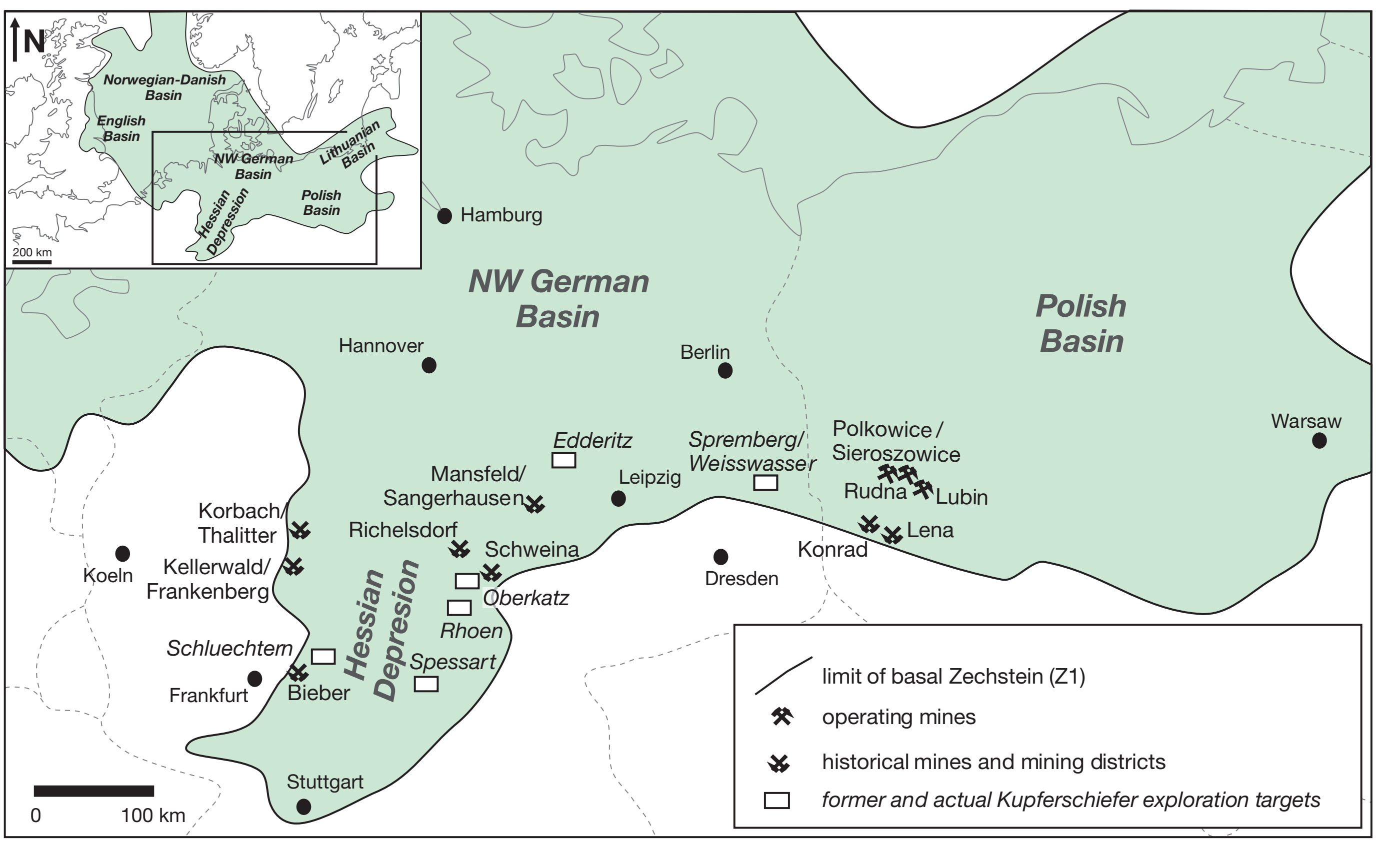

FIG. 1. Simplified map of the central part of the Kupferschiefer basin in northern central Europe (see insert map for orientation). Shown is the maximum extent of deposition of the basal Zechstein and the various Cu mining districts and exploration areas; near-mine exploration in Poland is not shown.

the history of science related to this remarkably complex type of ore deposit. The overview itself comprises a summary of all relevant features of the Kupferschiefer mineralization, the most important genetic concepts, and new insights from absolute age dating. The review also includes summaries of historical mining information from those ore districts that were mined in medieval times but not actively exploited in modern times any longer. A holistic investigation of all of the mining districts in the Cu-mineralized part of the basin is probably the key to the understanding of the metallogeny and particularly to the metal sources of the Kupferschiefer ores. More general summaries of certain aspects of the Kupferschiefer have been given by Deans (1950), Kulick et al. (1984), Speczik and Püttmann (1987), Vaughan et al. (1989), Wodzicki and Piestrzyński (1994), Speczik (1995), Oszczepalski (1999), Blundell et al. (2003), Paul (2006), Liedtke and Vasters (2008), and Hitzman et al. (2010).

Mining History

Germany

Prehistoric finds of slag and bronze from smelting sites on top of or immediately adjacent to outcropping Kupferschiefer ores at Wettelrode, Mohrungen, and Bottendorf in Central Germany give evidence of Early to Middle Bronze Age utilization of the Kupferschiefer ores (Leipold, 2007). The medieval mining history of the Kupferschiefer ores is documented in written sources since at least 1,199 A.D. from the Mansfeld district in Central Germany (Spangenberg, 1572; Fig. 1). The Counts of Mansfeld developed several copper mines, smelters, and a mint at the town of Eisleben, where copper and silver coins were minted from the metals of the Kupferschiefer ores. Although the Mansfeld and subsequently the Sangerhausen districts (Fig. 1) remained the centers of German Kupferschiefer mining and processing (Plate 1A-C), there were numerous other locations where the Kupferschiefer mineralization was mined in medieval and early industrial times. Unfortunately, there are only scarce records of past production for most of these mines but historical records of the number of miners, adits, and smelters document that the copper production must have been substantial at times between the 12th and 19th centuries. Examples of these other mining districts include the Richelsdorf district (Fig. 1) with the Schnepfenbusch mine, near Nentershausen (Kulick et al., 1984). This mine operated during two periods, from 1460 to 1850 and from 1934 to 1955, with some 400 miners working prior to the mine's closure. A significant portion of the ore in the Richelsdorf district has been contained in the footwall sandstones ("Sanderz") and in hanging-wall carbonate although this observation has not been quantified (Schnorrer-Köhler, 1983).

Another prominent historical mining district was the region around Schweina in Thüringen, Central Germany (Eisenhuth and Kautzsch, 1954; Fig. 1). Here, the mining targeted rich ores of up to 10% Cu, hosted by both the Kupferschiefer stratum sensu stricto and particularly by the underlying sandstones and conglomerates. Copper mining prevailed from 1441 to 1714 and was succeeded by the mining of rich cobalt ores, which ceased in 1714. At the height of production, the region had 100 producing adits and 12 smelters. The high-grade mineralization is fault controlled on bounding faults of the basement block of the Thuringian Forest.

Modern Kupferschiefer mining in Germany took place predominantly in the districts of Mansfeld and Sangerhausen. The Sangerhausen district still employed an impressive, though markedly uneconomic, work force of some 5,000 miners at the end of the mining operation in 1990, who mined to a maximum depth of 995 m below surface. The ore was mined predominantly from the Kupferschiefer black shale sensu stricto and from the immediate contact bedding planes with the footwall and subordinately with the hanging wall (Plate 1B, C). However, a narrow zone of rich sandstone- and conglomerate-hosted footwall ore and a more diffuse zone of carbonate-replacement and vein-type hanging-wall ore have been mined as well (Knitzschke, 1995; Knitzschke and Spilker, 2003). Highly mineralized hanging-wall and footwall rocks are common on mine dumps of the Mansfeld and Sangerhausen districts, suggesting that mining partly ignored these ore types, possibly for technical reasons. The orebodies of the Mansfeld syncline have been completely exploited (Table 1), but a small portion of already delineated ore blocks have remained intact within the Sangerhausen district (Stedingk et al., 2002). Here, proven ore reserves still remain on the order of 35.4 million metric tons (Mt) with an average grade of 2.34% Cu, containing 0.86 Mt Cu, 0.11 Mt Pb, 0.10 Mt Zn, and 4,650 t Ag, at a depth between 500 and 800 m (Knitzschke, 1995).

The area of Spremberg/Weisswasser in Brandenburg, eastern Germany, is situated between the German mining districts of Mansfeld and Sangerhausen and the mining districts in SW Poland (Fig. 1). Here, East German state exploration identified substantial Kupferschiefer mineralization under thick cover rocks and explored these between 1965 and 1980. Most of the exploration results have been documented in unpublished internal reports of the state exploration company "VEB Geologische Forschung und Erkundung Halle," some of which have been summarized and illustrated by Kopp et al. (2008). The Kupferschiefer ores occur at a minimum depth of 800 m below surface within the fold axis of the Mulkwitz anticline (Kopp et al., 2006, 2008). According to these authors, the ore zone has an average thickness of 2.4 m but locally can reach a thickness of 8.2 m and is transgressive to stratigraphy at a shallow angle from footwall conglomerate and sandstone (ca. 31%) through the Kupferschiefer black shale (ca. 46%) into the hanging-wall carbonates (ca. 23%). Overall, the orebodies dip along the fold hinges and the mineralization is open at depth. The state exploration company reported an indicated reserve (originally a C2 reserve according to the Russian reserve estimation scheme) of ca. 98 Mt ore with an average grade of 1.53% Cu, containing a total of 1.5 Mt Cu metal (Kopp et al., 2006, 2008). The Spremberg/Weisswasser district is being actively explored at the time of publication.

Poland

In the 16th century, extraction of copper from Kupferschiefer ores started in the North-Sudetic trough area (Fig. 2), however systematic exploration began only in 1930 (Eisentraut, 1939). By 1936 some 40 drill holes had been completed within the Grodziec syncline, outlining a copper deposit some 14 km long and 5 km wide and extending to a depth of 1,000 m. In the years

TABLE 1. Copper and Silver Production and Current Reserves of Major Kupferschiefer Mining Districts of Germany and Poland (data from www.kghm.com, Knitzschke, 1995, and Kopp et al., 2006)

Period	District	Ore (Mt)	Cu metal (t)	Ag metal (t)
Germany				
1200 to 1990	Mansfeld			
	mined	80.76	2,009,800.00	11,111.00
	remaining reserves	none	none	none
	Sangerhausen			
	mined	28.14	619,200.00	3,102.00
	remaining proven reserves	35.40	860,000.00	4,650.00
Exploration	Spremberg/Weisswasser			
1953 to present	indicated reserves	97.70	1,486,000.00	no data
Total Germany	Mined and proven	242.00	4,975,000.00	
Poland				
1949 to present	North-Sudetic trough			
	mined	37.91	212,894.00	756.7.00
	remaining reserves	104.26	1,460,000.00	no data
	Fore-Sudetic monocline			
	mined	>1,000,00	>20,000,000.00	>14,085.00
	remaining proven reserves	1,470.00	29,790,000.00	no data
	remaining indicated reserves	212.50	3,990,000.00	no data
Total Poland	Mined, proven, and indicated	>2,824.67	>55,452,894.00	
Total Germany and Poland	Mined plus remaining	>3,066.67	>60,427,894.00	

1936 to 1937, 20 additional drill holes were sunk to the depth of 480 m in the Zotoryja syncline, delineating a copper deposit with an extent of 20.9 km². In 1938, the first public mining company, BUHAG ("Berg- und Hütten-Aktiengesellschaft", i.e. Mining and Smelting Corporation) was launched. This company owned and operated four mines: Mittlau mine (1938–1945), Mühlberg mine (1938–1945), and the Libichau and Wahlstadt mines (1936–1945). After World War II, Poland reactivated all former German mines and in 1949, the Konrad mine (Figs. 1, 2) was reopened and operated until 1987. A total of 37,914,702 t of ore containing 212,894 t of metallic copper and 756.7 t of silver were extracted from the Konrad mine.

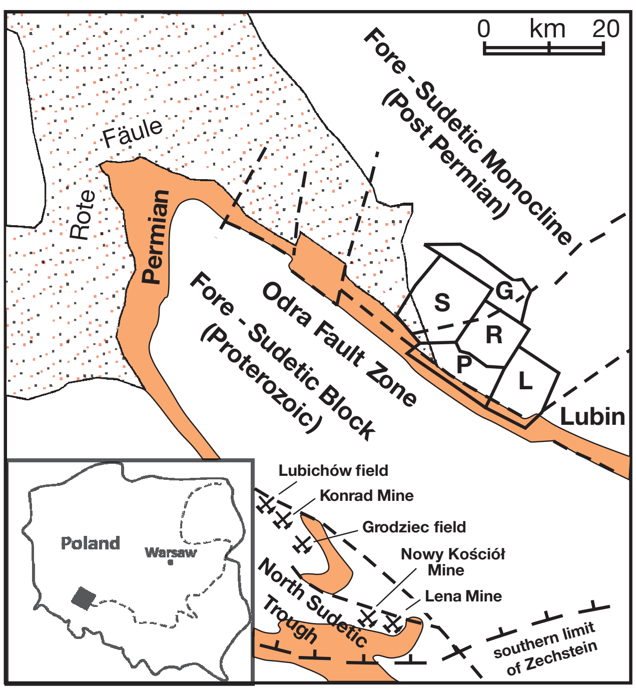

FIG. 2. Simplified map (Cenozoic not shown) of SW Poland (see insert map) with the deposits of the North-Sudetic trough and Fore-Sudetic monocline (Lubin-Sieroszowice mining district). Abbreviations: G = Głogów industrial field, L = Lubin mine, P = Polkowice mine, R = Rudna mine, S = Sieroszowice mine.

The Lena mine became the first new mining operation in the Zotoryja syncline after World War II (Figs. 1, 2). This mine was active from 1948 to 1974, with a maximum annual production of 0.5 to 0.7 Mt of ore with a Cu grade of 0.6%. The adjacent Nowy Kościół mine, located also in the Zotoryja syncline, operated from 1952 to 1968, with a maximum production of 0.42 Mt ore at 0.50 to 0.55% Cu. The first exploration within the Fore-Sudetic monocline (Fig. 2) begun during the late 19th century with drill holes located in Krajków, 15 km south of Wrocław (Roemer, 1876). Until the end of 1944, several other holes were drilled in the vicinity of Wrocław. Until the end of World War II, no drilling took place in the area of the current Polish copper deposits, the position of which was marked on Eisentraut's maps (1939) as non-prospective. Polish geologists began to explore this area in 1951. In the years 1951 to 1952 a seismic profile along the line Bolesławiec-Głogów was completed (Zwierzycki, 1951). Based on seismic records, two conceptual models inferring a suboutcrop of Zechstein north of Bolesławiec were prepared. Based on the first model, a drill hole was positioned in the Gromadka village but was stopped in 1955 after tapping metamorphic schists below the Quaternary and Tertiary sediments of the Fore-Sudetic block. Switching to the second prospecting model, the next four drill holes were planned by Jan Wyżykowski. The first three were stopped due to technical problems. However, today we know that they were located within the deposit area. In 1955, the fourth borehole was drilled by the Polish Oil Industry in Wschowa village, 20 km north of Głogów, which is presently the northern part of the known copper deposit. This borehole was the first to intersect the mineralized Kupferschiefer horizon. This discovery occurred in 1957, when borehole S-1, located at Sieroszowice village, intersected the Cu-mineralized section close to the contact between Lower and Upper Permian strata (Wyżykowski, 1958). The first report, based on 24 drill holes, was completed in 1959, delineating a deposit that extended over 175 km^2 and contained 1,364 Mt of ore at 1.42% Cu (19.3 Mt of contained Cu). Premining reserves in the early 1960s were calculated to a depth of 1,250 m and, together with inferred resources, were estimated at 2,700 Mt tons of ore, containing 52 Mt of Cu and 141,000 tons of Ag.

The so-called "Lubin mine under Development" was established in 1959 (Fig. 3a) with the first shaft intersecting the ore horizon at a depth of 610 m in 1963. Six years later, when the mine reached 25% of its annual output, it received its new and formal name, Lubin mine (Figs. 1–3a). The next mine, Polkowice, was opened in 1969, followed by the Rudna mine in 1974, and the Sieroszowice mine in 1986. Between 1960 and 1991, four mines, three flotation plants, and two smelters were operated by Copper Mining and Smelting Industrial Complex (KGHM), which was subsequently converted to KGHM Polska Miedź S.A. Today, extraction is predominantly by room and pillar mining although a first long wall mining system was implemented. Back-fill with extraction of remaining pillars is applied where orebodies reach a thickness of 15 m or more.

Even after 50 years of mining, the Kupferschiefer district of the Fore-Sudetic monocline is still host to proven reserves of 1.47 Bt of ore, containing 29.79 Mt of copper plus an indicated reserve of 212.5 Mt of ore, containing 3.99 Mt of copper in immediately adjacent areas (Fig. 3b). Overall, the largest volume of Cu ores of the Polish deposits is hosted by footwall sandstone (60%), followed by ores in hanging-wall carbonate rocks (30%), and only subordinately in the Kupferschiefer black shale (10%). However, the main host rock differs from mine to mine with sandstone ore amounting to 69.7 and 84.3% at the Lubin and Rudna mines, respectively (www.kghm.pl 2012). In contrast, 59.7% of the ore at Polkowice-Sieroszowice originates from hanging-wall carbonate rocks. KGHM, the owner of these mines and prospects has the mining and exploration rights over some 450 km^2 (Fig. 3b). All reserve calculation are based on a cut-off accumulation index of 50 kg/m^2 of Cu plus Ag equivalent (currently 10g Ag = 0.1% Cu), and 0.7% Cu as an overall cut-off grade, a minimum Cu content within the section of 0.7% Cu, and a depth limit of mining at 1,250 m below surface. However, it is important to note that the deposits are open to depth and the current limits are due to economic reasons only. Additionally, the Grodziec syncline within the North-Sudetic trough is still host to 104.26 Mt of copper ore containing 1.46 Mt of metallic Cu (Bachowski et al., 2011). These are joint reserves of the abandoned Konrad mine and the Wartowice II deposit.

The impressive tonnages of historical and modern mine production and remaining (minimum) reserves are summarized in Table1.

Mining and Stratigraphic Terminology—History and Inherent Problems

The strong influence of medieval mining of the Kupferschiefer in Germany is documented by several stratigraphic terms of the Permian in Germany and parts of Central Europe. Rotliegend translates to "red footwall," which was the rock that the miners were lying on (German: "liegen") during manual mining of the thin reef and refers to the terrestrial red-bed sediments. Weissliegend and Grauliegend refer to local color variations of the partly chemically reduced, uppermost Rotliegend, which are thus not a chronostratigraphic unit sensu stricto. The Kupferschiefer (literally and ambiguously translated as "copper shale/slate") is the basal stratigraphic unit of the Zechstein (Fig. 4) and was the reef that was originally mined, although, geologically, it is a nonmetamorphic, $C_{organic}$-rich black shale. The overlying Zechstein cycles of marl, limestone, and evaporites have their names from the descriptive term of a tough, well-supporting marl or limestone hanging-wall rocks; "tough rock" translating in medieval German as "der zaeche stein," i.e., Zechstein. Even the secondary oxidation, closely associated with ore-grade mineralization of the Kupferschiefer and its immediate footwall and hanging-wall rocks, has a descriptive mining name, the "Rote Fäule." Literally translated, this term means "red rot" and early miners attributed this negative connotation to the oxidized, barren rocks.

To complicate matters further, drastically different styles of mineralization have been referred to as Kupferschiefer ores. These ore types include disseminated sulfide ores within the Kupferschiefer stratum sensu stricto, sandstone- and conglomerate-hosted impregnation and replacement ores in the footwall of the Kupferschiefer stratum, mineralized veinlets and local carbonate replacement pockets in the Zechstein limestone of the hanging wall, and finally, clearly crosscutting vein-type and wall-rock impregnation-type ores (so-called "Rücken" or "ore ridges" due to their morphologically positive weathering gossans). As a lithostratigraphic unit, the Kupferschiefer black shale can be found throughout most of the basin although locally grading into marly facies equivalents, for example, in the North-Sudetic trough in SW Poland. However, the "Kupferschiefer" is, in most parts of the basin, nonmineralized or mineralized by Pb and Zn sulfides and pyrite only and thus does not qualify as a "cupriferous shale" (Oszczepalski, 1999).

With respect to another local mining term it is interesting to note that miners and ore deposit researchers in the Mansfeld/Sangerhausen region alike described the metal content of the ore—the term "grade" would not be appropriate as a translation—in kg/m^2. This unit was referred to as "Kupfer-Schüttung," which is literally translated most appropriately as "copper discharge" or "copper fill." The unit kg/m^2 does not take the thickness of the mineralized section and the density of the host rock and ore directly into account, although empirical correction factors were applied (Knitzschke, 1995, and pers. commun., 2011). The origin of the term is hard to trace but the earliest use of the unit kg/m^2 is in Hoffmann (1923). The concept of using the metal content per area is a direct reflection of the (assumed) reeflike, tabular geometry of the orebodies. Abundant hand specimens of sandstone- and conglomerate-hosted ore from old mine dumps in the Mansfeld/Sangerhausen district give evidence that the stratiform concept of

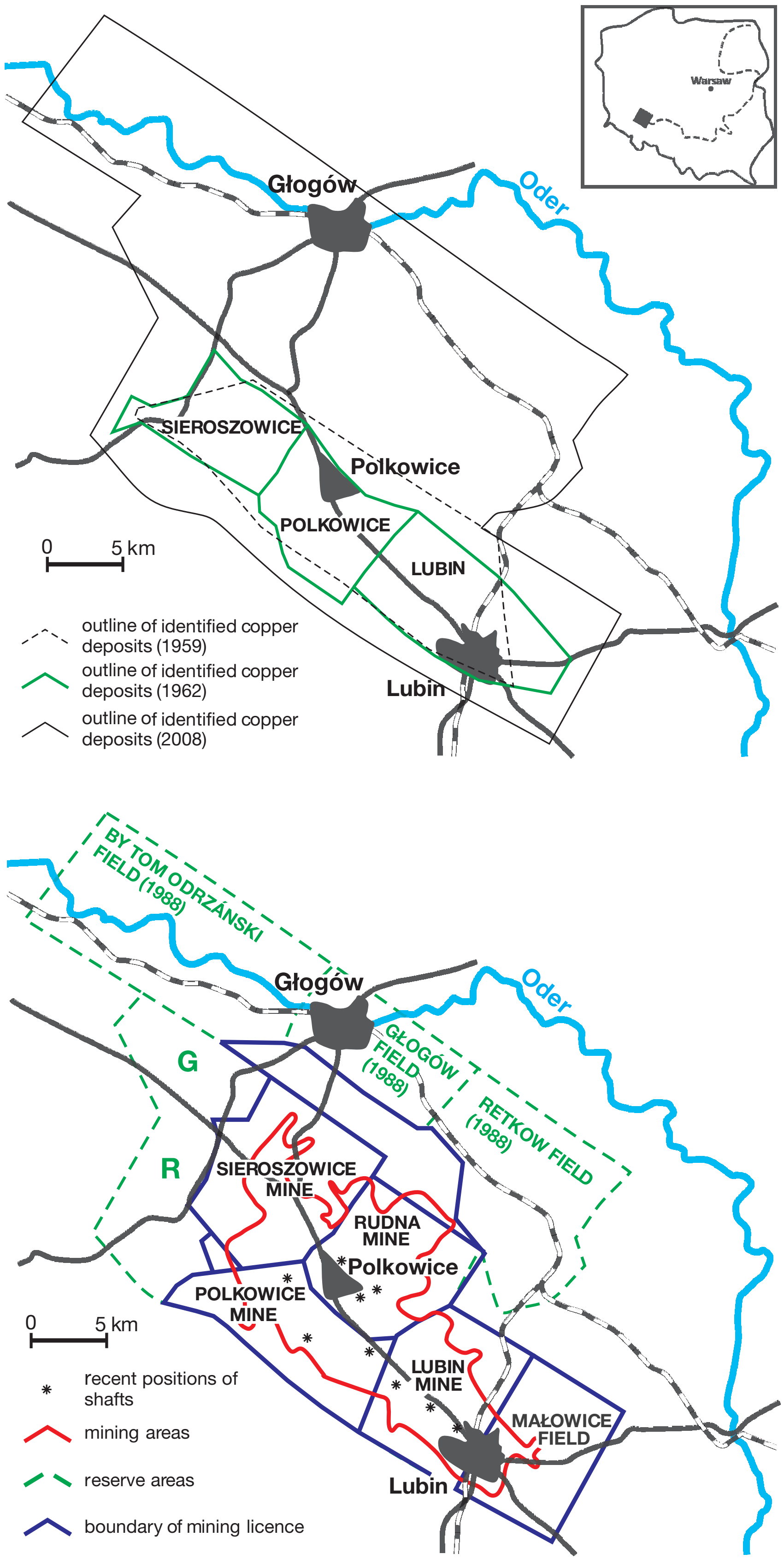

FIG. 3. Top: Outline of copper deposits of the Fore-Sudetic monocline, growing in size from 1959 through 1962 to 2008. Bottom: Recent positions of shafts, mining areas, and reserve areas (after Leszczyński, 2011).

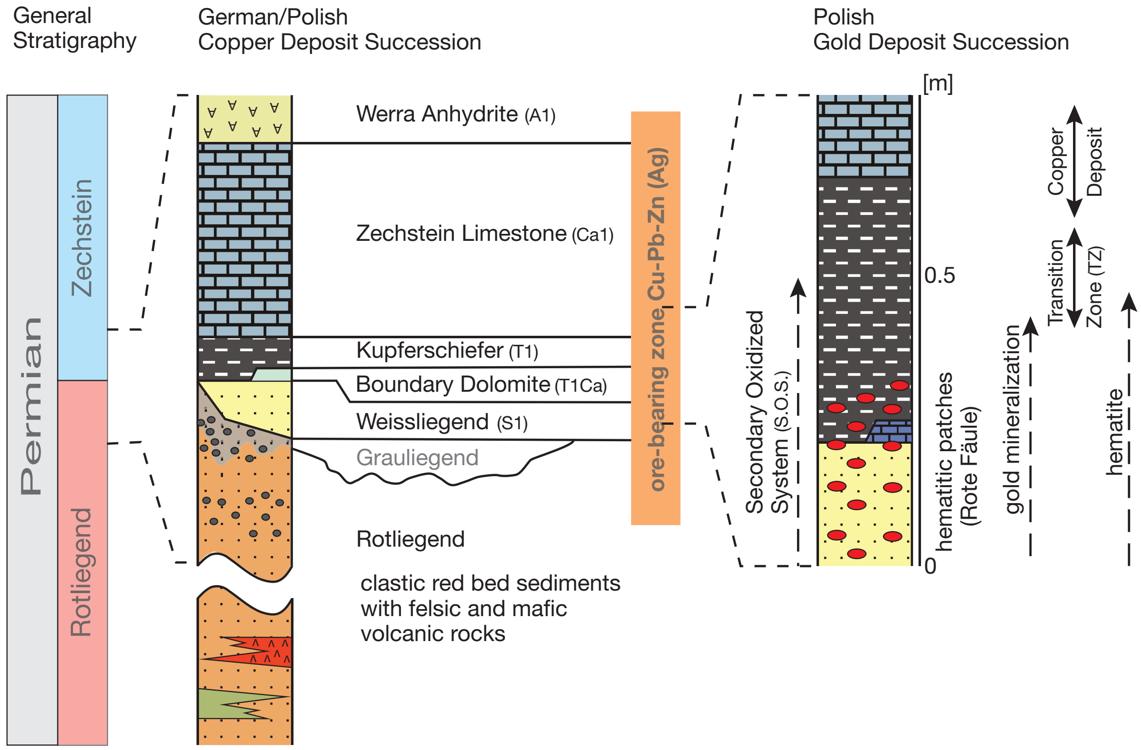

FIG. 4. Stratigraphic column of the Permian in Germany and Poland with typical mineralized successions in copper- and precious metal-dominated parts of the cupriferous belt. For practical reasons the Rotliegend/Zechstein boundary is at the base of the Kupferschiefer (T1). Note that secondary oxidation (Rote Fäule) is not shown for clarity in German/Polish succession and left column of general stratigraphy is not to scale.

purely black-shale-hosted ore in strictly reef-shaped orebodies did not apply. Locally and particularly adjacent to the Rote Fäule oxidation zone, the mineralization has long been known to grade into hanging-wall rocks, with the same metal content distributed over a thicker stratigraphic section at lower, subeconomic grades (Luge, pers. commun., 2009). However, the mines of the Mansfeld/Sangerhausen district used kg/m² as well as kg/t, although for different production parameters. The unit kg/m² was a measure for the extraction grade by mining (German: "Bauwürdigkeit") where 8 to 10 kg/m² was the typical range of "economic" ore grades (Knitzschke, 1995). The unit kg/t characterized the pyro-metallurgical recovery (German: "Schmelzwürdigkeit") from the ore by the smelter and a cut-off of 5.5 kg/t was applied during GDR times (Knitzschke, pers. commun., 2011). The kg/m² terminology for ore grades is also maintained in the Polish mining industry until today. Currently, an accumulation index of 50 kg/m² is used as economic cut-off grade for Polish copper ores. Interestingly, in modern metallogenic ore zonation or distribution maps, the unit kg/m² is a good measure of the total volume of metals introduced into a certain region.

Tectonic, Sedimentary, and Magmatic Evolution of the Central European Basin

The Kupferschiefer was deposited in the Central European Basin, which is roughly subdivided into three parts: the North Sea Basin, North German Basin, and Polish Basin (e.g., Ziegler, 1990; Littke et al., 2008; Doornenbal and Stevenson, 2010). The Central European Basin is an intracontinental (or cratonic) basin (Bachmann and Grosse, 1989; Ziegler, 1990) and came into existence after the Variscan Orogeny in latest Carboniferous times as a successor basin to the Variscan foredeep and on the northern margin of the orogen. The reasons for the origin and evolution of the basin include crustal extension, magmatic underplating, crustal heating, as well as the increasing weight of the basin fill (Bachmann and Hoffmann, 1997).

During latest Carboniferous and earliest Permian times (ca. 300 Ma ago), the eastward drift of the European Plate relative to the African Plate caused a stress field with E-W maximum extension in the region of the Variscan Orogen and its foreland. This in turn led to the formation of a large conjugate shear fault system (Arthaud and Matte, 1977; Ziegler, 1990). The faults strike predominantly NW-SE and NNE-SSW and large and small pull-apart basins formed due to transtension. The shearing opened up deep pathways for the intrusion of magma and the extrusion of volcanic rocks. Magmatism was markedly bimodal (Eckardt, 1979) with mafic magmas resulting from decompression melting of upper mantle and felsic magmatism from partial melting of lower continental crust. The main depocenter of the Central European Basin is located in northeastern Germany with a SSW-NNE trend. Up to 3 km of rhyolitic and basaltic to andesitic volcanic rocks as well as some terrestrial clastic sediments of the Lower Rotliegend were deposited in this basin (Plein, 1995; Breitkreuz and Kennedy, 1999). Crustal heating and extension caused widespread thermal uplift and erosion as manifested by the "Saalian Unconformity" between the Lower and Upper

Rotliegend (Ziegler, 1990; Bachmann and Hoffmann; 1997). The late Early, Middle, and Late Permian (Upper Rotliegend) were characterized by thermal subsidence of the basin as well as subordinate extensional tectonics that caused meridionally trending graben systems in Northwest Germany (Gast, 1988).

In the late Permian, the Central European Basin was situated approximately at 20° N latitude, within the influence of the northern “trade wind” system, leading to an arid climate (Ziegler, 1990). The basin was hydrologically closed and a large playa system developed, in which the more than 2-km-thick terrestrial red beds and evaporites of the Upper Rotliegend were deposited. Occasional tectonic pulses caused unconformities and some basaltic volcanism (Plein, 1995). Since the Upper Rotliegend, the trend of the basin was WNW-ESE, stretching from England to Poland with the most important depocenter in Northwest Germany. Some short-termed marine ingressions occurred in the uppermost Rotliegend along the same seaway from the Boreal Sea as during the subsequent Zechstein transgression (Littke et al., 2008).

In latest Permian (Wuchiapingian) times, the basin floor was some 200 to 300 m below sea level as a result of continued thermal subsidence. The ingression of the Zechstein Sea from the Boreal Sea happened very rapidly and catastrophically (Glennie and Buller, 1983) via a graben system between Scandinavia and Greenland, flooding the basin with seawater (Ziegler, 1990). Commonly thin, partly transgressional conglomerates and sandstones of the Weissliegend became subsequently covered almost basin-wide by the Kupferschiefer sediment. This unit is a typically 0.3- to 0.6-m-thick, black, bituminous and carbonaceous, laminated marine shale or marl that was deposited in anoxic, euxinic bottom waters (e.g., Paul, 2006). Subsidence of the Central European Basin was mainly due to further cooling and the weight of the sediments, with only minor extensional tectonics involved. The more than 1.5-km-thick basin fill of the Zechstein is characterized by up to eight major evaporite cycles (Littke et al., 2008).

The Central European Basin expanded and subsided significantly during the Triassic due to further cooling as well as extensional tectonics, heralding the break-up of Pangea. This resulted in the formation of local SSW-NNE–trending grabens, depressions, and swells, as well as salt diapirs of the underlying Zechstein salt (Doornenbal and Stevenson, 2010). More than 1.5-km-thick clastic fluvial and playa sediments dominated the basin fill (Buntsandstein, Keuper), with several hundred meters of marine carbonate and evaporite sandwiched in between (Muschelkalk). Repeated tectonic pulses caused significant unconformities.

The break-up of Pangea occurred in the Jurassic. Both the Middle Atlantic and Penninic Oceans opened and shallow seas covered the area of the Central European Basin for most of the time. During the Late Jurassic (ca. 150 m.y. ago), wrench tectonics uplifted the WNW-ESE–trending London-Bohemia Swell and the smaller Lusitania Swell, which was situated to the northeast (Ziegler, 1990). It is interesting to note that the Cu mineralization of the Kupferschiefer and several of the Kupferschiefer mining districts are situated close to the northern hinge zones of these uplifted swells. These include the Richelsdorf district immediately to the southwest, the Mansfeld and Sangerhausen districts right on top, the North-Sudetic trough between the Bohemia and Lusitania Swell, and the Spremberg/Weisswasser district to the northwest of the Lusitania Swell. Major NW-SE- as well as NNE-SSW–trending, crosscutting fault zones dissected the swell, thus accommodating differential lateral crustal movements. The differential crustal uplift in the southeast and renewed subsidence in the northwest caused tilting of crustal blocks and, as a consequence, allowed lateral and vertical large-scale fluid migration along major fault zones and suitable lithologic aquifers.

During the Early and particularly Late Cretaceous, large parts of the Central European Basin were flooded by a shallow sea due to a worldwide rise of the sea level. Parts of the Central European Basin underwent SW-NE compression due to convergence of the African and European plates, with a maximum between the latest Turonian and Campanian, ca. 86 to 70 m.y. ago (Kley and Voigt, 2008). The compression caused reactivation of NW-SE-trending faults and associated conjugate fault systems of originally Late Carboniferous and Permian age. Compressional tectonics also included thrusting of basement blocks up to several kilometers along reverse faults, causing “inversion” of the basin. Examples of uplifted basement blocks include many of today’s mountain ranges or highlands, for example, the Harz Mountains in North Germany or the Fore-Sudetic block in southwestern Poland. Other blocks, adjacent to the uplifts, for example, the northern foreland of the Harz Mountains, started to subside and accumulated large quantities of syntectonic clastic sediments, eroded from the uplifted areas in the Late Cretaceous (Littke et al., 2008). The paired uplift and subsidence caused local and regional tilting of crustal blocks, triggering renewed migration of basinal fluids. It was particularly near the tectonically uplifted blocks where historic mining activities began to target the economically viable orebodies of the outcropping Kupferschiefer mineralization.

The early Tertiary (Paleogene) was mostly characterized by extension. During the Paleocene, the northeastern part of the Central European Basin was flooded by the North Sea (Littke et al., 2008). In the early Eocene, around 53 m.y. ago, the Iceland plume became emplaced and the Middle Atlantic started to open, accompanied by crustal heating and lithospheric delamination (Nielsen et al., 2002). A further rise in sea level during the Eocene and Oligocene flooded even larger parts of the basin. The southern German Molasse Basin subsided to the north of the advancing Alpine nappes. At the same time, the SSW-NNE–trending volcanically active rift systems of the Upper Rhine graben and the Hessian Depression as well as the SSE-NNW–trending Lower Rhine graben developed due to E-W extension and were flooded, thus creating a seaway between the North Sea and the southern German Molasse Basin. Additionally, the WSW-ENE volcanically active Eger graben started to form. The Tertiary was a time of intense, mostly basaltic volcanism, spatially and petrogenetically associated with the rift systems, with maximum activity in the Miocene. The areas of intense Tertiary magmatism centered on zones of structurally controlled crustal weakness, particularly at the intersection of major fault and graben systems. Locally and regionally the magmatism transferred substantial heat and metal sources to upper crustal levels. The late Tertiary (Neogene) is characterized by generally N-S-directed compression, leading to mostly continental conditions in the basin.

Characteristics of "Kupferschiefer" Ores

The Kupferschiefer sensu stricto is a thin, commonly 0.3-m-thick layer of marine black, $C_{organic}$-rich shale (with the German stratigraphic abbreviation T1), which occurs at the base of the Zechstein succession. It is underlain by immature, coarse to fine clastic, continental red beds of the Rotliegend, which locally (ore-proximal) feature an upper part of up to several meters that has been bleached and chemically reduced to a white or gray color, the so-called Grauliegend (Fig. 4; Plate 1C-D). In detail, the Weissliegend (Fig. 4) consists of eolian, fluvial, and, locally, marine sandstones that remained white due to insufficient oxidation and hematitic reddening, immediately after deposition (Ehling et al., 2008). The Grauliegend sandstones and conglomerates, in contrast, had originally undergone terrestrial oxidation and hematitic reddening but became bleached (i.e., chemically reduced) due to the flooding by the subsequently stagnant, euxinic Kupferschiefer Sea. Kupferschiefer mineralization, however, is, at best, strata bound but not stratiform and occurs in coarse clastic footwall sediments ("sand-ore"), in the Kupferschiefer black shale sensu stricto, in the hanging-wall marl and limestone, and locally even in Werra Anhydrite. However, regional variations include a higher portion of the ore being contained in black shale in the Mansfeld/Sangerhausen district (Plate 1B-C) and a higher portion of footwall and hanging-wall ores in the Spremberg/Weisswasser district (Kopp et al., 2008) and particularly in the Sieroszowice/Rudna mines (www.kghm.pl, 2012). Rydzewski (1964) illustrated the various vertical positions of the Cu mineralization in relationship to stratigraphy, which locally does not even feature any black shale of the Kupferschiefer but is still well mineralized (Fig. 5). The thickness of footwall and hanging-wall ore can range from several decimeters to locally up to 50 m (Fig. 6). It is important to note that the vertical thickness of the mineralization varies gradually from east to west, i.e., from Poland to Germany (Wedepohl and Rentzsch, 2006). The thickness of the mineralization is greatest within the Polish deposits (Fig. 6), is still predominantly hosted in footwall and hanging-wall rocks in the Spremberg/Weisswasser area, and is more closely associated with the Kupferschiefer black shale (although certainly not only) in the Mansfeld/Sangerhausen (Plate 1B-C) and Richelsdorf districts (Fig. 7). However, an exploration borehole at the village of Queck in the far southwestern Kupferschiefer district of Kellerwald/Frankenberg in the Hessian Depression (Fig. 1) revealed 36% of the low-grade mineralization to be hosted by footwall sandstone (Kulick et al., 1984).

The styles of mineralization range from disseminated (Plate 2A) and veinlet-hosted ore in the Kupferschiefer sensu stricto to disseminated pore fillings, vein-type (Plate 2B) replacement of cements (Plate 2C-F), diagenetic pyrite, fossil shells, feldspar within lithic clasts in the footwall conglomerates and sandstones (Plate 3A-E), and sulfate and thiosulfate minerals (Plate 3G- H), to irregularly disseminated and spotted carbonate-replacement-style mineralization in the hanging-wall limestone and in the overlying Zechstein Werra Anhydrite. The ore zones of the Kupferschiefer mineralization show a broad but systematic metal and ore mineral zonation with a marked redox front at the proximal side (Plate 1E-F). The various zones are (1) a hematitic (Fe^{3+}) zone (the Rote Fäule; Plate 1E-F), (2) a copper zone with ore minerals ranging from chalcocite to bornite to chalcopyrite, (3) a widely overlapping

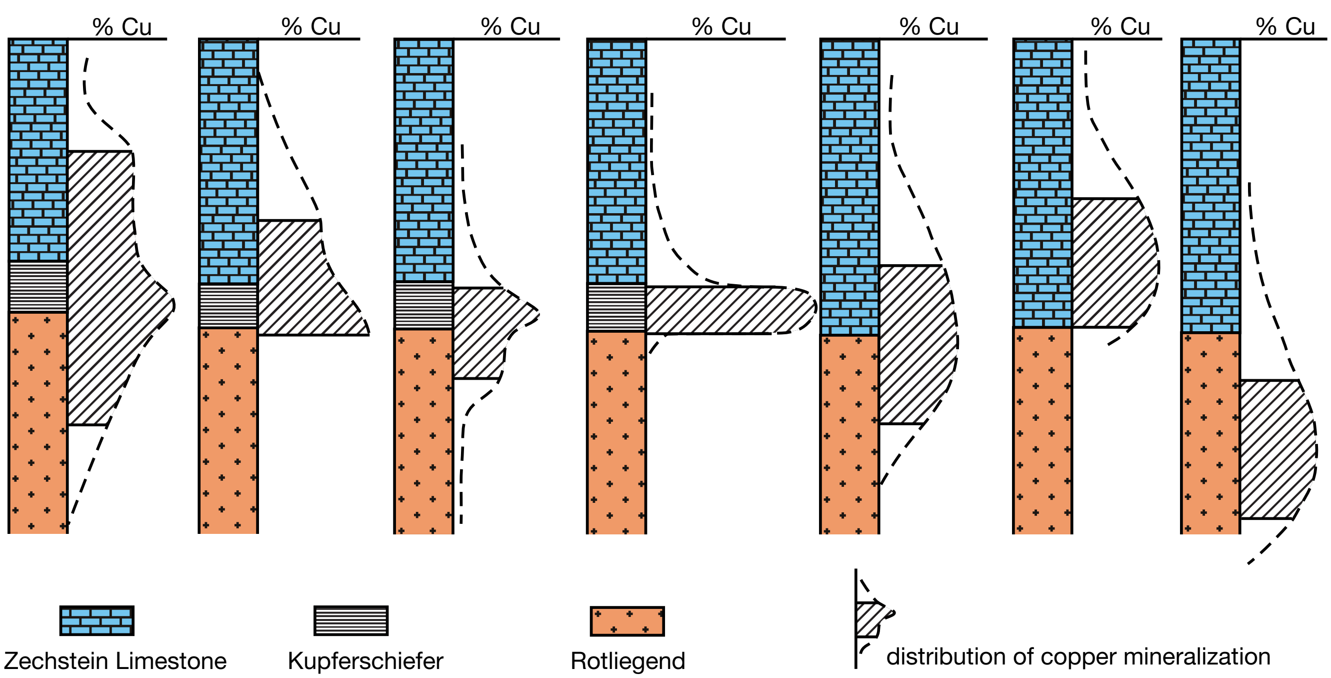

FIG. 5. Simplified lithologic profiles from various Polish deposits and boreholes, showing the different vertical positions of the copper mineralization, irrespective of the host rock (after Rydzewski, 1964). Note that the black shale of the Kupferschiefer is missing in several profiles.

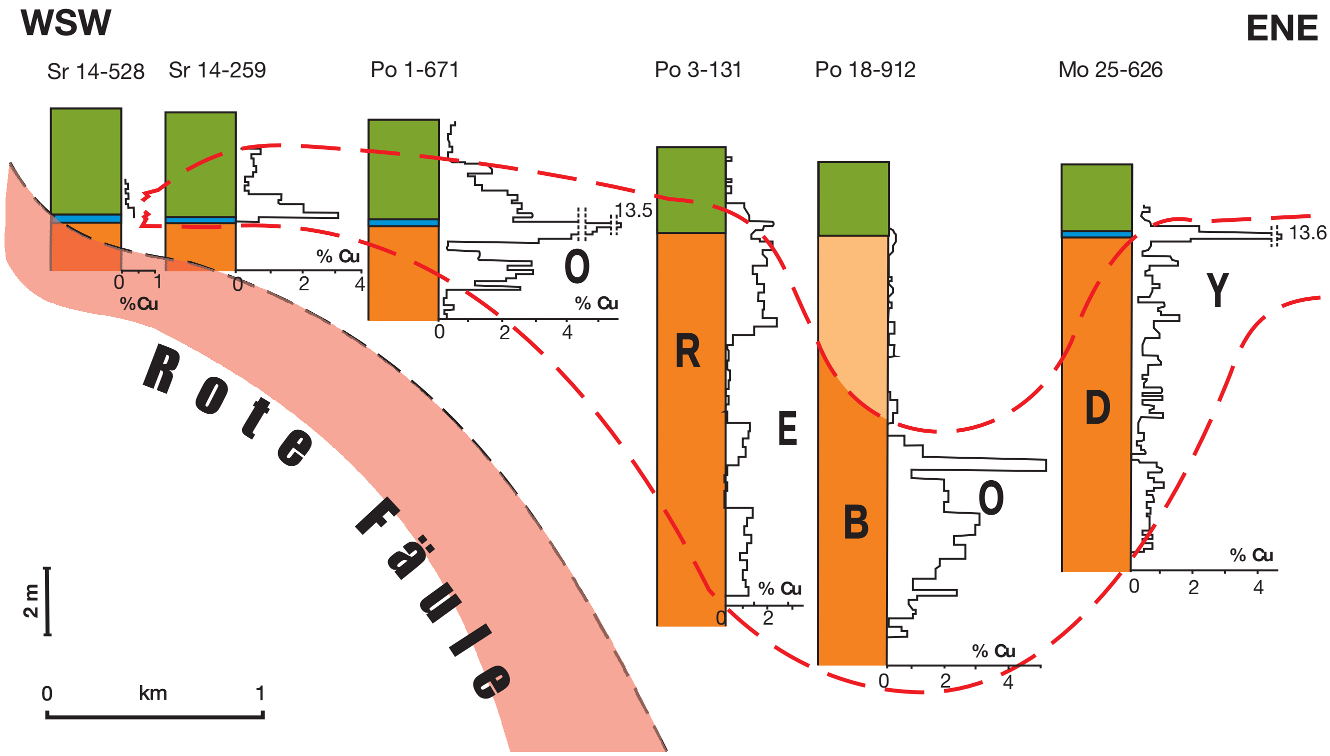

FIG. 6. Simplified cross section through the copper deposits of the Sieroszowice, Polkowice, Rudna, and Lubin mines within the Fore-Sudetic monocline, showing the thickness and strong vertical variation of the position of the ore zone relative to stratigraphy (adapted from Wodzicki and Piestrzyński, 1994).

lead-zinc zone with lead being more proximal and zinc more distal, and (4) an (Fe^{2+}) zone that is barren and contains only diagenetic pyrite. The first authors to recognize the full extent and relationship between lateral and vertical metal and ore mineral zonation were Rentzsch and Knitzschke (1968) and subsequently Rentzsch (1974). The laterally and vertically zoned mineralization front commonly documents a shallow oblique upward migration direction (Fig. 8). However, locally inverse zonation, i.e., downwardly zoned, has also been described (Kulick et al., 1984; Schmidt, 1987) and here a permeability controlled "roll over" effect of the migrating fluids has been assumed (Schmidt, 1987).

The transgressive to crosscutting nature of the metal and ore mineral zonation pattern, combined with the ubiquitous textures of ore minerals replacing preexisting early diagenetic pyrite, local carbonate cements, fossil shells, and even lithic clasts all document the late, epigenetic origin of the ore-grade mineralization. The redox front-related base and precious metal mineralizing system is thus a dynamic one that has ascended at a shallow, stratigraphy transgressing angle and has generally produced lobe-shaped metal and redox zones. The resulting style, geometry, texture, and grade of mineralization are strongly controlled by the respective host rocks, i.e., conglomerate and sandstone of the footwall, pyrite-bearing, $C_{organic}$-rich black shale of the Kupferschiefer sensu stricto, and marl, limestone, and locally even evaporitic rocks of the immediate and higher hanging wall. The metalliferous brines have interacted with early diagenetic pyrite in a systematic, dynamic, step-wise replacement process that caused the wide metal and ore mineral zonation pattern, which can be exemplified by the following general order of gradual replacement:

(preore) pyrite → sphalerite (+ galena) → galena (+ sphalerite) → chalcopyrite/bornite → chalcocite → hematite (the secondary Rote Fäule redox front).

It is important to note that, where present, a narrow precious metal-rich zone straddles the redox front and the highest values of gold and PGEs occur very close to the redox boundary (Fig. 7). The precious metals can occur locally in Cu-rich strata on the chemically reducing side (Walther et al., 2009) or on the immediately adjacent oxidized side of the redox front (Piestrzyński et al., 2002). The broadly zoned strata-bound to gently crosscutting mineralization described above has locally, in turn, been overprinted by even later, vein-type mineralization, e.g., in the German Spessart and Rhön areas (Friedrich et al., 1984; Fig. 1). Here, the subsequent mineralization was rich in As, Co, and Ni. Rich vein-type mineralization has also been described from several Polish deposits (Oszczepalski, 1999). Abundant ore petrographic studies have been carried out on the Kupferschiefer mineralization and these focused on both the broadly zoned and on the vein-type mineralization (e.g., Rentzsch and Knitzschke, 1968; Kulick et al., 1984; Mayer and Piestrzyński, 1985; Oszczepalski, 1999). More than 80 ore minerals have been described in several publications from Kupferschiefer ores in Poland, most of them are summarized in Piestrzyński (2007). Particularly the paragenesis of the secondary oxidation system, which locally contains native gold (Plate 3F) but also several noble metal alloys, tellurides,

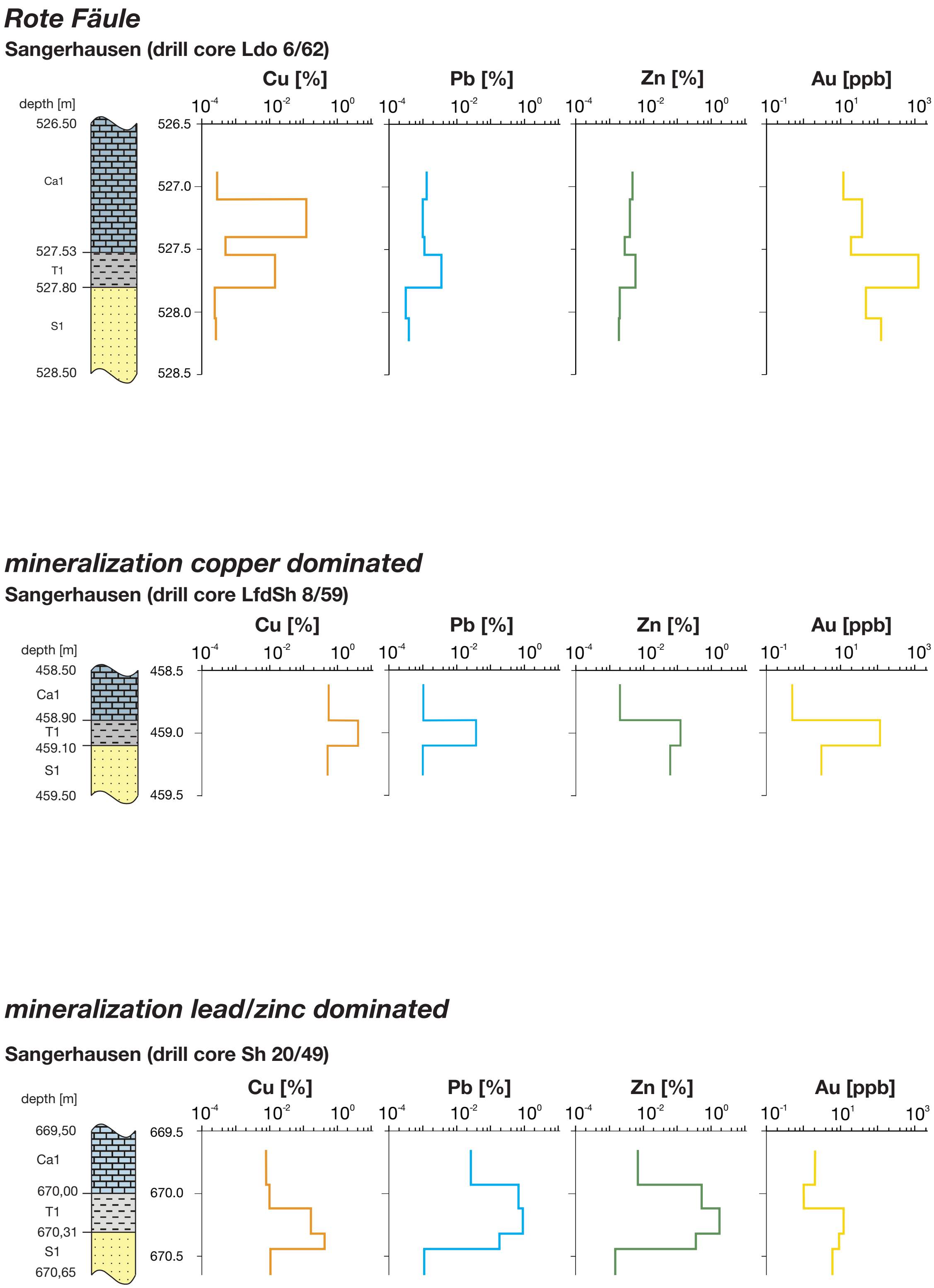

FIG. 7. Typical lithologic profiles with metal distribution from Sangerhausen (this page) and Spremberg, Germany, and various locations of the Fore-Sudetic monocline, Poland (following two pages). Note that Cu-mineralized intersections in Polish mines are not routinely assayed for precious metals. However, the precious metal zones occur characteristically between the Cu zone and the secondary oxidation of the Rote Fäule.

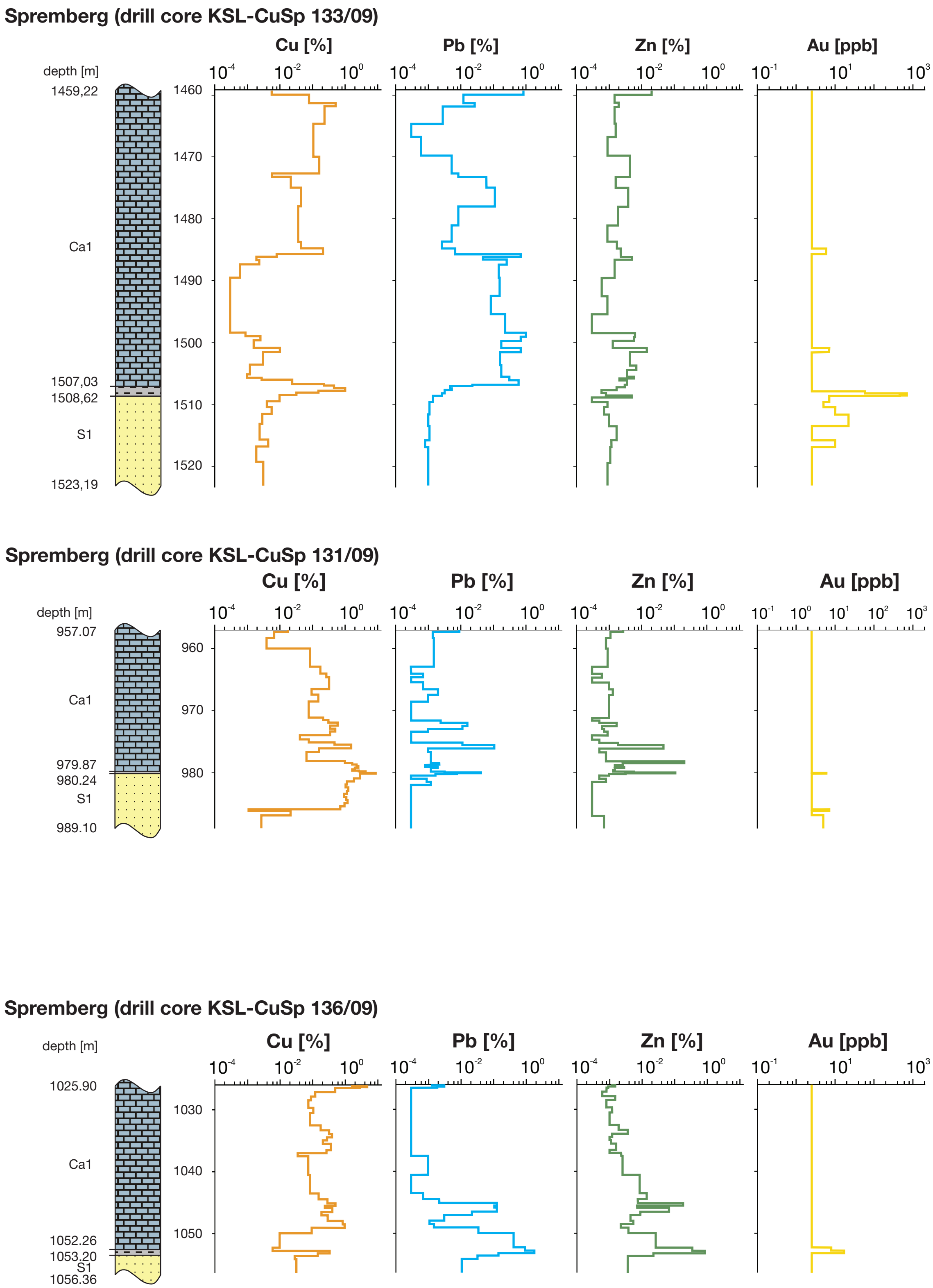
Spremberg (drill core KSL-CuSp 133/09)
Cu [%]
Pb [%]
Zn [%]
Au [ppb]
depth [m]
1459,22
Ca1
1507,03
1508,62
S1
1523,19
Spremberg (drill core KSL-CuSp 131/09)
Cu [%]
Pb [%]
Zn [%]
Au [ppb]
depth [m]
957.07
Ca1
979.87
980.24
S1
989.10
Spremberg (drill core KSL-CuSp 136/09)
Cu [%]
Pb [%]
Zn [%]
Au [ppb]
depth [m]
1025.90
Ca1
1052.26
1053.20
S1
1056.36

FIG. 7. *(Cont.)*

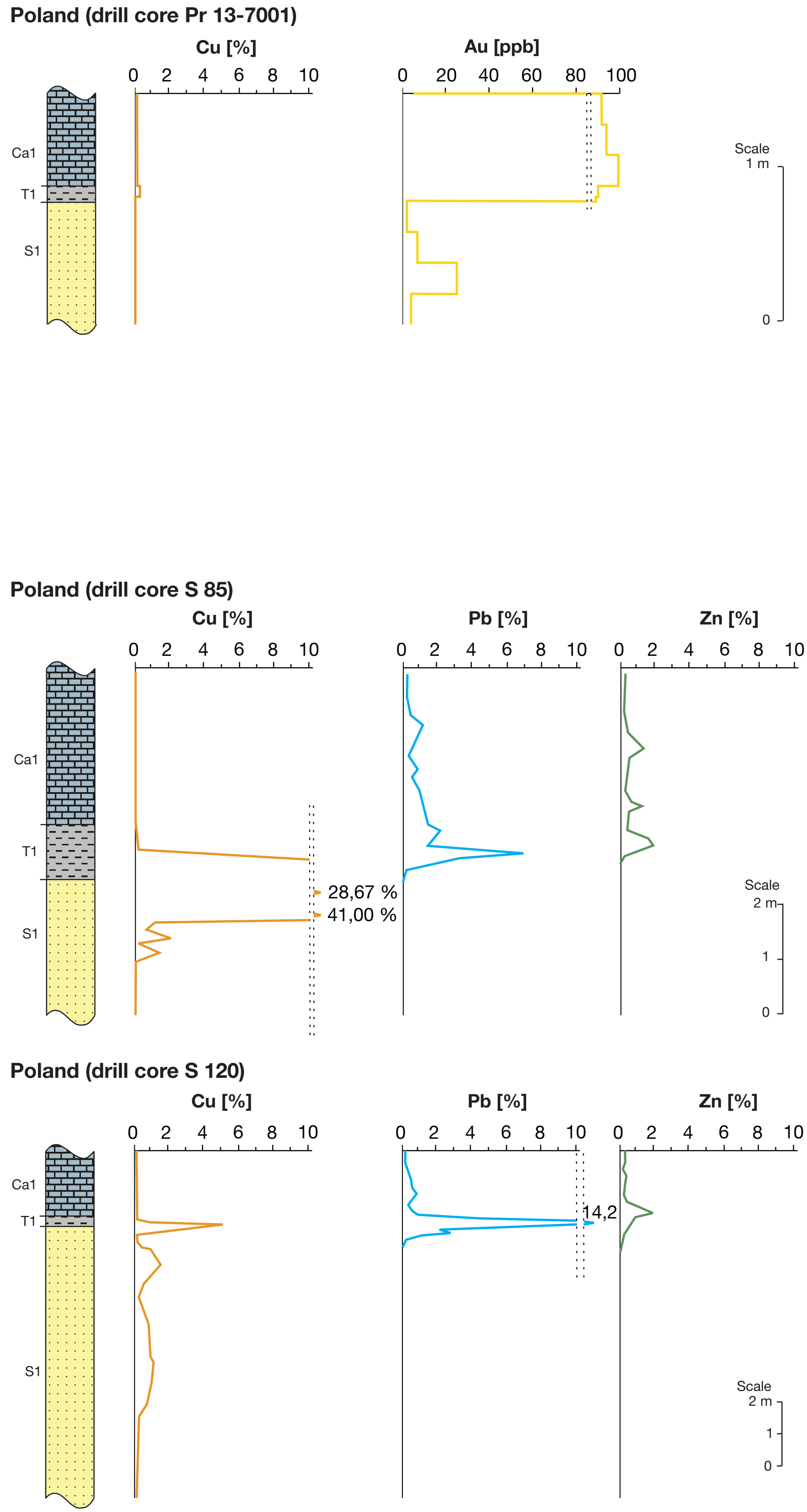
Poland (drill core Pr 13-7001)
Cu [%]
0 2 4 6 8 10
Au [ppb]
0 20 40 60 80 100
Ca1
T1
S1
Scale
1 m
0
Poland (drill core S 85)
Cu [%]
0 2 4 6 8 10
Pb [%]
0 2 4 6 8 10
Zn [%]
0 2 4 6 8 10
Ca1
T1
S1
28,67 %
41,00 %
Scale
2 m
1
0
Poland (drill core S 120)
Cu [%]
0 2 4 6 8 10
Pb [%]
0 2 4 6 8 10
Zn [%]
0 2 4 6 8 10
Ca1
T1
S1
14,2
Scale
2 m
1
0

FIG. 7. *(Cont.)*

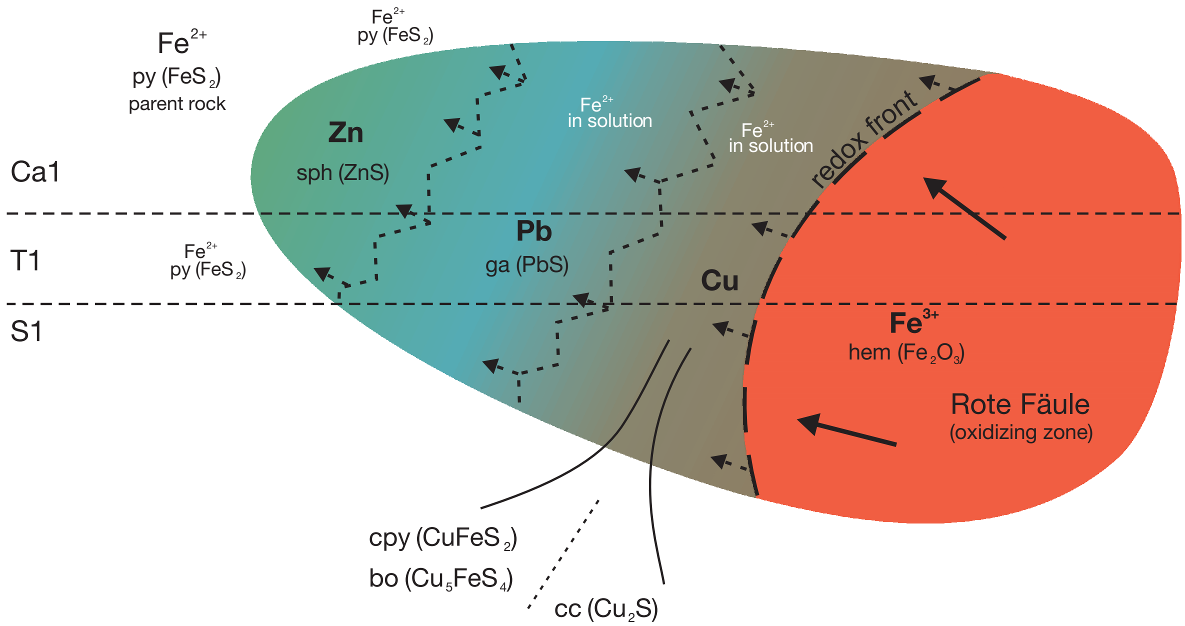

FIG. 8. Schematic illustration of metal and mineral zonation of the epigenetic Kupferschiefer system, transgressive to the stratigraphic units. The zonation and thus the interpreted fluid migration direction is more lateral in the German mining districts (e.g., Richelsdorf) and more vertically ascending in the Polish mining districts.

selenides, arsenides, and arsenates, has been described by Piestrzyński et al. (2002), Pieczonka and Piestrzyński (2008), and Pieczonka et al. (2008).

In Poland, mineralization of sandstone ore has typically replaced preexisting carbonate cement (Plate 2C-F). Mineralization occurs also as fine disseminations in all lithotypes forming micronests and mineralized veinlets. Locally, base metal sulfides have replaced clayey-carbonate cement, carbonate lamina and organogenic remnants such as shells of foraminifera (Plate 3C), as well as sulfate nodules and francolite, a carbonate-rich variety of fluorapatite. It is important to note that the base metal mineralization has commonly replaced preexisting (early diagenetic) pyrite (Plate 3A). A particularly instructive example from black shale-hosted ore from the Mansfield area is shown in Plate B, where the individual crystallites of framboidal pyrite have been replaced or partly replaced by chalcocite, documenting clearly the epigenetic origin of the copper-bearing ore paragenesis. Late emplacement of the Cu mineralization has not only affected preexisting sulfide minerals but also carbonate cements in clastic footwall rocks and even lithic (silicate) clasts or parts thereof (Ludwig and Rentzsch, 1967; Banas et al., 1982; Walther et al., 2007). As one particularly instructive example from the Schnepfenbusch mine, Richelsdorf district (Fig. 1), chalcopyrite-chalcocite has replaced parts of and even entire feldspar clasts in footwall conglomerate (Plate 3D-E) below the Kupferschiefer sensu stricto.

Mine Geology—the Example of the Lubin-Głogów Deposit

The present review does not allow an in-depth description of each Kupferschiefer deposit or mine. The present authors have thus concentrated on the particularly characteristic Lubin-Głogów deposit, located within the Fore-Sudetic monocline.

The deposit lies on the southwestern corner of the Fore-Sudetic monocline and is limited tectonically to the south by basement rocks of the Fore-Sudetic block (Figs. 2, 3). The Fore-Sudetic monocline is composed of three major geologic units, separated by unconformities. The first unit is the crystalline basement composed of crystalline schist, graywacke, hornfels, granodiorite, and gneiss of Precambrian and upper Paleozoic age and of Carboniferous sediments (Kłapciński et al., 1975; Tomaszewski, 1978). This basement unit is overlain by generally NE-dipping Permian, Triassic, and Cretaceous sediments deposited unconformably on the southern and northern parts of the Fore-Sudetic monocline and the Fore-Sudetic block (Konstantynowicz, 1971). Within the mining districts, the second unit comprises Rotliegend, Zechstein, and Buntsandstein strata covered unconformably by Paleogene, Neogene, and Quaternary sediments. Farther north, the Triassic units also comprise Middle and Upper Triassic rocks, which are missing in the mining districts.

The Rotliegend is subdivided in the Lower and Upper Rotliegend. The Lower Rotliegend is composed of red conglomerates and sandstones intercalated with shales and volcanic effusive rocks and tuffs (Ryka, 1981). The Upper Rotliegend comprises brownish-red sandstones, shales, conglomerates, and white sandstones at the top. The chrono- and biostratigraphic units "Autunian" and "Saxonian" of older literature are now obsolete. The overall thickness of the Rotliegend sedimentary red-bed succession reaches 300 m and that of the white Weissliegend sandstones 40 m. The volcanic rocks are up to 1,000 m thick near the German border.

The boundary between Rotliegend and Weissliegend sandstones is still discussed since the uppermost part was partly reworked during the transgression of the Zechstein Sea. The Zechstein Conglomerate is genetically classified as the basal marine sediment (Oszczepalski, 1999) although the uppermost part of the Rotliegend sandstone was decolorized during deposition of the Kupferschiefer black shale under euxinic conditions and with chemically reducing basin and pore fluids, resulting in the so-called Grauliegend. For practical reasons, the Kupferschiefer is regarded by the miners as the basal unit of the Zechstein (Kłapciński, 1971), which corresponds with the Rotliegend/Zechstein boundary of Germany. However, a carbonate horizon up to 30 cm thick occurs below the Kupferschiefer in the eastern part of the area. This unit is referred to as Boundary Dolomite, an equivalent of the Basal Limestone occurring in the North Sudetic trough (Krasoń, 1964) and the so-called "Mutterflöz" (mother seam) of the marginal Kupferschiefer facies of Germany. The Kupferschiefer is overlain by the Zechstein Limestone (Fig. 4), which is up to 110 m thick at the eastern flank of the deposit. The Zechstein Limestone, in turn, is overlain by the Lower Anhydrite and, in the western portion of the deposit, by the oldest rock salts and by the Upper Anhydrite strata (Krasoń, 1964; Tomaszewski, 1978), which can reach up to 130 m of evaporites. The upper units of the Zechstein strata are developed in typical evaporite cyclothems.

Lithology of the ore horizon

The mineralization, typically but inadequately referred to as "ore horizon," is hosted by several lithologic units and these comprise from bottom to top: white sandstones (Weissliegend), Boundary Dolomite, and the Kupferschiefer sensu stricto. In the mining area, the average thickness of the Weissliegend sandstones is approximately 18 m, although it can locally range from a few meters to 35 m. The white sandstones occur in a typical arenitic variety composed of quartz, feldspar, and lithic fragments of crystalline rock, commonly angular grains typically featuring cements composed of clay, carbonate-clay, clay-carbonate, anhydrite, and carbonate-clay-sulfide. The uppermost part of the white sandstones is more carbonaceous. Where mineralized, the Cu content of the sandstone ore can range from 0.7% Cu in disseminated impregnation-type ores to up to 30% Cu in massive replacement types of ore (cf. Plate 2C). The average grade of sandstone ore is 1.8% Cu. Lenses of anhydrite-cemented sandstones occur commonly in thicker and thus morphologically elevated parts of the Weissliegend sandstones, which represent coastline-parallel dunes or sandbars. Here the sandstones are usually barren with minor pyrite, marcasite, galena, sphalerite, and covellite only. Massive chalcocite and covellite sandstone ores are common where situated spatially adjacent to anhydrite-cemented sandstone bodies.

The Boundary Dolomite is developed in the eastern part of the deposit as a continuous and solid layer but occurs only locally as lenses in the western part. The Boundary Dolomite is developed as a bioclastic mudstone and locally as packstone and grainstone, rich in skeletons of foraminifers, brachiopods, and ostracod skeletons, and ore grades range from 1.1 to 12% Cu.

The Kupferschiefer at the Lubin mine is a typical metal-bearing black microlaminated shale composed of illite, mixed-layer clays, dolomite, organic matter, sulfides, calcite, and minor phosphates, gypsum, anhydrite, and clastic materials, for example, quartz, different types of mica and titanium oxides. From bottom to top the following mineralogical varieties have been recognized: pitchy shale, (clay-organic), clay-dolomitic, dolomitic-clay, and clay-calcareous. The thickness varies from absent to 0.7 m in the mining area with an average of 0.27 m. The average total organic carbon (TOC) content is 7.34% and the average Cu grade is 10%, locally ranging from a few percent up to maximum grades of 35% Cu. Locally some portions of the Kupferschiefer are rich in foraminifer and ostracod skeletons.

Hanging-wall carbonate rocks overlying the Kupferschiefer (i.e., Z1: Zechsteinkalk to Ca1-Werra Anhydrite) are typically fine-crystalline dolomite, characterized by a highly variable thickness ranging from a few meters up to 110 m. Generally, this unit ranges from several meters only in the western part of the mine to 40 m in the eastern part. From bottom to top three lithotypes can be distinguished: clayey dolomite, dolomite containing clay-rich laminae, and calcareous dolomite. In detail, this unit is composed of mudstone, bioclastic calcareous dolomite, packstone, and wackestone (Peryt, 1978). Some modifications comprise up to 35% of clay minerals and minor anhydrite, gypsum, and quartz both as clasts and authigenic. The copper content of this unit ranges from 0.7% to several percent.

Local tectonic setting and structural features of the Lubin deposit

The Lubin deposit is situated in the southeastern part of the Fore-Sudetic monocline, the middle part of the Odra fault zone, adjacent to the Fore-Sudetic block (Fig. 2). In general, all Permian and post-Permian sedimentary rocks of the Fore-Sudetic monocline dip shallowly toward the northeast although the dip can be locally as much as 25°. Four different fault systems have been identified in the mining area, trending NW-SE, W-E, N-S, and probably NNW-SSE. The latter fault system is represented by small degrees of strike-slip low-angle dislocations, fractures developed in brittle sandstone, and folds developed in ductile shale. Low-angle fissures and cracks represent the youngest tectonic deformational event. Fissures developed between the calcitic and dolomitic varieties of the Kupferschiefer are commonly filled by copper sulfides.

Mineralization at the Lubin mine

The Lubin copper deposit is located at the redox interface that crosscuts, peneconcordantly, both Rotliegend and Zechstein strata, including white sandstone, Kupferschiefer black shale (Plate 2E), and Werra clayey dolomite (Wodzicki and Piestrzyński, 1994). The Lubin deposit features three distinctly different lithologic host-rock sections (Fig. 7), one of which is the "classic" section. The second type is an oxidized host-rock section, with secondary red (hematitic) spots and patches (Plate 1E), which locally overprint footwall sandstone, Kupferschiefer black shale, and hanging-wall clayey dolomite. The third host-rock section is referred to as "anhydritic," where the Kupferschiefer is missing and the ore is hosted by anhydrite-cemented sandstone, with mineralized sections locally up to 68 m in thickness. Subordinate host rocks are the "boundary dolomite" and organogenic limestone. The orebody geometry and style of mineralization has been internally classified as (1) stratiform with one horizon, (2) stratiform with two horizons, (3) strata-bound nests and lenses, and (4) strata-bound but irregular. The ore minerals occur commonly disseminated, but zones with particularly high Cu contents feature massive (Plate 2C-D), lensoidal, nested, spotted, and vein-type ores (Plate 2B). A major system of secondary oxidation has been identified in the southwestern part of the deposit (Wodzicki and Piestrzyński, 1994; Piestrzyński at al., 2002).

Precious Metals in the Kupferschiefer Ores

Germany

Both research and analytical data on the occurrence and contents of gold and precious metals in German Kupferschiefer ores are scarce. Hammer et al. (1990) presented limited analytical data and gave concentration ranges for the main base metals (Cu, Pb, Zn) as well as for gold in the Kupferschiefer sensu stricto of the Sangerhausen syncline. These authors differentiated between several metallogenic zones and gave minimum and maximum values for the most common elements. Highest gold values were reported from the zone of secondary oxidation (Rote Fäule), locally with maximum gold values of 7,500 ppb. However, maximum gold concentrations within the copper zone were 275 ppb Au and 85 ppb Au in the Pb-Zn zone (Hammer et al., 1990). It is important to note that these results were published under the former East German state-controlled mining regime, when information on precious metals was treated as highly confidential. As a consequence, the given maximum and minimum ranges of precious metal contents, without detailed and reproducible information on sample sites and stratigraphic positions, were only of limited use.

The Cu-mineralized regions of the Kupferschiefer in southwestern Thuringia and southern Hessen contain precious metals in concentrations, which are commonly below or close to the detection limit. Here, gold shows maximum values of about 71 ppb, which is slightly elevated compared to a background value of 35 ppb, given for typical black shale by Kane et al. (1990). The concentrations of PGEs in samples from Thuringia and Hessen are commonly below the detection limit and show no significant enrichment, neither in Kupferschiefer sensu stricto, nor in adjacent strata or the secondary oxidation zone of the Rote Fäule.

Investigation of drill core samples from the Sangerhausen district south of the Harz Mountains revealed two locally restricted regions with elevated Au and PGE contents (Borg et al., 2005). The elevated precious metal values occur in a narrow fringe between the copper-rich Kupferschiefer and the Rote Fäule zone (Fig. 7). Follow-up research on drill core from the Sangerhausen district, south of the Harz Mountains, identified elevated gold concentrations of up to 1,200 ppb. The highest Au concentrations were detected in rocks that had undergone secondary oxidation (Rote Fäule) and occur spatially immediately below the zone with the highest copper contents within this borehole. Systematically elevated gold values (120–200 ppb) as well as slightly elevated platinum concentrations (up to 60 ppb) occur in samples that are situated adjacent to areas with high copper grades (Walther et al., 2009).

A small range of recently analyzed Cu- and Zn/Pb-rich ore samples of footwall sandstone, Kupferschiefer black shale, and hanging-wall limestone from the Mansfeld district generally contain only background concentrations of Au and PGEs (see data in digital Appendix). Pt and Pd concentrations are generally less than 4 ppb and Au concentrations below 5 ppb, with few samples containing between 20 and 90 ppb Au. However, initial sampling of historic, low-grade ore dumps has revealed significantly higher Au and—to a lesser extent—Pt and Pd concentrations in a first sample suite of sieved fractions of partly weathered and decomposed dump material. Sieved fractions of particles larger than 1.6 cm feature low Au, Pt, and Pd concentrations, indistinguishable from the concentrations reported above. The nine sieved fractions between 1.6 cm and the clay fraction (<63 μm) all contain between 300 to 800 ppb Au, 17 to 51 ppb Pt, and 9 to 30 ppb Pd (digital Appendix). The Au contents correlate largely with Cu contents and perfectly with V contents of the samples, the latter element being a reliable proxy for the $C_{organic}$ content. Although these new results document local and irregular precious metal mineralization in the Mansfeld district, further research is required to characterize the siting of the Au and PGE mineralization in detail.

A recent ore mineralogical investigation of the precious metal and selenides mineralization at Spremberg-Graustein has identified a hydrothermal late epigenetic ore paragenesis (Kopp et al. 2012). According to these authors, the mineralization has probably formed at relatively high temperatures between 230° and 290°C and has been compared to mineralization in Silesia in Poland as well as in the Harz Mountains and in the Richelsdorf district, Germany.

Recent exploration of a Kupferschiefer target area in the Spremberg/Weisswasser district by Kupferschiefer Lausitz GmbH at the German border with Poland has provided new analytical data from three diamond drill holes, which are between 1,007 and 1,545 m deep (Fig. 7). The analytical data include a full set of assays for precious metals (see digital Appendix). Generally, the precious metal contents are below detection limit (here 2.5 ppb). However, several analyses in all three boreholes show precious metal contents that are slightly above the detection limit, in the range of 10 to 20 ppb. Higher precious metal values occur in one of the boreholes (borehole Cu Sp 133/09), where the lowermost part of the Kupferschiefer has been oxidized (Rote Fäule). Here, assays from the basal 40 cm of Kupferschiefer yield up to 648 ppb Au, up to 318 ppb Pd, and up to 60 ppb Pt. The upper, nonoxidized part of the Kupferschiefer black shale, overlying the oxidized, precious metal-bearing Kupferschiefer contains up to 1% Cu and up to 100 ppm Ag, with elevated Pb values (<1%) in the Zechstein limestone above.

In summary, the spectacular maximum Au values (up to 7.7% Cu and 7,300 ppb Au) reported by Hammer et al. (1990) for the (East) German Kupferschiefer appear to have represented individual spots of mineralization, which have not been analytically reproduced or localized. Precious metal analyses of most Cu-mineralized districts of the German Kupferschiefer (Borg et al., 2005; Walther et al., 2009; and present data) show rather unspectacular precious metal contents, with the exception of a spatially restricted area in the Sangerhausen district, some erratic anomalously high gold values in random samples from low-grade ore dumps in the Mansfeld district, and one borehole in the Spremberg/Weisswasser exploration area. However, all of the anomalous Au contents reported from regionally and stratigraphically well-documented sampling sites occur in rocks that have undergone secondary oxidation (Rote Fäule) and/or near the main copper zone, close to the epigenetic redox front (Borg et al., 2005; Walther et al., 2009). Although the maximum concentrations of gold in the German Kupferschiefer are far below the values given for the Polish Kupferschiefer, for example, by Piestrzyński and Sawłowicz (1999), the geological and geochemical position of the precious metal mineralization appears to be similar in all regions. The zone of anomalous gold (and PGE) mineralization is generally situated in a geochemical zone that straddles the epigenetic redox front of the Rote Fäule.

Numerous other metals, besides Au and PGEs, have been recovered from the German Kupferschiefer. These metals include Ag, Ni, and Co, the latter being particularly rich where late crosscutting veins have upgraded earlier phases of mineralization. The topographically elevated gossans associated with such Co-Ni-rich ores have been baptized "Rückenvererzung" or "Kobalt-Rücken" (German for cobalt-ridge). These vein systems locally follow reactivated basement structures as shown by Friedrich et al. (1984). Other than Cu, Pb, Zn, Ag, Au, Pt, Pd, several other metals such as Co, Ni, Mo, Se, Re, V, Cd, Tl, and I have also been industrially recovered by the processing plants of the Mansfeld and Sangerhausen districts (Eisenhuth and Kautzsch, 1954). However, most of the metals were produced in relatively small quantities and information on grades and tonnages (or rather kilograms) was highly restricted during state mining in the former GDR. It is interesting to note that the recovery of most of these elements was even acknowledged at the time to have been uneconomic (Eisenhuth and Kautzsch, 1954, p. 44). These authors had already pointed out that a private enterprise could neither have developed the necessary recovery processes nor could they have recovered these metals economically. The metals Ag, Au, Pd, Pt, and Se were recovered from electrolytic (anode) mud, accumulated from the dissolution of huge quantities of copper anodes (Eisenhuth and Kautzsch, 1954). One might argue that, although totally uneconomic at the time, the East German state mining and recovery scheme was an early way of sustainable recovery of the maximum range of metals from the Kupferschiefer ores.

Poland

Gold in Kupferschiefer ores from Lubin was mentioned first by Kucha (1982) but economic concentrations of gold (Plate 3F) have been studied systematically first by Piestrzyński et al. (2002). A comprehensive summary of the gold mineralization within the Kupferschiefer ores with abundant photo documentation and analytical data is given by Pieczonka et al. (2008) and the reader is referred to this publication. Overall, the level of documentation and investigation of the precious metal mineralization within the Kupferschiefer metallogenic system is more advanced in Poland compared to Germany.

The Polish Kupferschiefer ores are known for significantly elevated concentrations of gold, with up to 2,500 ppb Au in the Lubin-Głogów district as well as anomalous concentrations of PGEs of up to 186 ppb Pt and 88 ppb Pd in the Lubin area (e.g., Kucha and Przyłowicz, 1999; Piestrzyński and Sawłowicz, 1999; Oszczepalski et al., 2002). Particularly spectacular values for gold (up to 3,000 ppm), Pt (up to 370 ppm), and particularly for Pd (up to 1,000 ppm) have been reported from the 0.5-m-thick Kupferschiefer sensu stricto of the Lubin West orebody (Kucha, 1982) but subsequent studies were unable to reproduce these results at the same sites. More recently, Piestrzyński et al. (2002) documented up to 94.9 ppm Au in the Polkowice-Sieroszowice mine with a 0.22-m-thick horizon yielding 2.25 ppm Au, 0.138 ppm Pd, and 0.082 ppm Pd.

The Metallogenic Role of Carbon, Sulfur, Iron, and Oxygen

Organic carbon is one of the most important constituents of the Kupferschiefer mineralizing system. The highest concentrations of TOC occur in the black shale of the Kupferschiefer sensu stricto (Tokarska, 1971; Sawłowicz, 1989). The organic matter consists predominantly of the marine type of kerogen II, followed in quantity by kerogen I, with kerogen III occurring in minor amounts only (Kirst, 1994; Więcław et al., 2007).

The average content of TOC in footwall sandstone is 0.4%, in the Kupferschiefer black shale 7.5 to 8.0%, and 0.72% in hanging-wall dolomite in Poland (Kucha and Mayer, 2007; see also Table 1A in digital Appendix). The present-day TOC content depends on the state of oxidation of the Kupferschiefer. The Kupferschiefer from a primary, reduced environment (R zone) is characterized by a high TOC content and high hydrogen index (HI index; mg_{HC}/g_{TOC}) and low oxygen index (OI index; mg_{CO_2}/g_{TOC}). In contrast, the red, hematitic secondarily oxidized Kupferschiefer is characterized by small TOC contents and high HI and OI indices (Pieczonka et al., 2008). In Poland, the Kupferschiefer zone with the lowest TOC (below 0.1%) coincides spatially with high precious metal contents (Piestrzyński et al., 2002). A catalytical role of U for the fixation of precious metals, as pointed out by Kucha and Przybyłowicz (1999), can be neglected due to its small content in the red, oxidized variety of the Kupferschiefer (Pieczonka et al., 2008).

The diagenetic maturation of organic matter and particularly the influence of a magmatic intrusion on the extent of isomerism in acyclic isoprenoids have been studied by Diedel and Püttmann (1988) and Püttmann and Eckardt (1989) for the Pb-Zn–mineralized Kupferschiefer of the Lower Rhine embayment in northwestern Germany. These authors identified a cryptic alteration halo, defined by anomalous aromatic hydrocarbons, that is related to a regional intrusion-related thermal event. Although some studies on the organic geochemistry have been carried out on parts of the Polish Kupferschiefer (Püttmann et al., 1988, 1989), this method still holds considerable potential for other parts of the Kupferschiefer metalliferous belt.

It goes without saying that sulfur in primary and secondary sulfide minerals, as well as in sulfate minerals, is another crucial constituent in the Kupferschiefer metallogenic system. The Cu sulfides are characterized by light sulfur, ranging from –10 up to –45‰ σ^{34}S (Piestrzyński, 2007). Several sulfur sources have been identified and these include early diagenetic irregular, cube-shaped, and partly framboidal pyrite, the latter being commonly interpreted as bacteriogenic (e.g., Wodzicki and Piestrzyński, 1994; Oszczepalski, 1999). Other sources comprise organic sulfur and sulfates, as well as various sulfoxy species, and extrinsic H_2S (Oszczepalski, 1999).

Abundant iron (ca. 3%) was precipitated throughout the Zechstein Sea during deposition of the black shale along the former shore line. The iron is largely present as framboidal iron sulfides but also as ankerite (Sun and Püttmann, 1997). The presence of ankerite in the immature Kupferschiefer from the Lower Rhine basin in northwestern Germany indicates that the availability of iron has not been the limiting factor for the formation of iron monosulfides as a result of bacterial sulfate reduction during sedimentation. The sulfur content of the organic matter is consequently very low.

In Cu-mineralized areas, the secondary oxidation front (Rote Fäule) caused the dissolution of pyrite and other metal sulfides, resulting in a metal-rich solution at the front or even in front of the Rote Fäule and a metal-poor residual rock behind the redox front. The mobilization and transport of metals in solution can be easily explained by the leaching of the highly oxidized Rote Fäule. However, the process of precipitation of metals from these solutions is more complex and requires abundant reducing equivalents, which can be provided either by the presence of sulfidic sulfur or by hydrocarbons, which commonly co-occur in black shale such as the Kupferschiefer sensu stricto. The contact of the oxidizing Rote Fäule with the reducing Kupferschiefer caused redox reactions leading to the precipitation of the metals dissolved in the fluid.

The processes responsible for metal precipitation in the Kupferschiefer and adjacent strata are summarized in Figure 9. During sedimentation and early diagenesis, bacterial sulfate reduction (BSR) will provide hydrogen sulfide, which reacts with simultaneously generated Fe^{2+} to precipitate iron monosulfides. These monosulfides are subsequently transformed to framboidal pyrite by reaction with an excess of hydrogen sulfide, as shown by laboratory experiments at a temperature above 60°C (Butler and Rickard, 2000). According to Machel et al. (1995) BSR is restricted to sedimentary environments at temperatures below 80°C, although some hyperthermophilic sulfate-reducing bacteria have been discovered, which can live at temperatures as high as approximately 110°C. BSR is well known to occur in tailings of former base metal mining areas (i.e., Parys Mountain, Anglesey, Wales), where Cu sulfides with a chalcopyrite-like structure have been detected in anoxic black mud (Parkman et al., 1996).

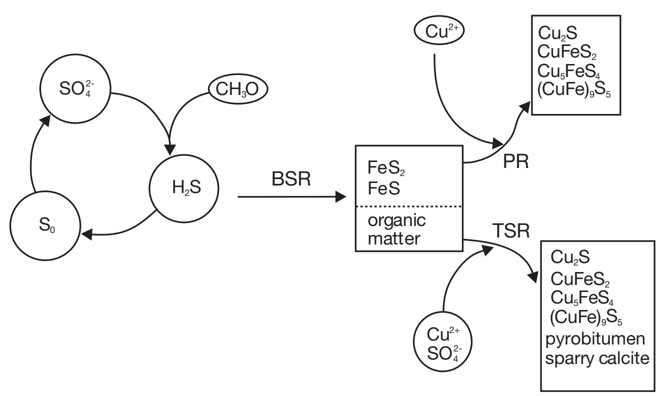

FIG. 9. Proposed model for the formation of ore sulfides in Kupferschiefer (adapted from Sun and Püttmann, 1997). BSR = bacterial sulfate reduction, PR = pyrite replacement, TSR = thermochemical sulfate reduction.

Incorporation of high amounts of Cu into the iron monosulfides already during BSR is unlikely since this would require abundant Cu to be dissolved in the water column or the pore water. Cu was shown to be toxic to sulfate-reducing bacteria (SRB) at concentrations as low as 30 μmol/L (Kumar Sani et al., 2001). Therefore, other processes have to be considered for the formation of Cu-rich iron sulfides in sedimentary environments. Cowper and Rickard (1989) have demonstrated in laboratory experiments at temperatures <100°C a rapid conversion of pyrrhotite ($Fe_{0.9}S$) to chalcopyrite ($CuFeS_2$) under acidic conditions. In similar experiments with an excess of Cu in solution, Zies et al. (1916) had shown already in 1916 that chalcopyrite was further replaced sequentially by bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S), native Cu, and Cu oxides (Zies et al., 1916). However, the extent of pyrite replacement for the enrichment of Cu in sediments is limited by the amount of reduced sulfur provided by the sedimentary pyrite. In Kupferschiefer provinces such as the Sangerhausen district the amount of Cu can locally increase in the bottom section of the black shale unit to values up to 20% and is characterized by a concomitant increase of the sulfidic sulfur, clearly exceeding the amount originating from BSR. This additional sulfur, required for precipitation of large amounts of base metals (mainly Cu), originated from thermochemical sulfate reduction (TSR), which is possible at temperatures above 80° to 100°C according to Machel et al. (1995). Four lines of evidence are available for the additional metal accumulation by TSR: (1) during TSR, organic matter is partly oxidized to carbon dioxide, which is precipitated as saddle (sparry) dolomite and/or calcite; (2) the remaining organic matter is converted to solid bitumen (pyrobitumen), which is microscopically visible; (3) the H_2S generated by TSR is isotopically heavier compared to H_2S generated by BSR; and (4) the carbon isotope composition of the diagenetic saddle dolomite/calcite is lighter than that of sedimentary carbonates. All of these effects have been observed in highly mineralized Kupferschiefer from the Sangerhausen area (Sun und Püttmann, 1997; Bechtel et al., 2001). The occurrence of TSR as the final step of base metal enrichment is consistent with the proposed temperatures of up to 130°C that affected the Kupferschiefer in the Sangerhausen area.

Metal Sources of the Kupferschiefer Ores

Chasing the metal sources of ore deposits can be a speculative venture since the original source rocks are commonly inaccessible due to erosion, tectonic removal, or deep burial. However, several regional features of the location and distribution of the ore districts within the Kupferschiefer basin are worth discussing in some detail. Potential source rocks of sediment-hosted strata-bound copper deposits can either be found in the internal (volcano-) sedimentary basin fill, derived from an eroded hinterland, or in external, underlying basement rocks (accessible by fault and shear zones with tectonically induced permeability). In general, mafic mineral assemblages are more favorable copper sources compared to felsic mineral assemblages, which are more suitable sources for lead. The principal copper sources of the Kupferschiefer mineralizing system are thus either the mafic volcanic rocks in the deep and central parts of the Rotliegend basin (Leeder et al., 1982) or basement rocks such as the metamorphosed magmatic arc rocks of the Mid-European Crystalline High, which underlies part of the Kupferschiefer basin, or both of these.

The eponymous Kupferschiefer sediment, i.e., the basin-marginal $C_{organic}$-rich black shale unit, occurs throughout a major portion of Northern Europe along most of the western, southern, and eastern coastal region of the Kupferschiefer basin (Fig. 1). However, only a relatively small, arc-shaped portion of the central southern basin margin—and even areas south of the depositional boundary of the Kupferschiefer sediment sensu stricto—are host to the economically significant copper ores and copper mineralization (Borg, 1991). Similarly suitable pyrite- and $C_{organic}$-rich host rocks for base metal mineralization occur in areas from England to Lithuania but, in these places, are merely typical metal-anomalous black shales and economically barren. Locally restricted regions, such as the Lower Rhine embayment in northwestern Germany, appear to mimic the Pb-Zn base metal endowment of the locally underlying basement rocks (Diedel and Friedrich, 1986). Borg (1991) demonstrated that the Cu-mineralized part of the southern basin margin coincided with areas where basinal brines could have been expelled due to sediment compaction, having percolated through thick, metal-endowed but now metal-depleted mafic volcanic and subvolcanic rocks of the Lower Rotliegend (Ryka, 1981). Lead isotope data by Wedepohl et al. (1978) identified basement rocks as a major source of lead in the Kupferschiefer ores. Wodzicki and Piestrzyński (1994) and Rentzsch and Friedrich (2003) estimated the original and depleted metal contents of all possible intrabasinal metal sources as well as the underlying basement rocks. The source rocks most favored by these authors for the majority of the economic metal accumulations are the basement rocks of the Mid-European Crystalline High and the Lower Rotliegend basalts, basaltic andesites, and subordinately rhyolites (e.g., for Pb) in northeastern Germany and northwestern Poland, for which a metal depletion has even been documented (Ryka, 1981; Borg, 1991). The best spatial match of the Cu-Pb-Zn-Ag(-Au-PGE)–rich part of the Kupferschiefer sensu lato is with the Late Proterozoic to Variscan domain of the Mid-European Crystalline High, where these rocks have been intersected by major NW-SE- as well as NNE-SSW-trending fault structures (Fig. 10a-c; Rentzsch et al., 1997; Wedepohl and Rentzsch, 2006). These rocks of the Mid-European Crystalline High have formed in a magmatic arc setting, are well endowed with base and precious metals, and coincide best with the arc-shaped copper-rich domain. Wedepohl and Rentzsch (2006) postulated the origin of basement-derived metalliferous fluids from the Mid-European Crystalline High as having emanated from “tectonic vents,” percolated through permeable strata and along faults within the Lower Rotliegend, and finally having precipitated at the redox front in or in the vicinity of the pyrite-bearing and chemically reducing Kupferschiefer and Zechstein limestone. The combination of underlying suitable source rocks and fault intersections is also evident in the German mining districts of Richelsdorf (Fig. 10d) and Mansfeld/Sangerhausen (Fig. 11), where richest ores occur immediately at prominent fault intersections or in tectonic domains that have been strongly faulted by sets of NW-SE– and NNE-SSW–trending faults, respectively.

Absolute Age Dating of Host Rocks and Mineralization

Logical age dating of mineralization in relationship to the host rocks or to tectonically induced fluid pathways, but particularly the absolute age dating by suitable methods, is crucial in any ore deposit or metal district. Here, the spatial distribution of the mineralization, which is clearly transgressive to both litho- and chronostratigraphy, precludes simplistic synsedimentary metallogenic concepts. Particularly, mineralization that reaches locally into carbonate rocks and evaporites of the Werra Anhydrite, within the lowermost evaporitic cycle of the Zechstein, clearly documents an epigenetic origin of the ores and the associated metal zonation patterns. Major remobilization from synsedimentary mineralization can also be precluded due to the lack of textural or geochemical depletion halos within the Kupferschiefer black shale sensu stricto. Absolute sedimentation ages of the rocks at the boundary between the Rotliegend and Zechstein have been comprehensively summarized by Symons et al. (2010). The various age-dating studies summarized therein have determined ages for the Kupferschiefer strata and for the immediately overlying Werra Anhydrite sequence, respectively. All available absolute sedimentation ages cluster in a relatively narrow interval between 260.4 ± 0.4 Ma (Slowakiewicz et al., 2009), 258 ± 19 Ma (Menning, 1995), 257.3 ± 1.6 Ma (Brauns et al., 2003), 258 ± 2 Ma (Menning et al., 2006), 260 Ma (Slowakiewicz et al., 2009), and 247 ± 20 Ma (Pašava et al., 2010).

Recently, Symons et al. (2010) have conducted paleomagnetic age dating of the mineralization in the Sangerhausen district. These authors demonstrated that initial attempts for paleomagnetic dating of the Rote Fäule in Poland by Jowett et al. (1987), already giving an epigenetic, Mid-Triassic mineralization age, had been too imprecise, with recalculated ages being indistinguishable from the Kupferschiefer sedimentation age (Symons et al., 2010). However Symons et al. (2010) conducted extensive paleomagnetic and rock magnetic measurements on a total of 205 specimens from 15 underground sites within the abandoned but still accessible Wettelrode mine in the Sangerhausen district. Here, the Cu mineralization is richest in the Kupferschiefer black marly shale (nine sampling sites; Plate 1C) but extends also into footwall sandstone (three sampling sites) and hanging-wall limestone (two sampling sites). The results of Symons et al. (2010) give a Late Jurassic paleopole at 149 ± 3 Ma on the apparent polar wander path for Europe of Besse and Courtillot (2002) but also a second paleopole at 53 ± 3 Ma.

It is interesting to note that paleomagnetic ages, not too different from these 149 and 53 Ma ages for the Kupferschiefer ores at Sangerhausen, have been determined as potential mineralization ages at two other European base metal districts. One is the district of the Cevennes in southern France with a (second) pulse of mineralization at 60 to 50 Ma (Henry et al., 2001). The other—perhaps more importantly—is the giant MVT Pb-Zn district of Upper Silesia in southern Poland (Heijlen et al., 2003; Muchez et al., 2005), where two mineralization ages have been determined. For the Upper Silesian Pb-Zn ores, Rb/Sr dating of insoluble residues from sulfide minerals yielded a Middle Cretaceous age of 135 Ma (Heijlen et al., 2003; Muchez et al., 2005). Paleomagnetic dating of the same deposit determined also a Tertiary age (Symons et al.,

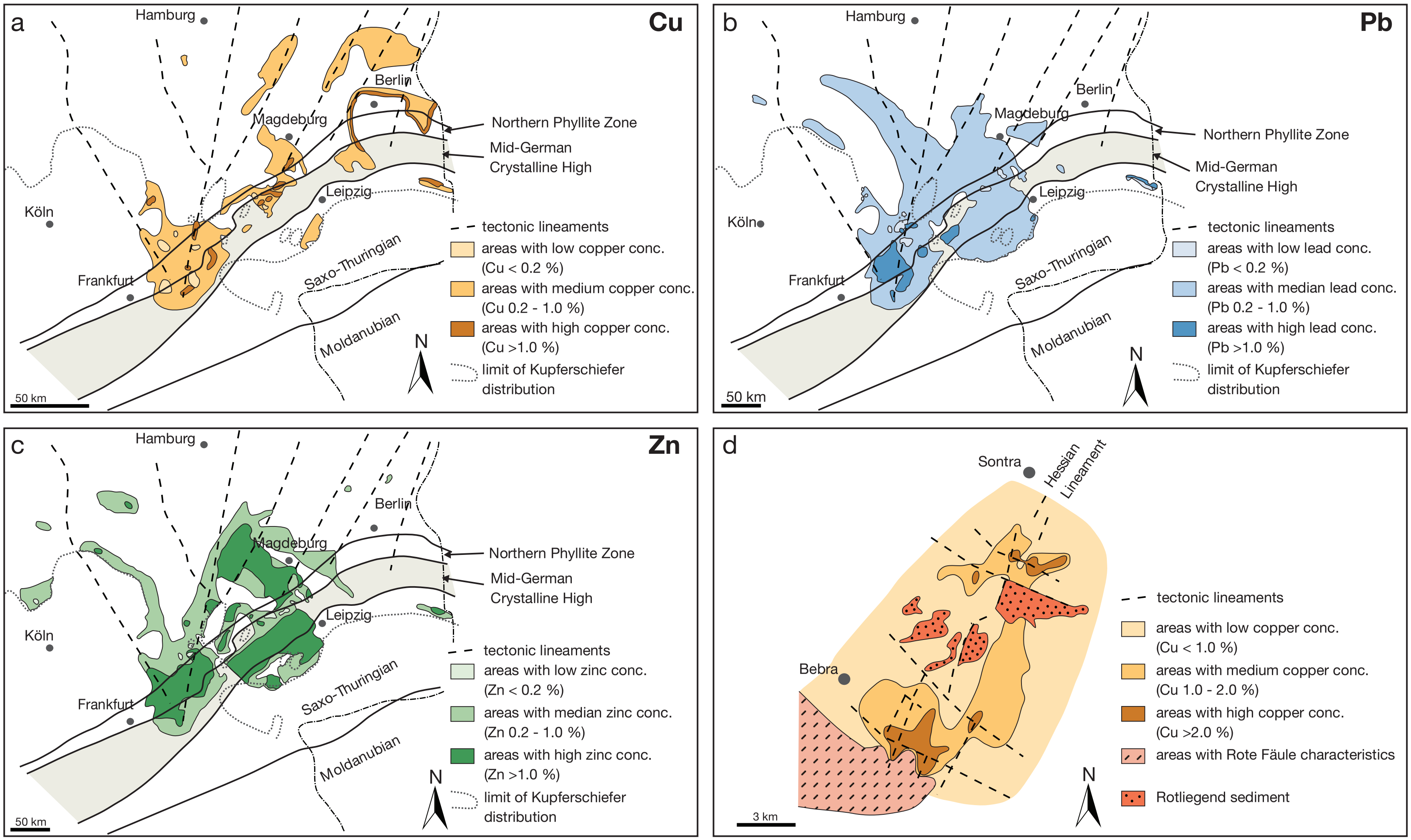

FIG. 10. Schematic diagrams of supraregional and local distribution of metal grades in relationship to lineaments and fault structures and major underlying crustal units (potential source rocks). a-c. Cu, Pb, and Zn distribution in the German part of the Kupferschiefer metallogenic belt. Note the spatial match between the Mid-German Crystalline High and crosscutting lineaments (after Wedepohl and Rentzsch, 2006). d. Distribution of Cu grades in relationship to fault structures and secondary hematite alteration (Rote Fäule) in the Richelsdorf district. Modified after Rentzsch and Franzke (1997).

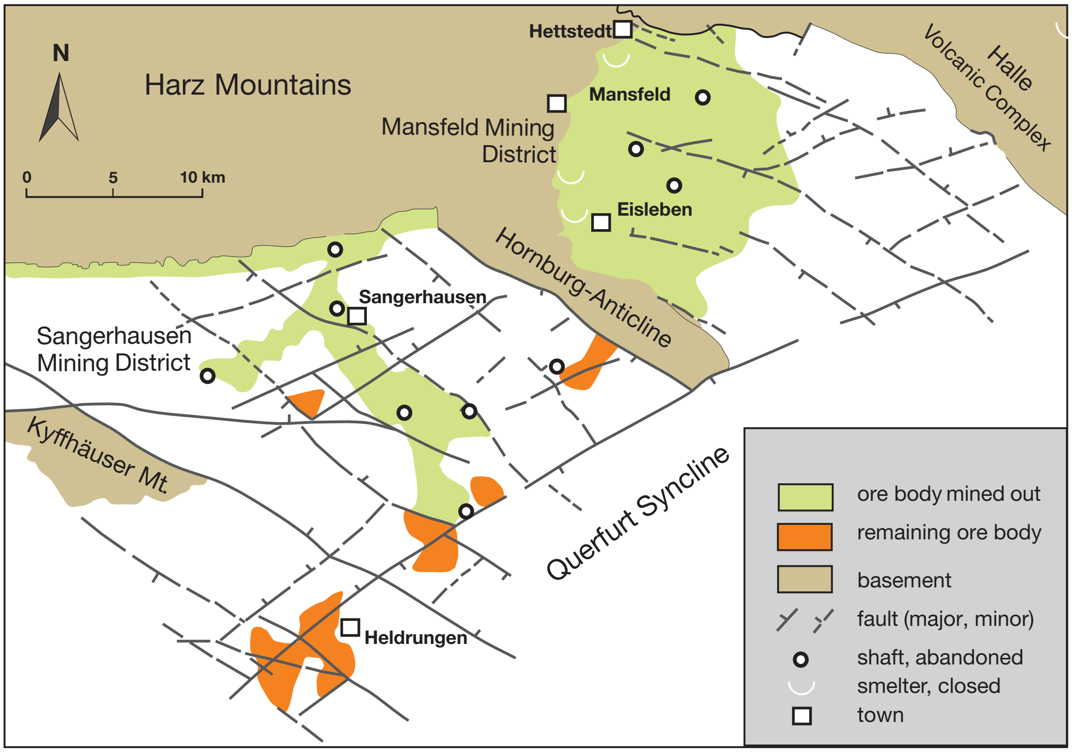

FIG. 11. Schematic map of the mining districts of Mansfeld and Sangerhausen, showing orebodies, both mined out and remaining, in relationship to the local fault pattern (adapted from Stedingk et al., 2002).

1995). The two ages, or rather the dated mineralizing episodes, have been attributed by these authors to the Late Jurassic to Mid-Cretaceous break-up of Pangea and to extensional faulting during the closure of the Tethyan Ocean during the Carpathian orogeny, respectively. The importance of basin-wide mobilization of mineralizing fluids by major tectonic events in the north German and Polish basin has been pointed out already by Schmidt Mumm and Wolfgramm (2004). Fluid inclusion studies are lacking for the Kupferschiefer ores since they are severely hindered by the lack of suitable carrier minerals. However, mineralizing fluids with temperatures of 145° to 160° and 180° to 200°C have been determined by Strengel-Martinez et al. (1993) for Polish vein-type Kupferschiefer ores. Muchez et al. (2005) presented a first integrated interpretation of the absolute ages and interrelated mechanisms of European ore district formation. These authors have pointed out the importance of basin-hosted and basement-fault-hosted brines with a long residence time (tens of millions of years) and the tectonic remobilization and propulsion of metal-bearing brines toward favorable trap sites. Such a mechanism has been proposed by Muchez et al. (2005) for—among other deposits—both the (SW-Polish) Kupferschiefer and the Upper Silesian Pb-Zn district. Although not including the Kupferschiefer mineralization as having formed specifically from an epigenetic metallogenetic episode, these authors have also recognized the regional, late epigenetic mineralizing potential of metalliferous fluids with temperatures of up to 200°C that had been stored in fault structures and other basinal reservoirs for a long period of time.

When compared with the stages of tectonic and magmatic evolution of the Central European basin (see chapter above), both potential mineralization ages coincide markedly with major crustal events of tectonic and/or magmatic activity. These tectonic events included the wrench tectonics with resulting transpressional uplift of the London-Bohemia Swell during the Late Jurassic at approximately 150 Ma and the opening of the Middle Atlantic, associated by hot-spot magmatism in the early Eocene at about 53 Ma. Thermal and magmatic pulses, supraregional tilting of major crustal blocks, and the reactivation of deep-reaching, basement-tapping large-scale fault structures are all known as being capable of providing, mobilizing, and channeling metalliferous brines. Particularly transpressive wrench movements along major subcontinental-scale fault structures can actively drive huge volumes of (metalliferous) fluids over large lateral and vertical distances by seismic pumping, a process described in detail by Sibson et al. (1975).

Previous Metallogenic Models

The Kupferschiefer sediments were deposited in an anoxic, euxinic environment (e.g., Pompeckj, 1914; Paul, 2006). The origin of the Kupferschiefer ore deposits sensu lato has been debated controversially for many decades. The various proposed models have reflected—at times—both sound observation but also concepts from relatively dogmatic schools of thought. The numerous metallogenic models have been summarized rather comprehensively by authors such as Kulick et al. (1984), Vaughan et al. (1989), and Oszczepalski (1999). In the following section, we will point out the most prominent theories and their proponents. This summary can only quote a brief selection of authors, due to the limitations of this text. However, a more comprehensive list of authors is included in the digital Appendix for further reading.

According to the earliest model, the base metal sulfides were precipitated in a strictly synsedimentary process, directly from the Zechstein sea in an euxinic environment following ideas of German geologists like Freiesleben (1815), Pompeckj (1914), Gillitzer (1936), Eisenhuth and Kautzsch (1954), Wedepohl (1971), and Jung and Knitzschke (1976). Several Polish authors adopted this model (e.g., Konstatynowicz, 1973; Sawłowicz, 1990). A similar concept was presented by Brongersma-Sanders (1966), who suggested base metal sulfide precipitation directly from sea water in estuarial sediments. However, Jung and Knitzschke (1976) discarded this model as unrealistic, due to a mass balance of metals, which could not be derived from the body of marine sea water alone. Epigenetic models were presented by Beyschlag (1900) and Lisiakiewicz (1959) and—as a special twist—hydrothermal fluids emanating metals into the partly biogenic Kupferschiefer sediment were proposed by Ekiert (1960) and Wyżykowski (1971). Recently, Kopp et al. (2012) attributed the precious metal and selenides mineralization at Spremberg, southeastern Germany, to a late epigenetic, hydrothermal event.

An early diagenetic formation of the base metal sulfide ores was proposed by authors such as Rentzsch (1964) and Oszczepalski (1989). In contrast, precipitation of sulfides during late diagenesis was assumed by Jowett et al. (1987), Hammer et al. (1990), and Oszczepalski and Rydzewski (1991). Multistage models were presented by Beyschlag (1900, 1921) and Vaughan et al. (1989) and the various facets of multistage models proposed by Polish authors have been summarized comprehensively in Piestrzyński (2007). Two separate oxidation events that resulted in the "reddening" of originally chemically reduced black or gray sediments have been distinguished by Piestrzyński et al. (2002). These authors distinguish a "diagenetic oxidation stage (DOS)," associated with copper mineralization and a "secondary oxidation stage (SOS)," associated with epigenetic Au mineralization. Finally, Rentzsch and Friedrich (2003) took the multistage genesis of the (German) Kupferschiefer ores to the extreme and distinguished a total of ten mineralizing stages and substages. These authors also attempted to estimate the relative proportion of metals introduced and the local or regional lateral extent of each of the ten stages of mineralization. A five-stage model was also used by Wodzicki and Piestrzyński (1994) and Piestrzyński et al. (2002).

The initial, strictly synsedimentary models for the origin of the Kupferschiefer ores were based on arguments such as the assumption of fossilized fish being poisoned by metalliferous seawater, from which the mineralization was supposed to have been precipitated (Freiesleben, 1815). The first epigenetic concepts of ascending metalliferous fluids that have mineralized the Kupferschiefer must be credited to Beyschlag (1900). Subsequently, several renewed syngenetic proposals have been published and the evidence of late emplacement of copper mineralization has been largely ignored or interpreted as local secondary remobilization. This includes mineralized lithic clasts in the Weissliegend conglomerates (similar to the ones shown in Plate 3D, E), which had been interpreted as sulfide pebbles of porphyry copper ores from the hinterland and transported by rivers in a terrestrial environment toward the Kupferschiefer Sea (Schüller, 1959). Brongersma-Sanders (1966) suggested that the entire metal content of the Kupferschiefer ores had been supplied by precipitation from seawater and the Kupferschiefer ores were even referred to as the "prototype of syngenetic sedimentary deposits" by Wedepohl (1971). The synsedimentary models all envisaged the metals to have been supplied by the erosion of a partly mineralized hinterland, the Variscan orogen with its prominent examples of massive sulfide ores (e.g., Rammelsberg and Meggen) and vein-type ore districts (e.g., the Harz Mountains in Germany). The Variscan mineralization should have been transported in particulate form as sulfides (Schüller, 1959) or oxidized ore particles in suspension or dissolved in river water (Brongersma-Sanders, 1966; Wedepohl, 1971). Metal precipitation and metal zonation was envisaged, by this school of authors, as occurring upon entering a chemically reducing lagoonal, deltaic, or marginal marine part of the euxinic Kupferschiefer Sea. However, this model did not take into account that the metal zonation did not match a basin-margin-to-basin-center-directed chemical zonation with solubility-controlled metal precipitation and particularly not that the mineralization is not restricted to the Kupferschiefer sensu stricto.

One particular feature associated with the mineralization has caught the attention of geologists from early times on and, in fact, the attention of the miners right from the start. This is the secondary oxidation zone, the Rote Fäule (Plate 1E, F), which has been discussed in detail already by Freiesleben (1815) and its spatial relationship to features that intersect the black shale layer of the Kupferschiefer sensu stricto. Such features include aeolian sand dunes of the Weissliegend that had formed at the end of the terrestrially deposited uppermost Rotliegend sediments and which were not covered by the subsequently deposited black shale of the Kupferschiefer. Gillitzer (1936) mapped large numbers of such sand dunes in great detail in the Mansfeld district. These sand dunes, together with fault structures crosscutting the Kupferschiefer, have been widely interpreted as permeable zones (or valves) for epigenetically migrating ore fluids through the relatively impermeable Kupferschiefer (Rentzsch and Langer, 1963; Rentzsch, 1964, 1974; Rentzsch and Knitzschke, 1968). These authors must be credited with having first proposed the general metallogenic model of a systematically zoned three-dimensional mineralizing system, transgressive to stratification (Fig. 12), which until now, accommodates many metallogenically relevant observations in virtually all Cu-mineralized districts of the basin. However, systematically and both vertically and laterally zoned sulfide (chalcocite-bornite-chalcopyrite-pyrite) mineralization, originating from crosscutting faults and extending up to 200 m away from the fault in the Mansfeld district was described by Hecker as early as 1859. The epigenetic transgressive brine model and the resulting three-dimensional metal and ore mineral zonation model have been refined and modified (Fig. 12) by authors such as Schmidt (1987) and Vaughan et al. (1989). The relative timing of the epigenetic mineralizing event is implied by the fact that the ore and redox zones have locally transgressed stratigraphy well into the hanging wall, affecting not only the basal limestone cycle of the Zechstein but locally even the

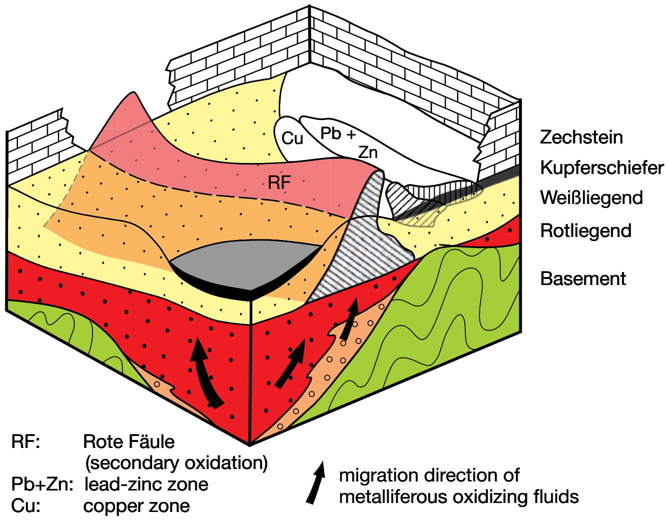

FIG. 12. Three-dimensional illustration of the (early) diagenetic metallogenic model (adapted from Rentzsch, 1974, and Schmidt, 1987). Note the valve-like function of the permeable rocks of the sand dune in contrast to the more impermeable black shale and the lack of fault structures in this model.

lowermost evaporite unit of the Werra Anhydrite (Rentzsch, 1974). Thus the metallogenic model is clearly epigenetic although the term has apparently been avoided at the time and for many years to follow, with the exception of few early authors (e.g., Kaemmel, 1965). The origin of the mineralization was instead referred to as being early to late diagenetic (e.g., Kulick et al., 1984; Blundell et al., 2003; Hitzman et al., 2010).

Given the long-lasting, historic to subrecent debate on the metallogenesis of the Kupferschiefer ores, it is surprising that regional to local structural evidence has been taken into account only very early (Beyschlag, 1921) and again much more recently and by comparatively few authors (Rentzsch and Franzke, 1997; Rentzsch et al., 1997; Muchez et al., 2005; Wedepohl and Rentzsch, 2006; Symons et al., 2010).

Conclusions and a New Holistic Model

The Kupferschiefer metallogenic belt of Germany and Poland is one of three "supergiant" sediment-hosted copper deposits of the world and is among the largest 1% of deposits with >60 Mt contained Cu. The belt is hosted by the much more extensive Central European basin, but the individual Kupferschiefer mining districts cluster in a comparatively small, kidney-shaped area at the central southern basin margin. The economic deposits spatially overlie a basement of magmatic arc rocks of the Mid-European Crystalline High.

Probably the most important observation on the ore deposit style and geometry is the shallow transgressive to crosscutting nature of the mineralization relative to stratigraphy. Overall, at least half of the ore is hosted by footwall sandstones and conglomerates and by hanging-wall carbonate rocks rather than by the $C_{organic}$-rich, originally pyritic black shale of the Kupferschiefer sensu stricto. Except for examples on hand specimen to outcrop scale, the mineralization is not stratiform. The transgressive mineralization is systematically zoned with respect to both metals and ore minerals and this zonation is developed both vertically (upward) and laterally. The zoned mineralizing system consistently includes a marked redox front with a characteristic hematitic alteration zone, the Rote Fäule. A migration direction of the mineralizing system from the hematite (Fe^{3+}) zone through a Cu zone, Pb zone, and Zn zone to a (pre-ore) pyritic (Fe^{2+}) zone is generally accepted. Highest Cu grades occur proximal (on the chemically reducing side) to the redox front and precious metal mineralization—where present—straddles the redox front or occurs very proximal on the oxidizing side of it.

The vast majority of evidence from ore textures, regional metal zonation, spatial relationship to fault structures, and mass-balance considerations (e.g., the insufficiency of biogenic sulfur from the black shale to produce the total Cu sulfide ores) all document the epigenetic origin of the economic Kupferschiefer orebodies. Additionally, recent absolute age dating, both for the Kupferschiefer and other European ore districts, also revealed epigenetic ages of ore formation, significantly later than the formation of the host rocks and much later than previously anticipated. A clear spatial and most likely genetic relationship exists between favorable intrabasinal and particularly basement source rocks, major regional, deep basement-tapping fault structures, and the location and outline of the most important Kupferschiefer deposits.

The last decade has seen a liberation from early but persistent syngenetic to early diagenetic metallogenic models. This liberation has allowed relating the Kupferschiefer metallogenic system to the entire tectonic and magmatic evolution of the wider region, particularly the Central European basin and its neighboring crustal domains. Allowing such an approach, it turns out that many of the active stages in the formation and subsequent and episodic extensional and compressional tectonic evolution are reflected in the metallogenic history of the Kupferschiefer ore deposits.

Our present compilation of results from ore textures, regional spatial coincidence of copper mining districts with major crustal zones, and regional to local coincidence of orebodies with fault structures and crustal lineaments and absolute age dating does not support any of the previously proposed metallogenic models for the Kupferschiefer ores. We therefore propose the following model as illustrated in Figure 13. The present authors are aware that this model represents "work in progress," since the metallogenic implications of many of the phenomena described above have only recently been recognized. The present model and review paper show the need for a holistic evaluation of all available evidence and the improved understanding of the significance of tectonic structures and tectonically induced secondary permeability. This evaluation will hopefully result both in new research and new exploration of areas previously considered as low-priority targets.

The model presented here is a composite from and for both German and Polish deposits, each of which will invariably differ in specific details. The first four stages (Fig. 13a-d) do not differ significantly from various previous models described above and are merely a summary of the current knowledge. Major differences, however, exist for the main metallogenic stages that have produced the economically viable orebodies (Fig. 13e, f).

The fault-bounded terrestrial Rotliegend basin has been filled rapidly with immature red beds, evaporites, and bimodal volcanic rocks (Fig. 13a). Basinal fluids were moderately warm,

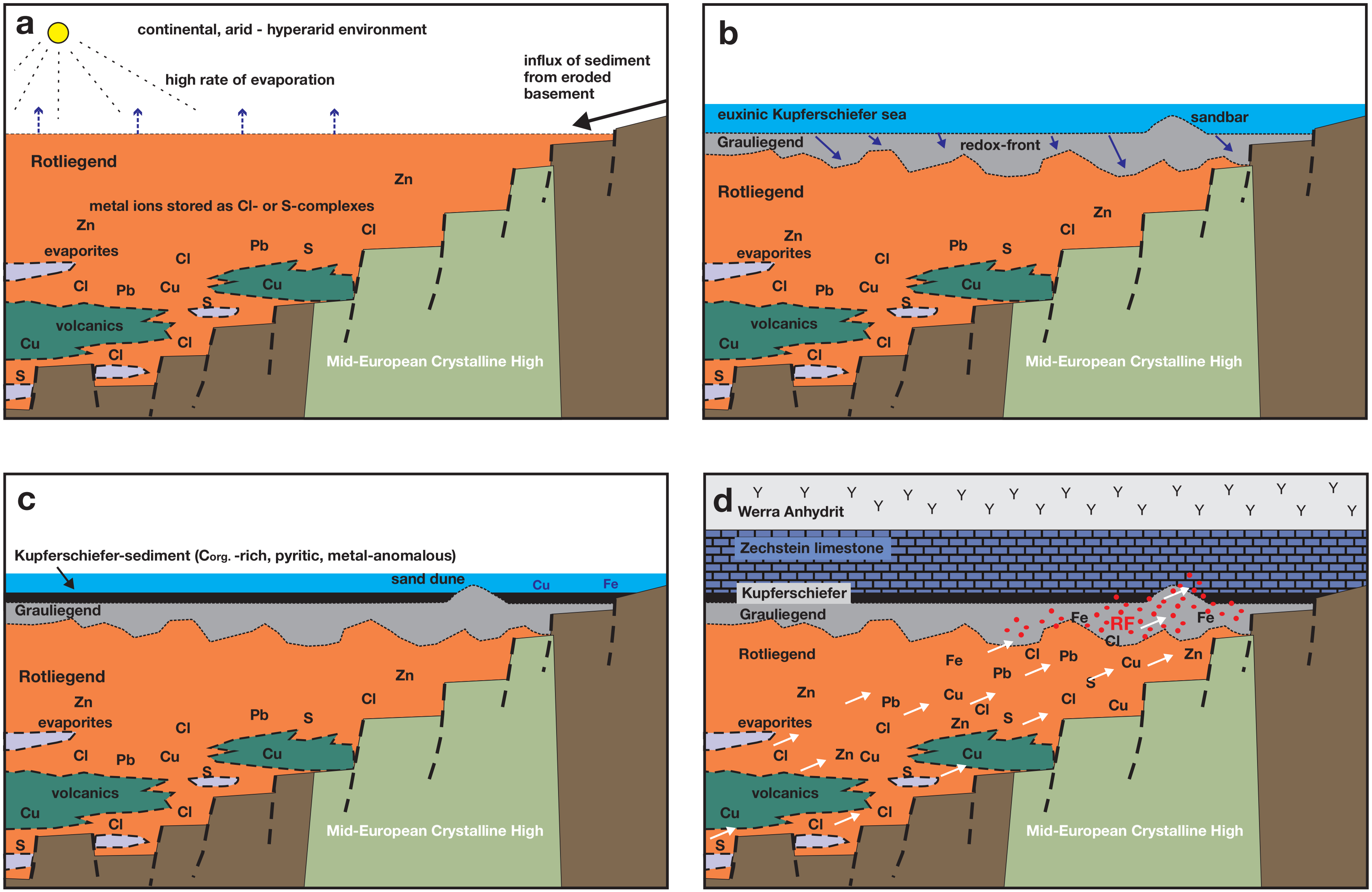

FIG. 13. Proposed metallogenic model for the Kupferschiefer ores with two late epigenetic stages being responsible for the economic orebodies (see text for explanation).

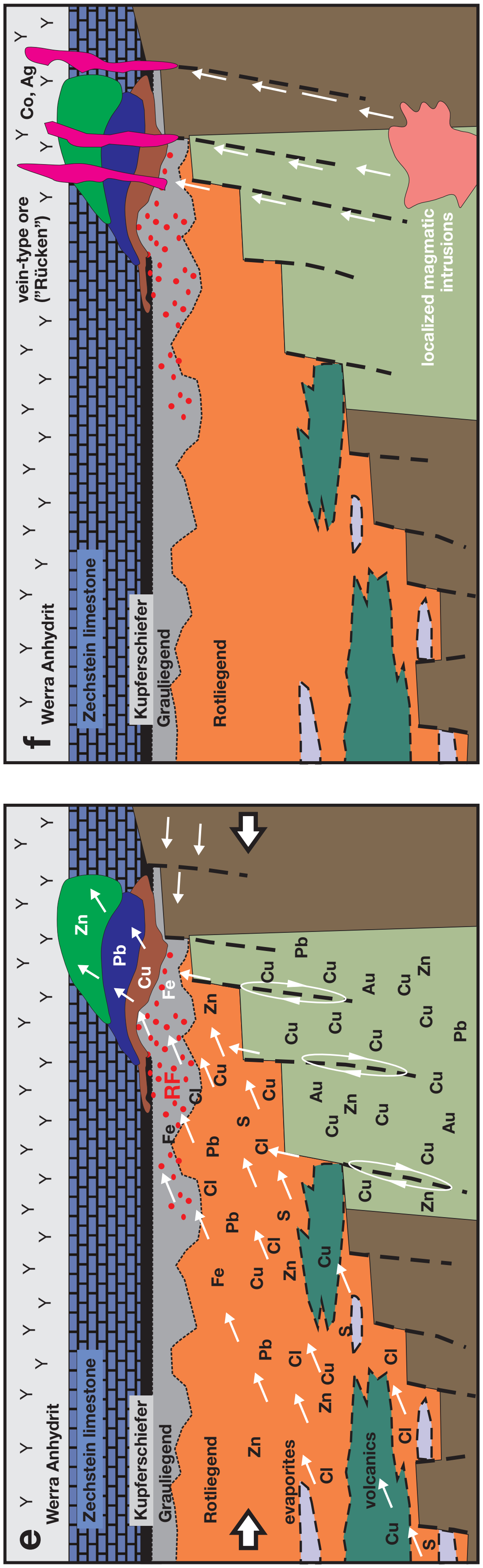

Fig. 13. (*Cont.*)

oxidizing, saline, and thus capable of altering all rock types of the basin fill and of basement rocks in permeable faults and shear zones. The rapid transgression by the Kupferschiefer Sea subsequently resulted in a stagnant and euxinic body of water, which infiltrated the topmost red beds in a descending and irregular fashion thus creating the bleached and chemically reduced Grauliegend (Fig. 13b). Deposition of $C_{organic}$-rich mud, the Kupferschiefer sediment sensu stricto, some 255 m.y. ago, acted as a chemical sink with the precipitation of framboidal pyrite and minor accumulation of available base metals (Fig. 13c). Sediment compaction led to partial basin dewatering and mobilization of metalliferous brines from deeper parts of the basin (Fig. 13d). The fluids have possibly partly oxidized rocks of the Grauliegend, Kupferschiefer sensu stricto, and Zechstein. However, this process has been increasingly hindered by low primary permeability and diagenetic cementation of the clastic sedimentary basin fill and is thus most probably not responsible for the major pulse of mineralization. A major central European transpressional tectonic event at the end of the Jurassic, some 150 m.y. ago, also involved some regional crustal tilting. Major NW-SE– and NNE-SSW–trending fault systems, dissecting both basement rocks and the basinal volcanosedimentary succession, had acted as a reservoir for moderately heated and metal-charged fluids. Upon reactivation of these fault structures, the fluids became mobilized and transported over large vertical and lateral distances, spreading slowly laterally in the uppermost Rotliegend and Weissliegend clastic rocks to suitable, structurally controlled trap sites (Fig. 13e). The thin, quasihorizontal Kupferschiefer black shale acted as a severe hydrodynamic and geochemical barrier to the migrating fluids. This barrier will have slowed down or stopped ascending fault-propagated fluid flow and caused "ponding" of the metalliferous fluids below the black shale aquiclude. The mineralizing fluids will thus have had a long residence time within and reaction time with the uppermost, partly sulfate-cemented Rotliegend or Grauliegend coarse clastic sediments and with the more impermeable but also more reactive $C_{organic}$-rich, pyritic black shale. Slow hydrodynamic valves through the black shale, such as slowly decemented sand dunes and fault and shear zones would have released the metal-bearing fluids into overlying, reactive carbonate and evaporite rocks of the hanging wall. This low fluid velocity has probably been the main reason for the development of the particularly pronounced metal and mineral zonation pattern of the mineralization (for comparison, see Merino et al., 1986). It is open for debate if the higher velocities of basin dewatering fluids in noncemented clastic sediments would have allowed the development of such a broad and persistent zonation pattern. Most of the economic copper orebodies have formed during this metallogenic stage, even though the details of formation of the secondary oxidation (or various oxidations?) are still not fully understood and need further research. An even later metallogenic pulse occurred during the Tertiary, some 53 m.y. ago, when subcontinental-scale tectonic structures underwent another phase of reactivation and hot-spot magmatic activity provided additional sources of metals and local heat (Fig. 13f). This stage is responsible for localized high-grade, massive vein- and breccia-type ores that have overprinted earlier types of ores in many of the mining districts.

Outlook

Ore geologic research on the genesis of the Kupferschiefer ores sensu lato is far from being complete or obsolete. Particularly the various redox processes still need scientific clarification and research, since the different basinal fluids, their origin, properties, and effect on source and host rocks are still incompletely understood. Particularly the role of hydrocarbon- and evaporite-related fluids within the Central European basin and their relationship to the Kupferschiefer ores and alteration patterns hold considerable research potential. Additionally, future research needs a fully integrated approach to the European dimension of the metallogenic systems that have been triggered and driven by major crustal tectonic and magmatic events. These continental-scale processes have formed regional metallogenic districts and local ore deposits and orebodies, which still carry the—sometimes apparently cryptic—imprints of the underlying larger cause.

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REFERENCES

Arthaud, F., and Matte, P., 1977, Late Paleozoic strike-slip faulting in southern Europe and North Africa: Results of a right lateral shear zone between the Appalachians and the Urals: Geological Society of America Bulletin, v. 88, p. 1305–1320.

Bachmann, G.H., and Grosse, S., 1989, Struktur und Entstehung des Norddeutschen Beckens – geologisch-geophysikalische Interpretation einer verbesserten Bouguer-Schwerekarte: Niedersächsische Akademie der Geowissenschaften Veröffentlichungen, v. 2, p. 23–47.

Bachmann, G.H., and Hoffmann, N., 1997, Development of the Rotliegend basin in northern Germany: Geologisches Jahrbuch, v. D103, p. 9–31.

Bachowski, C., Kudelko, J., and Wirth, H., 2011, Copper reserves in Poland and their possible development, *in* Banaszak, A., Downorowicz, S., Leszczyński, R., and Mudry, D., eds., 50–years KGHM PM S.A. Anniversary Conference, Lubin, Finestra, p. 91–107 (in Polish).

Banas, M., Gluszek, A., Jarosz, J., and Salamon, W., 1998, Pollymetallic veins in the Permian coppper deposits in the Fore-Sudetic monocline: PT Min Special Paper 10, p. 43–49 (in Polish).

Bechtel, A., Sun, Y., Püttmann, W., Hoernes, S., and Hoefs J., 2001, Isotopic evidence for multi-stage base metal enrichment in the Kupferschiefer from the Sangerhausen basin, Germany: Chemical Geology, v. 176, p. 31–49.

Besse, J., and Courtillot, V., 2002, Apparent and true polar wander and the geometry of the geomagnetic field over the last 200 Myr: Journal of Geophysical Research, v. 107, p. 1–31.

Beyschlag, F., 1900, Beitrag zur Genesis des Kupferschiefers: Zeitschrift für Praktische Geologie, v. 8, p. 115–117.

——1921, Die Erzführung des Kupferschiefers: Zeitschrift für Praktische Geologie, v. 29, p. 1–9.

Blundell, D.J., Karnkowski, P.H., Alderton, D.H.M., Oszczepalski, S., and Kucha, H., 2003, Copper mineralization of the Polish Kupferschiefer: A proposed basement fault-fracture system of fluid flow: Economic Geology, v. 98, p. 1487–1495.

Borg, G., 1991, The significance of Rotliegend volcanics for the metal provinces of the Kupferschiefer basin: Zentralblatt für Geologie und Paläontologie, v. 1991, 4/1, p. 929–943.

Borg, G., Frotzscher, M., and Ehling, B., 2005, Metal content and spatial distribution of Au and PGE in the Kupferschiefer of the Mansfeld/Sangerhausen mining district, Germany, *in* Mao, J., and Bierlein, F. P., eds., Mineral deposit research: Meeting the Global Challenge. Proceedings of the Eighth Biennial SGA Meeting, Beijing, China, 18–21 August 2005: Berlin, Springer Verlag, p. 885–888.

Brauns, C.M., Pätzold, T., and Haack, U., 2003, An Re-Os study bearing on the age of the Kupferschiefer mineralization at Sangerhausen [abs.]: XVth International Congress of Carboniferous and Permian Stratigraphy, Utrecht, Abstracts, p. 66.

Breitkreuz, C., and Kennedy, A., 1999, Magmatic flare-up at the Carboniferous/Permian boundary in the NE German basin revealed by SHRIMP zircon ages: Tectonophysics, v. 302, p. 307–326.

Brongersma-Sanders, M., 1966, Metals of Kupferschiefer supplied by normal sea water: Geologische Rundschau, v. 55, p. 365–375.

Butler, I.B., and Rickard, D., 2000, Framboidal pyrite formation via the oxidation of iron(II) monosulfide by hydrogen sulphide: Geochimica et Cosmochimica Acta, v. 64, p. 2665–2672.

Cowper, M., and Rickard, D., 1989, Mechanism of chalcopyrite formation from iron monosulphides in aqueous solutions (<100°C, pH 2–4,5): Chemical Geology, v. 78, p. 325–341.

Deans, T., 1950, The Kupferschiefer and the associated lead-zinc mineralisation in the Permian of Silesia Germany and England: International Geological Congress, 18th, Report, v.7, p. 340–352.

Diedel, R., and Friedrich, G., 1986, Buntmetall- und Schwerspatmineralisation im Kupferschiefer des niederrheinischen Tieflandes: Fortschritte der Geologie Rheinland und Westfalen, p. 221–241.

Diedel, R., and Püttmann, W., 1988, Base metal mineralization and maturation of organic material in the Kupferschiefer of the Lower Rhine basin: SGA Special Publication 5, p. 60–73.

Doornenbal, J.C., and Stevenson, A., eds., 2010, Petroleum geological atlas of the southern Permian basin area: Houten, European Association of Geoscientists and Engineers (EAGE), 342 p.

Eckardt, F.J., 1979, Der permische Vulkanismus Mitteleuropas: Geologisches Jahrbuch, v. D35, p. 38–84.

Ehling, B.-C., Gebhardt, U., and Kampe, A., 2008, Rotliegend, *in* Bachmann, G.H., Ehling, B.-C., Eichner, R., and Schwab, M., eds., Geologie von Sachsen-Anhalt: Stuttgart, Schweizerbart'sche Verlagsbuchhandlung, p. 143–178.

Eisenhuth, K.-H., and Kautzsch, E., 1954, Handbuch für den Kupferschieferbergbau: Leipzig, Fachbuch Verlag, 358 p.

Eisentraut, O., 1939, Der niederschlesische Zechstein und seine Kupferlagerstätten: Archiv für Lagerstättenforschung des preußischen geologischen Landesamtes, v. 71, 116 p.

Ekiert, F., 1960, Neue Anschauungen über die Herkunft des in den Sedimenten des unteren Zechsteins auftretenden Kupfers: Freiberger Forschungshefte, v. C79, p. 26–45.

Freiesleben, J.C.V., 1815, Geognostischer Beytrag zur Kenntnis des Kupferschiefergebirges, auch einiger benachbarter Gebirgsformationen, mit besonderer Hinsicht auf Thüringen: Freiberg, Craz und Gerlach, 459 p.

Friedrich, G., Diedel, R., Schmitdt, F.P., and Schuhmacher, C., 1984, Untersuchungen an u-As-Sulfiden und Arseniden des basalen Zechsteins der Gebiete Spessart/Rhön und Richelsdorf: Fortschritte der Mineralogie, v. 62, p. 63–65.

Gast, R., 1988, Rifting im Rotliegenden Niedersachsens: Geowissenschaften, v. 4, p. 115–122.

Gillitzer, G., 1936, Die Geologie der Erzanreicherungen im mitteldeutschen Kupferschiefer: Jahrbuch des Halleschen Verbands zur Erforschung mitteldeutscher Bodenschätze, v. 15, p. 1–19.

Glennie, K.W., and Buller, A.T., 1983, The Permian Weissliegend of NW Europe: The partial deformation of aeolian dune sands caused by the Zechstein transgression: Sedimentary Geology, v. 35, p. 43–81.

Hammer, J., Junge, F., Rösler, H.J., Niese, S., Gleisberg, B., and Stiehl, G., 1990, Element and isotope geochemical investigations of the Kupferschiefer in the vicinity of "Rote Fäule," indicating copper mineralization (Sangerhausen basin, G.D.R.): Chemical Geology, v. 85, p. 345–360.

Hecker, J., 1859, Erfahrungen über das Vorkommen der Sanderze in den Sangerhäuser und Mansfeldischen Revieren: Zeitschrift der gesammelten Naturwissenschaften, Halle, v. 14, p. 445–474.

Heijlen, W., Muchez, P., Banks, D.A., Schneider, J., Kucha, H., and Keppens, E., 2003, Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: Origin and evolution of mineralizing fluids and constraints on genetic models: Economic Geology, v. 98, p. 911–932.

Henry, B., Rouvier, H., le Goff, M., Leach, D., Macquar, J.-C., Thibieroz, J., and Lewchuk, M.T., 2001, Palaeomagnetic dating of widespread remagnetization on the southeastern border of the French massif central and implications for fluid flow and Mississippi Valley-type mineralization: Geophysical Journal, v. 145, p. 368–380.

Hitzman, M.W., Selley, D., and Bull, S., 2010, Formation of sedimentary rock-hosted stratiform copper deposits through Earth history: Economic Geology, v. 105, p. 627–639.

Hoffmann, W., 1923, Erzführung und Erzverteilung des Mansfelder Kupferschiefers und die hieraus sich ergebenden mineralbildenden und -umbildenden Vorgänge im Kupferschiefer: Jahrbuch des Halleschen Verbandes für die Erforschung der mitteldeutschen Bodenschätze und ihrer Verwertung, v. 4, p. 278–328 (in German).

Jowett, E.C., Pearce, G.W., and Rydzewski, A., 1987, A Mid-Triassic paleomagnetic age of the Kupferschiefer mineralization in Poland, based on a revised apparent polar wander path for Europe and Russia: Journal of Geophysical Research, v. 92, p. 581–598.

Jung, W., and Knitzschke, G., 1976, Kupferschiefer in the German Democratic Republic (GDR) with special reference to the Kupferschiefer deposit in the southeastern Harz Foreland, *in* Wolf, K.H., ed., Handbook of stratabound and stratiform ore deposits II. Regional studies and specific deposits, v. 6: New York, Elsevier, p. 353–406.

Kaemmel, T., 1965, Die Stellung der Erzmineralisation innerhalb der Petrogenese des Aderstedter Kupferschiefers: Freiberger Forschungshefte, v. C193, p. 143–155.

Kane, J.S., Arbogast, B., and Leventhal, J., 1990, Characterization of Devonian Ohio Shale SDO-1 as a USGS geochemical reference sample: Geostandards Newsletter, v. 14/1, p. 169–195.

Kirst, G., 1994, Lagerstättenkundlich geochemische Untersuchungen an Kupferschiefer-profilen im Lagerstättenbericht der Vorsudetischen Monokline/SW Polen: Unpublished Diploma thesis, Germany, University of Bonn, 160 p.

Kłapciński, J., Juroszek, C. and Sachanbi ski, M., 1975, Geology of the crystalline basement of the Fore-Sudetic foreland, new data: Geologia Sudetica, v. 10/2, p. 7–46 (in Polish).

Kley, J., and Voigt, T., 2008, Late Cretaceous intraplate thrusting in central Europe: Effect of Africa-Iberia-Europe convergence, not Alpine collision: Geology, v. 36, p. 839–842.

Knitzschke, G., 1995, Metall- und Produktionsbilanz für die Kupferschieferlagerstätte im südöstlichen Harzvorland, *in* Jankowski, G., ed., Zur Geschichte des Mansfelder Kupferschieferbergbaus: Clausthal-Zellerfeld, GDMB-Informationsgesellschaft mbH, p. 270–284.

Knitzschke, G., and Spilker, M., 2003, Die Kupferschieferlagerstätte Mansfeld/Sangerhausen- Bergbauliche Nutzung und Verwahrung: Der Anschnitt, v. 3–5, p. 134–147.

Konstantynowicz, E., 1971, Geology of copper deposit and occurrences in Poland, *in* Warszawa, W.G., Monography of Polish copper industry: Warszawa, p. 27–412 (in Polish).

——1973, Genesis of Permian copper deposits in Poland: International Geological Review, v. 15, p. 1054–1066.

Kopp, J., Simon, A., and Götherl, M., 2006, Die Kupfer-Lagerstätte Spremberg-Graustein in Südbrandenburg: Brandenburgische Geowissenschaftliche Beiträge, v. 13, nos. 1–2, p. 117–132.

Kopp, J., Hermann, S., Höding, T., Simon, A., and Ullrich, B., 2008, Die Kupfer-Silber-Lagerstätte Spremberg-Graustein (Lausitz, Bundesrepublik Deutschland)-Buntmetallanreicherungen an der Zechsteinbasis zwischen Spremberg und Weisswasser: Zeitschrift für Geologische Wissenschaften, v. 36, p. 75–114.

Kopp J.C., Spieth V., and Bernhardt H.-J., 2012, Precious metals and selenides mineralisation in the copper-silver deposit Spremberg-Graustein, Niederlausitz, SE-Germany: Zeitschrift der deutschen Gesellschaft für Geowissenschaften, v. 163/4, p. 361–384.

Krasoń, J., 1964, Stratigraphic division of the northern Sudetic Zechstein unit based on facies development: Geologia Sudetica, v. 1, p. 323–325 (in Polish).

Kucha, H., 1982, Platinum-group metals in the Zechstein copper deposits, Poland: Economic Geology, v. 77, p. 1578–1591.

Kucha, H., and Mayer, W., 2007, Geochemistry, *in* Piestrzyński, A., ed., Monografia KGHM Polska Miedź SA, p. 197–207 (in Polish).

Kucha, H., and Przybyłowicz, W., 1999, Noble metals in in organic matter and clay-organic matrices, Kupferschiefer, Poland: Economic Geology, v. 94, p. 1137–1162.

Kulick, J., Leifeld, D., Meisl, S., Pöschl, W., Stellmacher, R., Strecker, G., Theuerjahr, A.-K., and Wolf, M., 1984, Petrofazielle und chemische Erkundung des Kupferschiefers der Hessischen Senke und des Harz-Westrandes: Geologisches Jahrbuch, v. D68, 223 p.

Kumar Sani, R., Peyton, B.M., and Brown, L.T., 2001, Copper-induced inhibition of growth of Desulfovibrio desulfuricans G20: Assessment of its toxicity and correlation with those of zinc and lead: Applied Environmental Microbiology, v. 67, p. 4765–4772.

Leeder, O., Weber, W., and Baumann, L., 1982, Kontinentale Riftprozesse und ihre minerogenetische Bedeutung im postvariszischen Mitteleuropa: Zeitschrift für Geologische Wissenschaften, v. 10, p. 501–510.

Leipold, J., 2007, Chronik des Kupferschieferbergbaus in Bottendorf/Unstrut: Bad Langensalza, Rockstuhl, 258 p.

Leszczyński, R., 2011, Deposit model - comparison of the first deposit models to the recent, *in* Banaszak, A., ed., Geologists in the Polish copper industry: Lubin, p. 21–35 (in Polish)

Liedtke, M., and Vasters, J., 2008, Renaissance des deutschen Kupferschieferbergbaus?: Hannover, Commodity Top News, Bundesanstalt für Geowissenschaften und Rohstoffe, 15 p.

Lisiakiewicz, S., 1959, W sprawie genezy złóż miedzi w niecce północno-sudeckiej: Przegląd Geologiczny, v. 3, p. 119–120 (in Polish).

Littke, R., Bayer, U., Gajewski, D., and Nelskamp, S., Eds., 2008, Dynamics of complex intracontinental basins: The Central European basin system: Berlin, Springer, 519 p.

Ludwig, H., and Rentzsch, J., 1967, Das Sanderzproblem—ein Beitrag zur Genese des Kupferschiefers: Bericht der deutschen Gesellschaft für geologische Wissenschaften, A. Geologie und Paläontologie, v. Reihe B, p. 3–12.

Machel, H.G., Krouse, H.R., and Sassen, R., 1995, Products and distinguishing criteria of bacterial and thermochemical sulphate reduction: Applied Geochemistry, v. 10, p. 373–389.

Mayer, W., and Piestrzyński, A., 1985, Ore minerals from Lower Zechstein sediments at Rudna mine, Fore-Sudetic monocline, SW Poland: Prace Mineralogiczne, v. 75, p. 1–80.

Menning, M., 1995, A numerical time scale for the Permian and Triassic periods: An integrated time analysis, *in* Scholle, P.A., Peryt, T.M., and Ulmer-Scholle, D.S., eds., The Permian of northern Pangea: Heidelberg, Springer, p. 77–97.

Menning, M., Alekseev, A.S., Chuvashov, B.I., Davydov, V.I., Devuyst, F.X., Forke, H.C., Grunt, T.A., Hance, L., Heckel, P.H., Izokh, N.G., Jin, Y.G., Jones, P.J., Kotlyar, G.V., Kozur, H.W., Nemyrovska, T.I., Schneider, J.W., Wang, X.D., Weddige, K., Weyer, D., and Work, D.M., 2006, Global time scale and regional stratigraphic reference scales of Central and West Europe, East Europe, Tethys, South China, and North America as used in the Devonian-Carboniferous-Permian Correlation Chart 2003 (DCP 2003): Palaeogeography Palaeoclimatology Palaeoecology, v. 240, p. 318–372.

Merino, M., Moore, C., Ortoleva, P., and Ripley, E., 1986, Mineral zoning in sediment-hosted copper-iron sulfide deposits—a quantitative kinetic approach, *in* Friedrich, G.H., Genkin, A.D., Naldrett, A.J., Ridge, J.D., Sillitoe, R.H., and Vokes, F.M., eds., Geology and metallogeny of copper deposits: Berlin, Springer, p. 559–571.

Muchez, P., Heijlen, W., Banks, D., Blundell, D., Boni, M., and Grandia, F., 2005, Extensional tectonics and the timing and formation of basin-hosted deposits in Europe: Ore Geology Reviews, v. 27, p. 241–267.

Nielsen, S.B., Paulsen, G.E., Hansen, D.L., Gemmer, L., Clausen, O.R., Jacobsen, B.H., Balling, N., Huuse, M., and Gallagher, K., 2002, Paleocene initiation of Cenozoic uplift in Norway: Geological Society London Special Publication 196, p. 45–65.

Oszczepalski, S., 1989, Kupferschiefer in southwestern Poland: Sedimentary environments, metal zoning, and ore controls: Geological Association of Canada Special Paper 36, p. 571–600.

——1999, Origin of the Kupferschiefer polymetallic mineralization in Poland: Mineralium Deposita, v. 34, p. 599–613.

Oszczepalski S., and Rydzewski A., 1991, The Kupferschiefer mineralization in Poland: Zentralblatt für Geologie und Paläontologie, v. 1/4, p. 975–999.

Oszczepalski, S., Nowak, G.J., Bechtel, A., and Zak, K., 2002, Evidence of oxidation of the Kupferschiefer in the Lubin-Sieroszowice deposit, Poland: Implication for Cu-Ag and Au-Pt-Pd mineralisation: Geological Quarterly, v. 46, p. 1–23.

Parkman, R.H., Curtis, C.D., Vaughan, D.J., and Charnock J.M., 1996, Metal fixation and mobilization in the sediments of the Afon Goch estuary, Dulas Bay, Anglesey: Applied Geochemistry, v. 11, p. 203–2010.

Pasava, J., Oszczepalski, S., and Du, A., 2010, Re-Os age of non-mineralized black shale from the Kupferschiefer, Poland, and implications for metal enrichment: Mineralium Deposita, v. 45, p. 189–199.

Paul, J., 2006, Der Kupferschiefer: Lithologie, Stratigraphie, Fazies und Metallogenese eines Schwarzschiefers: Zeitschrift der Deutschen Gesellschaft für Geowissenschaften, v. 157, p. 57–76.

Peryt, T.M., 1978, Characteristic of microfacies of the Zechstein carbonate sediments of the first and second cyclotems in the Fore-Sudetic monocline: Geologia Polonica, v. 54, p. 1–88 (in Polish).

Pieczonka, J., and Piestrzyński, A., 2008, Mineralogy and geochemistry of ore minerals from secondary oxidized zones: Annales Societatis Geologorum Poloniae, v. 78, no. 3, p. 195–241.

Pieczonka, J., Piestrzyński, A., Mucha, J., Gluszek, A., Kotarba, M. and Wieclaw, D., 2008, The red-bed-type precious metal deposit in the Sieroszowice-Polkowice copper mining district, SW Poland: Annales Societatis Geologorum Poloniae, v. 78, p. 151–280.

Piestrzyński, A., 2007, Historical development of the ore genesis of the copper deposit (Fore-Sudetic monocline, SW Poland)—Discussion: Biuletyn Biuletyn Państwowego Instytutu Geologicznego, v. 423, p. 69–76 (in Polish).

Piestrzyński, A., and Sawłowicz, Z., 1999, Exploration for Au and PGE in the Polish Zechstein copper deposits (Kupferschiefer): Journal of Geochemical Exploration, v. 66, p. 17–25.

Piestrzyński, A., Pieczonka, J., and Gluszek, A., 2002, Redbed-type gold mineralization, Kupferschiefer, south-west Poland: Mineralium Deposita, v. 37, p. 512–528.

Plein, E., ed., 1995, Stratigraphie von Deutschland I, Norddeutsches Rotliegendbecken, Rotliegend-Monographie Teil II: Courier, Forschungs-Institut Senckenberg, v. 183, p. 1–193.

Pompeckj, J.F., 1914, Das Meer des Kupferschiefers: Leipzig, Branca Festschrift, p. 444–494.

Püttmann, W., and Eckardt, C.B., 1989, Influence of an intrusion on the extent of isomerism in acyclic isoprenoids in the Permian Kupferschiefer of the Lower Rhine basin, N.W. Germany: Organic Geochemistry, v. 14, p. 651–658.

Püttmann, W., Hagemann, H.W., Merz, C. and Speczik, S., 1988, Influence of organic material on mineralization processes in the Permian Kupferschiefer Formation, Poland: Organic Geochemistry, v. 13, p. 357–363.

Püttmann, W., Merz, C., and Speczik, S., 1989, The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland: Applied Geochemistry, v. 4, p. 151–161.

Rentzsch, J., 1964, Der Kenntnisstand über die Metall- und Erzverteilung im Kupferschiefer: Zeitschrift für angewandte Geologie, v. 10, p. 281–288.

——1974, The Kupferschiefer in comparison with the deposits of the Zambian copperbelt: Centeniary Societé Géologique Belgique, Gisements Stratifomes et Provinces Cupriferes, p. 395–418.

Rentzsch, J., and Franzke, H.J., 1997, Regional tectonic control of the Kupferschiefer mineralization in Central Europe: Zeitschrift für Geologische Wissenschaften, v. 25, p. 121–139.

Rentzsch, J., and Friedrich, G., 2003, Zur Herkunft der Metalle der Kupferschiefervererzung in Deutschland: Hallesches Jahrbuch für Geowissenschaften, v. B25, p. 1–20.

Rentzsch, J., and Knitzschke, G., 1968, Erzmineralparagenesen des Kupferschiefers und ihre regionale Verbreitung: Freiberger Forschungsheft, v. C 231, p. 189–211.

Rentzsch, J., and Langer, M., 1963, Fazielle Probleme des Kupferschiefers von Spremberg-Weißwasser: Zeitschrift für angewandte Geologie, v. 9, p. 507–513.

Rentzsch, J., Franzke, H.J., and Friedrich, G., 1997, Die laterale Verbreitung der Erzmineralassoziationen im deutschen Kupferschiefer: Zeitschrift für Geologische Wissenschaften, v. 25/1-2, p. 141-149.

Roemer, F., 1876, Ergebnisse eines Tiefbohrlochs bei Kraika Bez: Breslau, Jahresbericht der Schlesischen Gesellschaft für Vaterländische Kultur, 54 p.

Rydzewski, A., 1964, Petrography and mineralization of the Zechstein deposits in the areas of Fore-Sudetic monocline and pericline of Zary: PrzeglaÎd Geol., v. 12, p. 476–480.

Ryka, W., 1981, Some problems of the Autunian volcanism in Poland: International Symposium Central European Permian, Warsaw, Proceedings, p. 165–179.

Sawłowicz, Z., 1989, Organic matter in the Zechstein Kupferschiefer from the Fore-Sudetic monocline. I. Bitumen: Mineralogia Polonica, v. 20, p. 69–86.

——1990, Primary copper sulphides from the Kupferschiefer, Poland: Mineralium Deposita, v. 25, p. 262–271.

Schmidt, F.P., 1987, Alteration zones around Kupferschiefer-type base metal mineralization in West Germany: Mineralium Deposita, v. 22, p. 172–177.

Schmidt Mumm, A., and Wolfgramm, M., 2004, Fluid systems and mineralization in the north German and Polish basin: Geofluids, v. 4, p. 315–328.

Schnorrer-Köhler, G., 1983, Die minerale des Richelsdorfer Gebirge: Aufschluss, v. 34, p. 535–540.

Schüller, A., 1959, Metallisation und Genese des Kupferschiefers von Mansfeld: Abhandlungen der deutschen Akademie der Wissenschaften zu Berlin, Klasse Chemie, Geologie Biologie, 1958, v. 6, p. 62–89.

Sibson, R.H., Moore, J.Mc.M., and Rankin, A.H., 1975, Seismic pumping—a hydrothermal fluid transport mechanism: Journal of the Geological Society of London, v. 131, p. 653–659.

Slowakiewicz, M., Kiersnowski, H., and Wagner, R., 2009, Correlation of the Middle and Upper Permian marine and terrestial sequences in Polish, German and USA western interior basins with reference to global time markers: Palaeoworld, v. 18, p. 193–211.

Spangenberg, C., 1572, Mansfeldische Chronica: Eisleben, Germany, Petri, 503 p.

Speczik, S., 1995, The Kupferschiefer mineralization of Central Europe: New aspects and major areas of future research: Ore Geology Reviews, v. 9, p. 411–426.

Speczik S., and Püttmann W., 1987, Origin of Kupferschiefer mineralization as suggested by coal petrology and organic geochemical studies: Acta Geologica Polonia, v. 37, p. 67–187.

Stedingk, K., Rentzsch, J., Knitzschke, G., Schenke, G., Heinrich, K., and Schefler, H., 2002, Potenziale der Erze und Spate in Sachsen-Anhalt: Rohstoffbericht 2002: Mitteilungen zur Geologie Sachsen-Anhalt, LAGB Sachsen-Anhalt, v. 5, p. 75–131.

Strengel-Martinez, M., Spezik, S., and Jankowski, J., 1993, Epigenetic veins in Kupferschiefer deposits of SW Poland: Archiwum Mineralogiczne, v. 46, p. 202–203.

Sun Y., and Püttmann W., 1997, Metal accumulation during and after deposition of Kupferschiefer from the Sangerhausen basin, Germany: Applied Geochemistry, v. 12, p. 577–592.

Symons, D.T.A., Sangster, D.F., and Leach. D.L., 1995, A Tertiary age from paleomagnetism for the Mississippi Valley-type zinc-lead mineralization in Upper Silesia, Poland: Economic Geology, v. 90, p. 782–794.

Symons, D.T.A., Kawasaki, K., Walther, S., and Borg, G., 2010, Paleomagnetism of the Cu-Zn-Pb-bearing Kupferschiefer black shale (Upper Permian) at Sangerhausen, Germany: Mineralium Deposita, v. 46, p. 137–152.

Tokarska, K., 1971, Geochemiczna charakterystyka substancji bitumicznej cechsztyń-skich łupków miedzionośnych: Kwartalnik Geologiczny, v. 15/1, p. 67–76.

Tomaszewski, J.B., 1978, Geology of the Lubin-Sieroszowice vicinity (Lower Silesia): Geologia Sudetica, v. 13/2, p. 85–132 (in Polish).

Vaughan, D.J., Sweeney, M.A., Friedrich, G., Diedel, R., and Haranczyk, C., 1989, The Kupferschiefer: An overview with an appraisal of the different types of mineralization: Economic Geology, v. 84, p. 1003–1027.

Walther, S., Borg, G., and Ehling, B.C., 2009, The German Kupferschiefer deposits—what about the precious metals, smart science for exploration and mining: Townsville, Australia, Economic Geology Research Unit, James Cook University, v. 2, p. 502–504.

Walther, S., Borg, G., and Kopp, J., 2007, The significance of footwall and hanging wall ore in the German Kupferschiefer of Richelsdorf and Spremberg/Weisswasser, *in* Andrew, C., ed., Digging deeper—Proceedings of the Ninth Biennial SGA Meeting, Dublin, Ireland 2007, 1: Dublin, Irish Association for Economic Geology, p. 229–232.

Wedepohl, K.H., 1971, Kupferschiefer as a prototype of syngenetic sedimentary ore deposits: Japan, Society for mineralogy and Geology, v. 3, p. 268–273.

Wedepohl, K.H., and Rentzsch, J., 2006, The composition of brines in the early diagenetic mineralization of the Permian Kupferschiefer in Germany: Contributions to Mineralogy and Petrology, v. 152, p. 323–333.

Wedepohl, K.H., Delevaux, M.H., and Doe, B.R., 1978, The potential source of lead in the Permian Kupferschiefer bed of Europe and some selected Paleozoic mineral deposits in the Federal Republic of Germany: Contributions to Mineralogy and Petrology, v. 65, p. 273–281.

Więcław, D., Kotarba, M., Pieczonka, J., Piestrzyński, A., Oszczepalski, S., and Marynowski, L., 2007, Reduce, transitional and oxidized zones distribution in the Kupferschiefer in Fore-Sudetic monocline based on indices of organic matter: Biuletyn Państwowego Instytutu Geologicznego, v. 423, p. 125–138. (in Polish).

Wodzicki, A., and Piestrzyński, A., 1994, An ore genetic model for the Lubin-Sieroszowice mining district, Poland: Mineralium Deposita, v. 29, p. 30–43.
Wyżykowski, J., 1958, Prospecting of copper ores on the Fore-Sudetic zone: Przegląd Geol., v. 1, p. 17–22 (in Polish).
——1971, Zechstein copper formation in Poland: Przegląd Geol., v. 3, p. 117–122.
Ziegler, P. A., 1990, Geological Atlas of Western and Central Europe: Den Haag, Elsevier, 2nd ed., 239 p.
Zies, E.G., Allen, E.T., and Merwin, H.E., 1916, Some reactions involved in secondary copper sulfide enrichment: Economic Geology, v. 11, p. 407–503.
Zwierzycki, J., 1951, Sole potasowo-magnezowe na północ od Wrocławia: Prace Państwowego Instytutu Geologicznego, v. 7, p. 257–295.

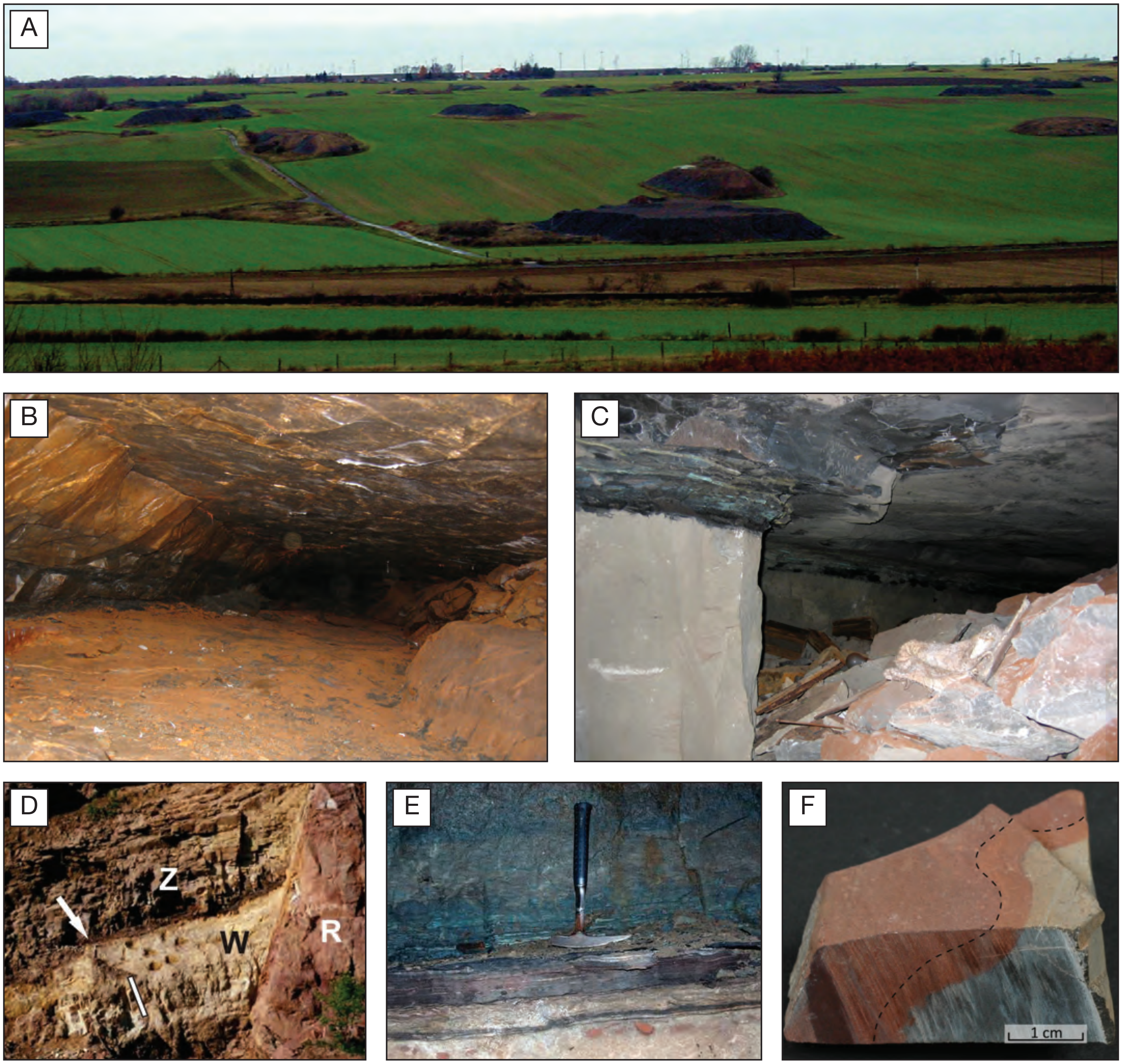

Plate 1. A. Medieval and early industrial Kupferschiefer mine dumps at Hettstedt, near Mansfeld. Note the increasing size of the waste dumps due to the increasing depth of the Kupferschiefer, dipping toward the photographer. B. Stope face in historic part of the Wettelrode mine, Sangerhausen district. Mining width is 0.45 m with Kupferschiefer black and basal Zechstein limestone (yellow-brown) being extracted prior to 1950. C. Kupferschiefer ore above barren Weissliegend sandstone, Wettelrode mine, Sangerhausen district. Modern mining width 1.4 m. D. Quarry near Münden, Richelsdorf district. Rotliegend (R), down-faulted Weissliegend (W), Kupferschiefer (arrow), Zechstein limestone (Z). Hammer for scale below arrow. The Cu zone is indicated by a white bar. E. Kupferschiefer altered and oxidized by Rote Fäule on top of Weissliegend with hematitic spots. Polkowice mine, Poland. F. Two zones within secondary hematitic oxidation front (Rote Fäule) in Zechstein limestone, Mansfeld district. Image: Saskia Meißner.

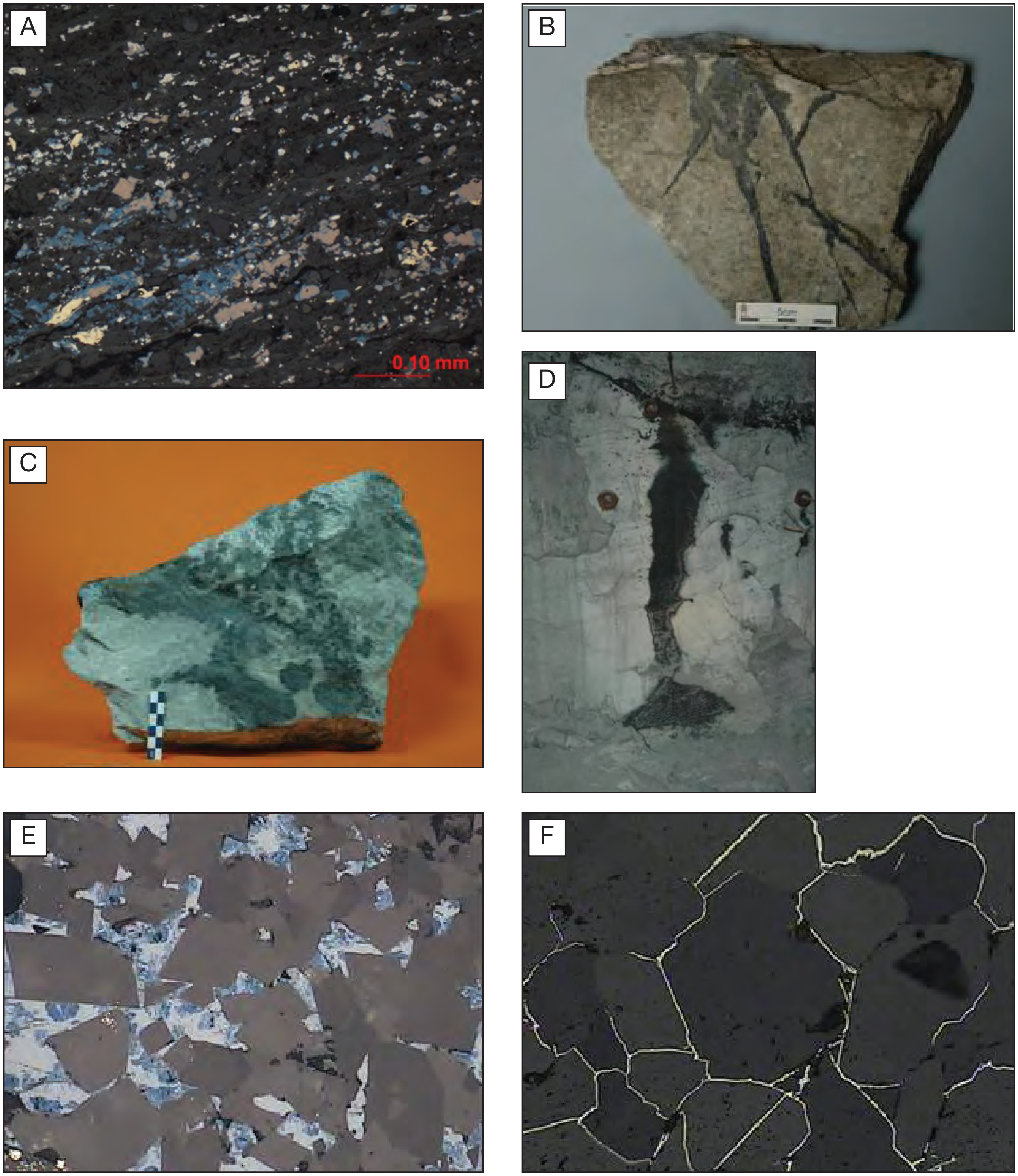

PLATE 2. A. Photomicrograph of finely disseminated chalcocite-bornite-chalcopyrite ore in black shale, partly replacing diagenetic pyrite cubes (reflected light). Mansfeld district. Image: Manuela Frotzscher. B. Chalcocite veins in uppermost part of Weissliegend sandstone, Rudna mine. C. Massive chalcocite impregnating Weissliegend sandstone, Rudna mine. D. Massive chalcocite impregnation crosscutting Weissliegend sandstone, Rudna mine. E. Photomicrograph of chalcocite (light gray) and covellite (blue) cementing dolorhombs in hanging-wall dolomite ore, Sieroszowice mine (reflected light, field of view 0.86 × 0.6 mm). F. Photomicrograph of thin coatings of chalcopyrite (white) in calcite crystal boundaries, Sieroszowice mine (reflected light, field of view 0.86 × 0.6 mm).

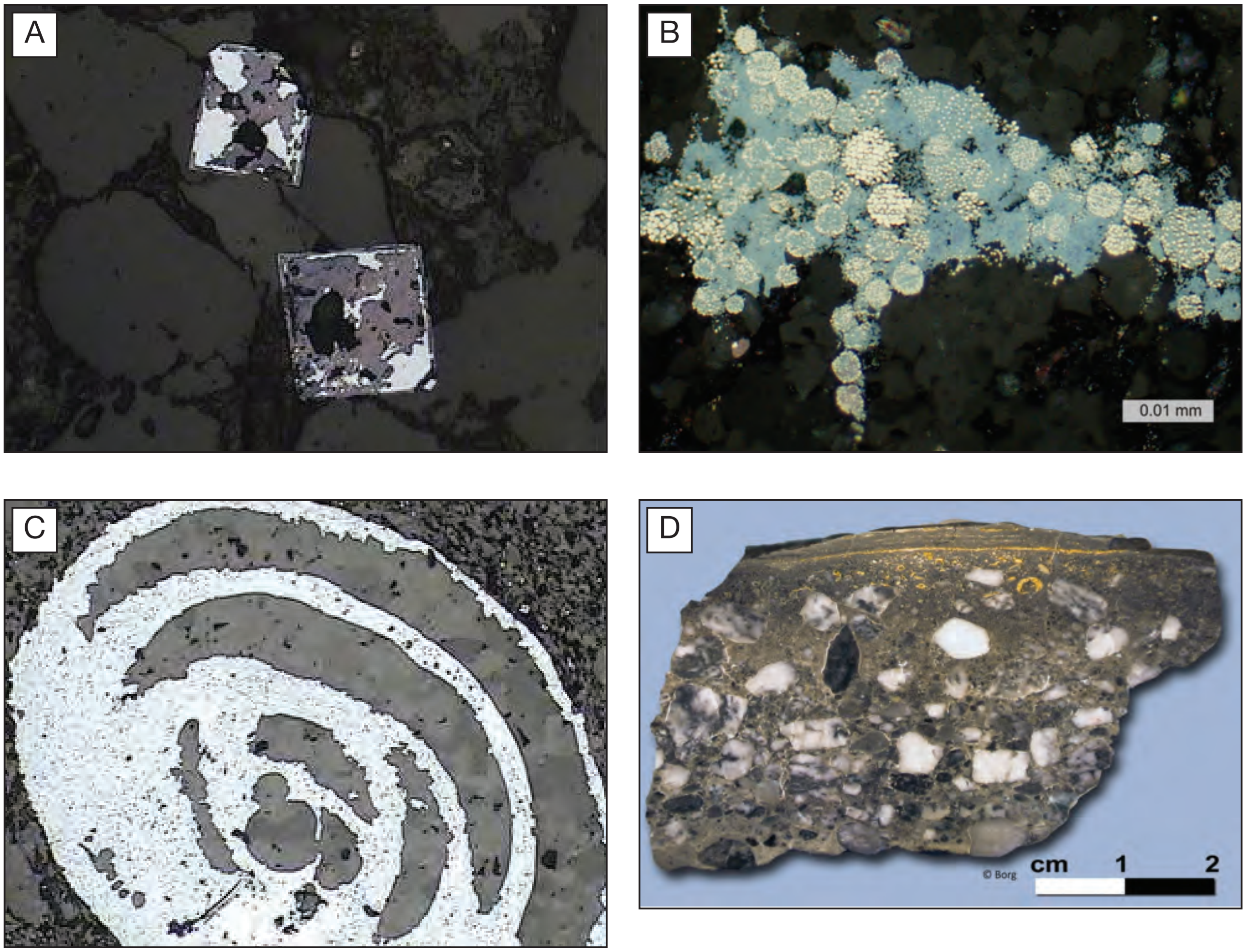

PLATE 3. A. Photomicrograph of chalcocite (white) and bornite (mid-gray) pseudomorph after diagenetic pyrite cubes in Weissliegend Sandstone, Lubin mine (reflected light, field of view 0.86 × 0.6 mm). B. Photomicrograph of early diagenetic framboidal pyrite (white) being replaced to varying degrees by chalcocite (light blue), Mansfeld district (reflected light). Image: Saskia Meißner. C. Photomicrograph of a foraminifer skeleton replaced by chalcocite, Grodziec syncline (reflected light, field of view 1.6 × 1.2 mm). D. Hand specimen of uppermost Weissliegend conglomerate and basal Kupferschiefer with rich chalcopyrite (yellow) and chalcocite (not visible) mineralization partly replacing lithic clasts, Schnepfenbusch mine, Richelsdorf district. E. (following page) Photomicrograph (reflected light) showing replacement of feldspar component of lithic clasts by chalcopyrite (yellow) and chalcocite (light gray). F. Photomicrograph of intergrown native gold (yellow) and secondary hematite in Weissliegend sandstone, Polkowice mine, western ore field (reflected light, field of view 0.4 × 0.2 mm). G. Photomicrograph of thiosulfates as cement in sandstone, Lubin mine (reflected light, field of view 0.86 × 0.6 mm). H. Photomicrograph of botryoidal bornite (brownish pink), covellite (blue), and marcasite (white), pseudomorph after thiosulfates, Lubin mine (reflected light, field of view 0.4 × 0.2 mm).

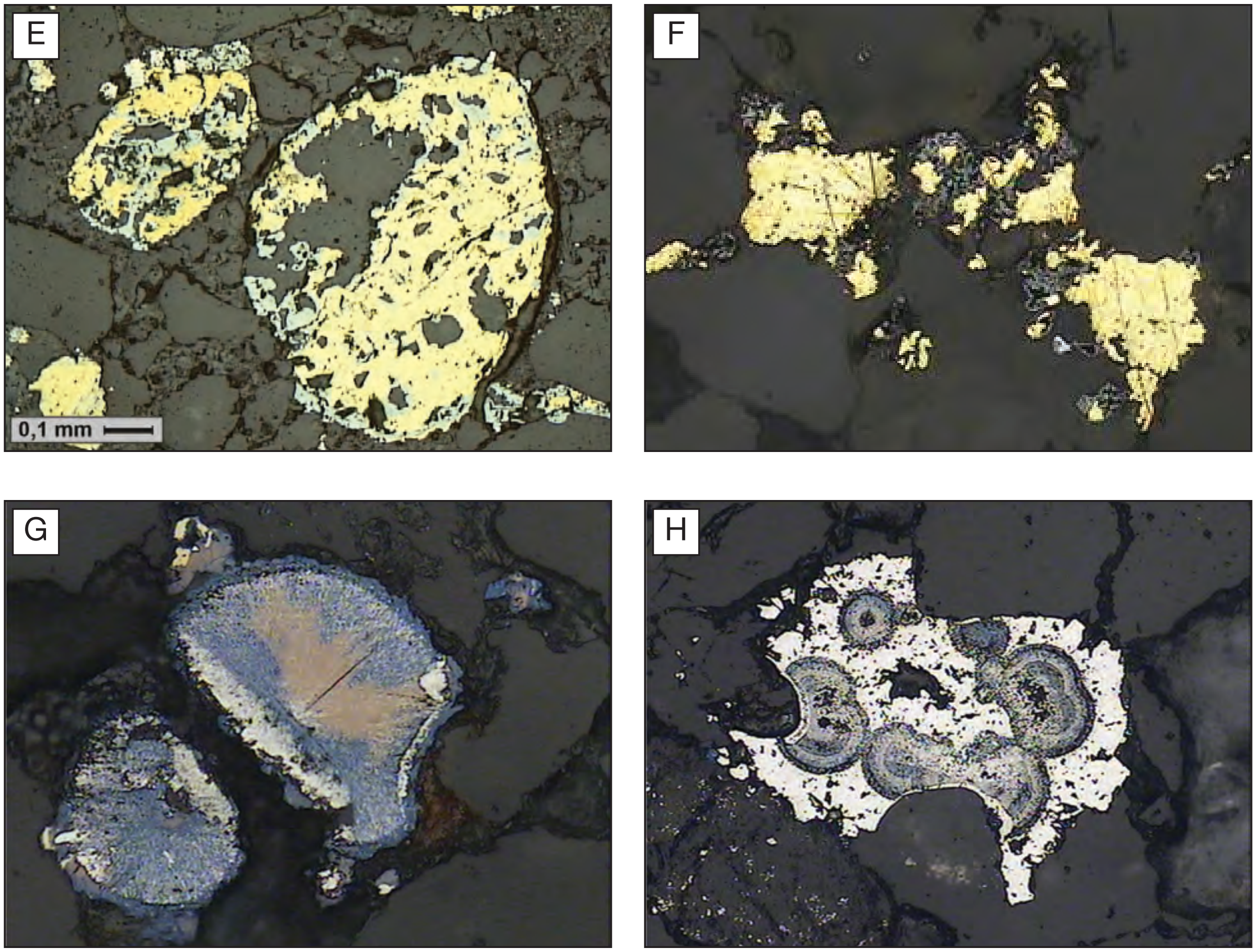

PLATE 3. *(Cont.)*