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Zechstein-Kupferschiefer Mineralization Reconsidered as a Product of Ultra-Deep Hydrothermal, Mud-Brine Volcanism

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Abstract

The Kupferschiefer is a copper-, polymetallic-, hydrocarbon-bearing black shale of the lowermost Zechstein Group of Permo-Triassic age (252 Ma) in Germany and Poland. It is usually 1 m thick and underlies 600,000 km², extending from Great Britain to Belarus for a distance of over 1500 km. At a district scale, copper has been mined for over 800 years since its discovery circa 1200 A.D. Mineralogical, chemical, and geological analyses of the combined Zechstein-Kupferschiefer show strong chemical and paragenetic relationships between the Zechstein salines, Kupferschiefer, and Weissliegend sandstones that lead to a broader, more unified, genetically linked model related to deep-sourced, hot, hydrothermal, mud-brine volcanism. The overall Zechstein-Kupferschiefer chemical stratigraphy suggests density-/composition-driven fractionation of deep-sourced, metal-rich, alkali-rich, silica-aluminum-rich, halogen-rich, high-density brines. The ultimate brine source is interpreted to be serpentinized peridotite in the lower crust near the Moho transition to the mantle. Dehydration of the serpentinite source to talc (steatization) by mantle heat during failed, intra-continental rifting of the Pangaea supercontinent at the end of Permian time released vast amounts of element-laden, high-density brines into deep-basement fractures, depositing them into and above the Rotliegend Sandstone in the shallow Kupferschiefer Sea, which is analogous to the modern northern Caspian Sea.

Keywords: Kupferschiefer, Permian, copper, silver, hydrocarbons, hydrothermal, ultra-deep hydrothermal, UDH, Zechstein, mud volcanism, exotic

1. Introduction

The Kupferschiefer is copper-bearing black shale of lowermost Zechstein Group of Permo-Triassic age (252 Ma) in Germany and Poland. The black shale is approximately 1-m thick and

underlies 600,000 km² of northern Europe, extending from Poland to eastern England (**Figure 1**). The Kupferschiefer is thinly laminated, bituminous, calcareous and clayey shale at the base of the Zechstein Group. The Kupferschiefer is a small part of a larger, Permo-Triassic, genetically linked geosystem that includes the underlying Rotliegend (red sandstone) and Weissliegend (white sandstone), Kupferschiefer (black copper shale), and overlying Zechstein chemical sedimentary rocks (Werra carbonates, dolomite, anhydrite, and saline rocks) (**Figure 2**) that are cross cut by the hematitic Rote Fäule. In this chapter, this broader system (**Figure 3**) is designated the Zechstein-Kupferschiefer system, following the precedent of Kucha [1].

The literature that has accumulated since Agricola is extremely robust and this chapter does not attempt to summarize the pre-existing genetic models. Instead, this chapter offers a broader perspective and hypothesis that the entire Weissliegend-Kupferschiefer-Zechstein system can be reconsidered as product of ultra-deep, high-energy, high temperature, mud volcanism. These rocks are produced by a deep-sourced, hydrothermal plume system of high-density brines, and mud slurries that transported the above materials from a steatized serpentinite reaction chamber near the base of the crust to a low-energy, low temperature, exhalative system at the crust-hydrosphere interface.

The ultra-deep hydrothermal (UDH), mud-volcanic model resolves a number of paradoxes that have arisen in the abundant Kupferschiefer literature. One main contrast in concepts is between high temperature, hydrothermal mineral assemblages, and low temperature mineral

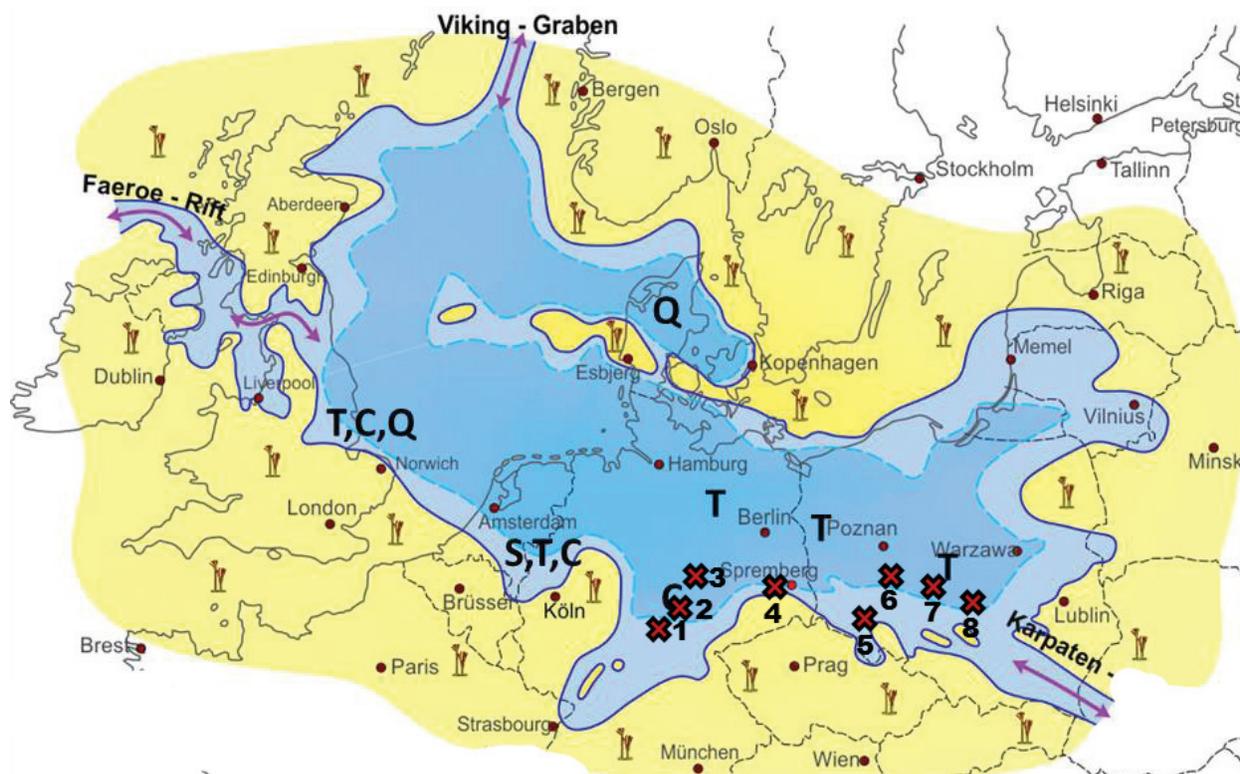


Figure 1. Map of Zechstein basin showing locations of exotic magnesium-rich mineral suites and euhedral quartz [T = talc; S = serpentinite; C = clinocllore; Q = euhedral quartz]. From west to east (left to right), the locations are Yorkshire, England [TCQ], Emsland, southwest Germany [STC], Mors diapir, northern Denmark [Q], Gorbelen salt dome north central Germany [T], Königschall-Hindenburg salt mine, southern Germany [C], dolomite 'reef'. Mines: 1 = Melsungen, 2 = Sangerhausen, 3 = Mansfeld, 4 = Spremberg, 5 = Konrad, 6 = Polkowice-Sieroszowice, 7 = Rudna, 8 = Lubin.

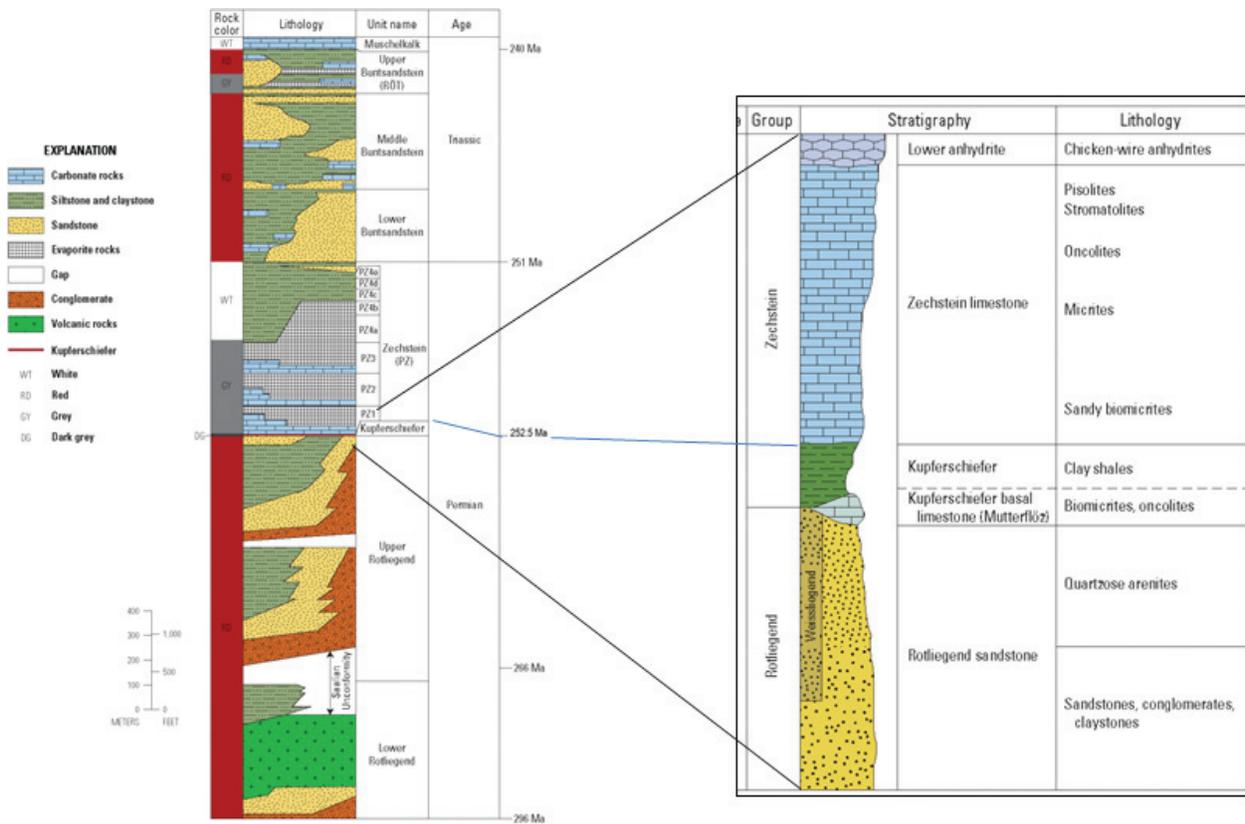


Figure 2. Stratigraphic sections (broader area on left, narrow zone on right) (modified from Zientek et al. [2]).



Figure 3. The upper Permian-lower Triassic sequence is from upper (Sandsteinschiefer) Rotliegend sandstone in the footwall, the mineralized Weißliegend white sandstone and Kupferschiefer metallized black shale, and the hanging wall of Zechstein dolostone. Location: Roerigschacht, Wettelrode/Sangerhausen mine, Mansfeld district, Germany. The Permo-Triassic boundary is placed at the Kupferschiefer-Zechstein contact. (Photo by Juergen Kopp showing the mine manager Dipl.-Ing. Erich Hartung).

assemblages indicative of surface environments. The UDH mud volcanism model merges both syngenetic and epigenetic processes. The UDH model also considers the oxidized and reduced mineralization styles to be independent, age distinct components of an ongoing, pulsed process that occurred over a period of geologic time from 265 to 235 Ma. Within this sequence, each pulse represents a thermodynamically distinct episode that is not rigorously connected to the other episodes. The connection only occurs at the scale of the entire system that is broadly related to a process of dehydration of ultramafic serpentinites in the lower crust that were episodically affected by influxes of mantle heat.

The UDH, mud-volcanic concept posits that much of the Kupferschiefer-Zechstein represents metalliferous slurry flows that were erupted from numerous mud vents. A spectacular example of where epigenesis meets syngeneses is present at Rudna where chalcocite veins transgress metallized Weissliegend and appear to erupt chalcocite slurry flows into the overlying Kupferschiefer. The slurries can contain exotic, hydrothermal components as clasts that may have originally formed deep within the mud-volcanic system at various times and temperatures. This explains the equivocal results from dating individual clasts within the Kupferschiefer. Once erupted onto the seafloor (circa 255 Ma), the deep-sourced mud slurries were able to interact with the low-energy, biogenic environment. In some cases, especially in the distal pyrite environments, microbial reduction of the sulfur could have produced light sulfur isotopes. This process, however, would have been superimposed on already very light sulfur isotopes inherited from deep sources.

The southern rim of the Kupferschiefer carries enriched polymetallic mineralization near large shear zones (**Figure 4**). Mineralization occurs as: (1) large amounts of copper sulfides in the upper part of the Weissliegend sandstones, (2) reduced, black to dark gray, kerogen-rich, metal sulfide-bearing deposits of the Kupferschiefer and overlying Zechstein carbonates, and (3) oxidized, reddish, hematitic rocks (Rote Fäule) that contain gold and platinum group elements (PGE). Mineralization consists of fine disseminations and as coarse-grained aggregates, lenses, streaks, and veinlets of sulfide minerals. Mineralization of the Rote Fäule transgresses all three units at very low angles (**Figure 5**).

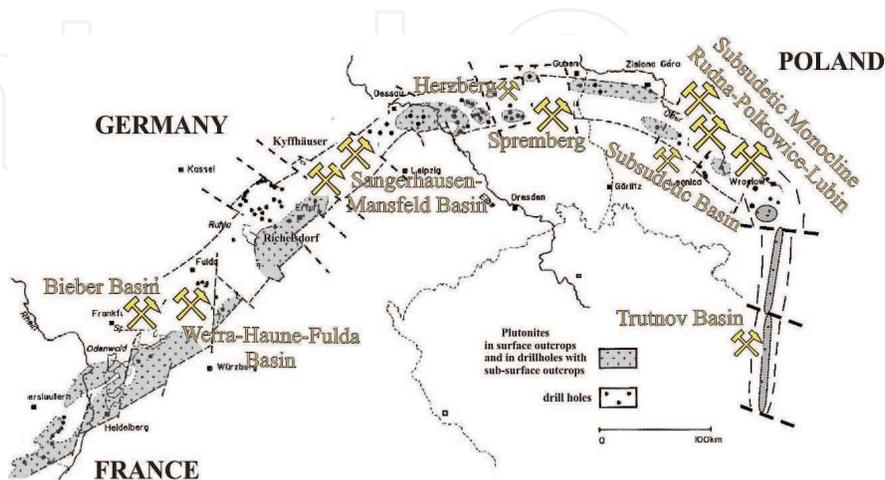


Figure 4. The copper-polymetallic-gold belt of central Europe showing exploration drill holes, deposits and mines (names of the mines are in **Figure 1**). The mineralized belt overlies the post-Variscan-crystalline zone at the southern rim of the Zechstein-Kupferschiefer Sea [62].

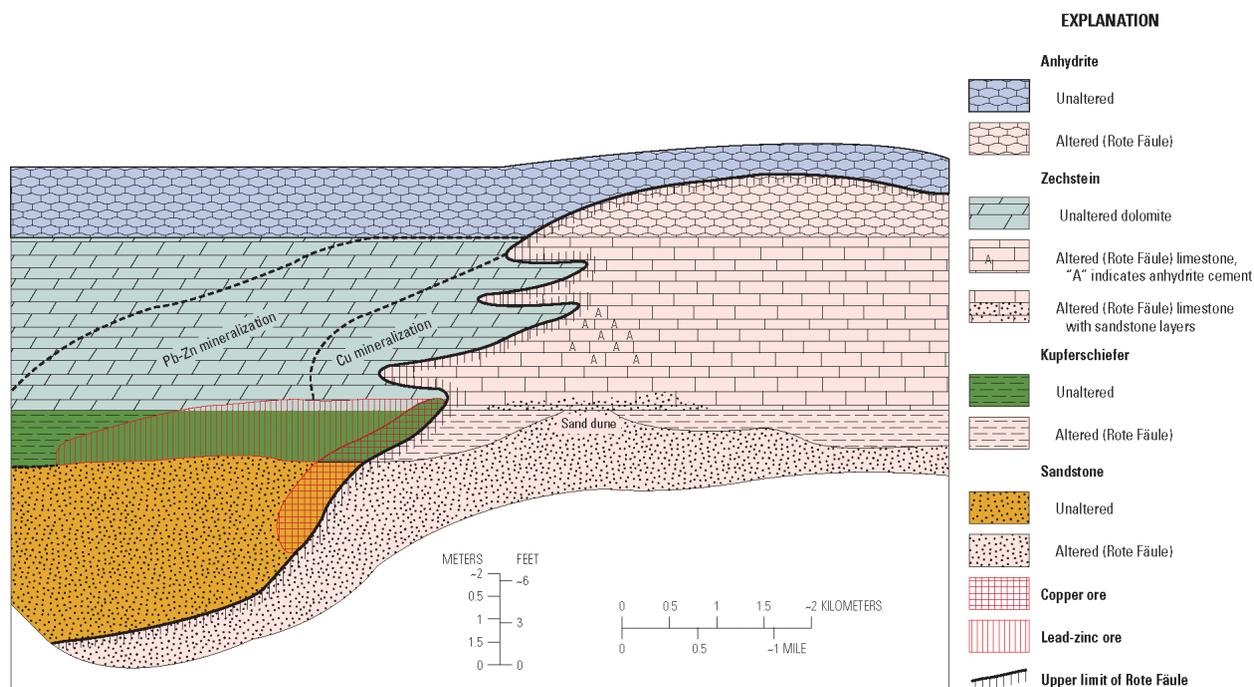


Figure 5. Schematic cross-section showing the Zechstein-Kupferschiefer metallization as part of the greater Zechstein sequence in the Lubin district (from Zientek et al. [2]).

Since about 1200 A.D., some 78 million metric tons of copper metal have either been produced or are delineated as reserves in Germany and Poland, according to an assessment of undiscovered copper resources for the Kupferschiefer (as documented as production and reserves by Zientek and others [2]). Some of the significant mines are shown in **Figure 1**. Zientek and others [2] estimate that 126 million metric tons of copper metal may remain undiscovered.

2. Formations underlying the Kupferschiefer

2.1. Rotliegend Group

The Lower Rotliegend consists of volcanic rocks and interbedded fluvial and lacustrine sedimentary strata of Early Permian age. The Upper Rotliegend consists of clastic, red bed sedimentary rocks of Middle and Late Permian time that were deposited in desert environments over broad areas of northern Europe. These rocks extend from Poland to western England and from the German-Danish border to northeast of Frankfurt, Germany [2]. The Rotliegend is approximately 300 m thick [1]. The abundant areas of oil and gas fields in the Rotliegend (**Figure 6**) (one [Groningen] of which is world class [3]), follow a similar regional orientation as the metallic mines and are partly hosted in the same units (especially pure silica sand of the Weissliegend). The economic significance of the oil and gas resource overshadows the economic significance of the metal production in the Zechstein-Kupferschiefer.

The Rotliegend underlying the black shale of the Kupferschiefer is inferred to be a pre-ambly to the ultra-deep hydrothermal (UDH) process. The UDH process of the Zechstein-Kupferschiefer super system is likely to have subjected the Rotliegend rocks to alteration along feeder zones and



Figure 6. Oil (green squares) and gas (red dots) fields in the Rotliegend (modified from Gautier [3]).

fluid pathways. The Rotliegend is locally very hematitic and contains wide spread anhydrite and locally bitumen hydrocarbon. The alteration is probably a regional scale footprint of a deeper process (similar to that causing the Rote Fäule) that continues downward into the lower crust along a series of deeply penetrating basement faults.

2.2. Weissliegend injectite/Extrudite facies

The Weissliegend white sandstone underlies the black Kupferschiefer shale in places and is 0.3–42 m thick in the mining areas [3]. The angular and unfrosted nature of the Weissliegend quartz grains in thin section (seen in Figure 3a of [4]) indicates the sand was not formed in an eolian environment. Silica dikes and sills in the Weissliegend in the United Kingdom North Sea (photographs in Figures 8 and 14 in [5]) and the Netherlands (Figures 9 and 11 in [6]) show textures that are very similar to quartz sand injectites, such as those in the Panoche Hills and Panther Beach, California [7].

The underlying Weissliegend is interpreted to be a sand extrudite or injectite, silica mud that locally contains a matrix of copper sulfide that could have been emplaced as mud slurry composed of chalcocite and silica. For example, the Rudna Mine, in the greater Lubin district in southwest Poland, has turned out to be the largest copper mine in the Kupferschiefer (and in Europe) with 513 million tons of ore grading 1.78% copper and 42 g/metric tons silver [2]. The mineralization in the Rudna Mine is not hosted in Kupferschiefer shale, but rather is hosted almost entirely in the Weissliegend. This mine alone has more copper than has been produced from the entire Kupferschiefer. The geometry of the Rudna ore body takes the form of a large mound-like feature composed mainly of silica with lesser amounts of illite and feldspar.

From a UDH perspective, this mound-shaped feature has the appearance of a pancake-like, silica-mud volcano that is 12 m high by 1 km diameter (see cross-section Figure 4 in [8]). The Kupferschiefer has accumulated as thin carbonaceous shale facies in depressions adjacent to the inferred silica-mud volcano(s) of the Weissliegend. The Kupferschiefer interfingers with the Boundary Dolomite (which was originally recognized by Krasoň [9]) on the tops of the Weissliegend silica mounds (see Figure 4 in [10]). The Boundary Dolomite is a dolomite-cemented sandstone that rapidly grades downward into the main, structureless sandstone of the Weissliegend. Thus, there appears to be a direct chemical and sedimentological connection between the Weissliegend chemical extrudites and the Boundary Dolomite, which is a magnesium carbonate fractionate at the top of the Weissliegend. On the flanks of the silica-mud mounds, the Boundary Dolomite then grades laterally into the carbon-rich, reduced Kupferschiefer. In effect, the Kupferschiefer in the greater Lubin area can be regarded as a volumetrically minor facies of the Weissliegend. All of the above units are regarded as chemical facies of deep-seated mud volcanism.

The Weissliegend silica extrudite mounds and ridges appear as high areas throughout the Lubin area (see cross-section in Figure 13 in [8]) and are the main hosts to the ore bodies (especially at the Rudna Mine). In the Lubin district at least, the Weissliegend and the processes that formed it are important to the genesis of the Kupferschiefer in southwestern Poland. In this sense, the Weissliegend is part of the process that is related to the broader Zechstein-Kupferschiefer mud-volcanic sequence. This interpretation is in agreement with the stratigraphic column presented in Figure 2 in [11] (as modified from Refs. [12, 13]).

The 'sandstone-hosted ore' can be further interpreted as a matrix-supported, high temperature, sulfide-rich, mud slurry that was extruded as a sulfide-matrix, mud slurry from an underlying vent source and accumulated into a chalcocite-silica-mud mound (Figure 3a of [4]). Furthermore, chalcopyrite-bornite, rhythmic laminae grade upward into layers of subangular to subrounded, quartz grains with a partial chalcopyrite-, bornite-, and covellite-filled matrix, as shown in Figure 4 in [14] and Figures 2–4 in [15]. The copper sulfide, rhythmic bands are distinguished by their extremely light $\delta^{34}\text{S}$ isotopes, which yield values between -39 and -44 . The sulfur isotopes consistently lighten upwards in a pattern that is consistent over five sections in the various parts of the Rudna, Polkowicze, and Lubin mines (Figure 3 in [15]).

From a UDH perspective, the laminae are interpreted as density-sorted, laminar flows, whereby the high-density sulfides were gravitationally sorted to the bottom of each rhythmic cycle. This gravitational sorting is consistent with slurry flowage and gravitational sorting within a silica-sulfide flow unit within the larger-scale, silica-sulfide mud mound, which is portrayed as an extrudite. The increasingly lightening upward pattern of the sulfur isotopes in

the Weissliiegend inferred extrudites is interpreted as being caused by progressive hydrogen reduction induced by hydrogen release from hydrogen sulfide gas during formation of various copper sulfides that were traveling as chloride complexes. The overall lightness of the sulfur isotopes may be explained by the light sulphurs that would be present in lizardite in the serpentine source region. Light sulphurs in oceanic lizarditic serpentine have been documented in an increasing number of cases summarized in **Table 1** of [16]. Hence, it is reasonable to suggest that lizarditic serpentinite might be a component of the ultramafic source near the Moho beneath the Lubin area.

3. Kupferschiefer

The Kupferschiefer (copper shale) consists of thinly laminated, bituminous, black mudstones, shales, marls, and carbonates. The Kupferschiefer traditionally is regarded as the basal member of the Zechstein Group and is 30–50 cm thick. In some areas, thin layers of carbonates are present under the Kupferschiefer. The lowermost, metal-rich, Kupferschiefer strata is 5–15 cm thick and contains the high-grade Cu-Ag-Au polymetallic and hydrocarbon mineralization in Germany and Poland at the southern rim of the Kupferschiefer Sea (**Figure 1**). If the Kupferschiefer is reconsidered as a facies of the Weissliiegend silica sands as discussed above, the base of the Zechstein can be assigned to the lowest of the Weissliiegend extrudites.

3.1. Kupferschiefer-Zechstein mineralogy

Copper mineralization in the Kupferschiefer *sensu stricto* consists of chalcocite, digenite, covellite, bornite, and chalcopyrite (**Figure 7**) associated with copper-arsenic ore consisting of tennantite and enargite. Galena and sphalerite commonly occur in the distal areas and only rarely in the Cu high-grade zones. Gold and silver occur as electrum in bornite and digenite (**Figure 8**). Pyrite

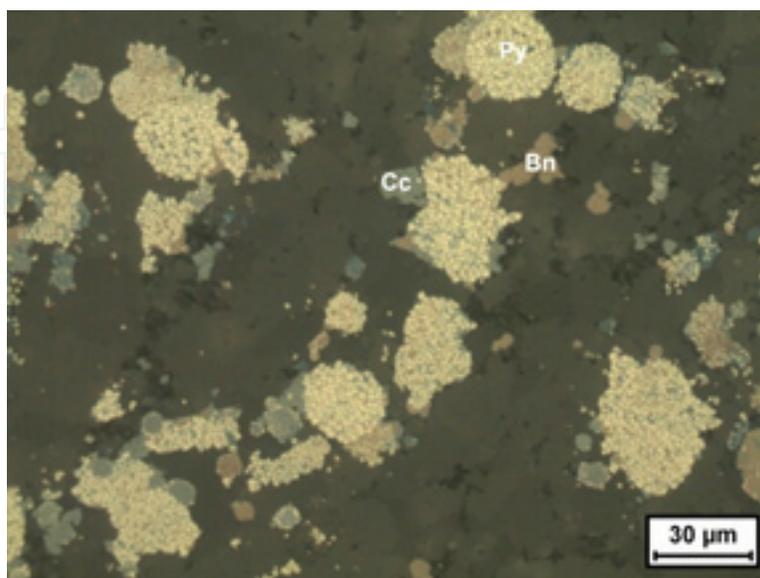


Figure 7. Microscopic mineralization in the Kupferschiefer, showing framboidal texture of copper and iron sulfides. Sample is from Spremberg drill hole 131, M 726b.4, KS T1, // ppl. Nicols.

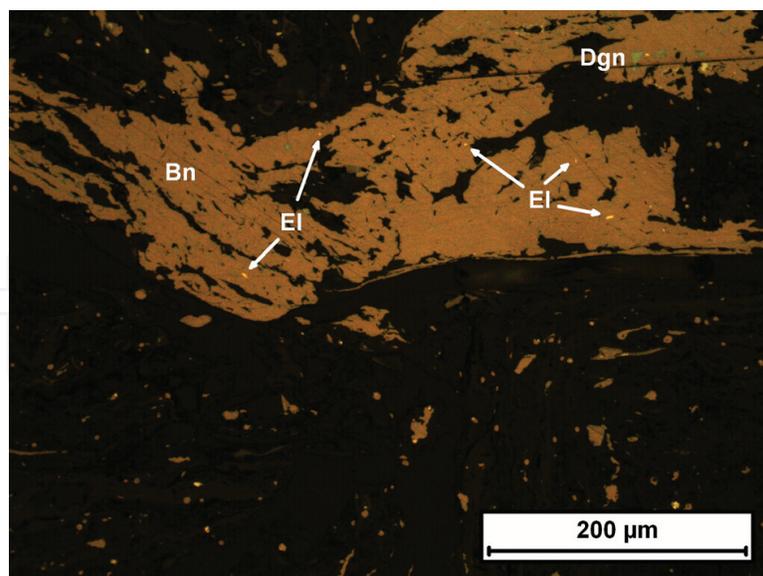


Figure 8. Massive and disseminated bornite with digenite and electrum exsolutions in kerogen- and hydrocarbon-rich Kupferschiefer shale layer T1. Sample is from Spremberg drill hole 131, M 735c, // ppl. Nicols. (Bn = Bornite, Dgn = Digenite, El = Electrum).

occurs in the Kupferschiefer and in the low-grade, mineralized zone distant from the high-grade copper mineralization. Silver and gold occur disseminated in copper sulfides as native metals and as exsolution in the form of electrum. Hematite occurs in the Rotliegend sediments and as a primary mineral in the Rote Fäule zone. Other minerals in the Kupferschiefer include marcasite, clausthalite, barite, and rutile, and also kerogen, hematite, calcite, quartz, clay minerals, and the detrital relicts of titanite, zircon, and apatite.

Copper sulfides are the main sulfides precipitated early in the mineral reaction sequence. Copper sulfides are widespread and are the major source of the economic extraction of copper. Digenite occurs as the major copper mineral. Chalcocite $[\text{Cu}_2\text{S}]$, digenite $[\text{Cu}_9\text{S}_5]$, djurleite $[\text{Cu}_{31}\text{S}_{16}]$, and anilite $[\text{Cu}_7\text{S}_4]$ are the copper-rich members of a mineral-series from covellite $[\text{CuS}]$ to chalcocite. Copper sulfide deposition is important in the process of liberating hydrogen.

In the UDH model, the brine plume, which contained copper, sulfur, iron, potassium, and chloride brines, quickly ascended, depressurized, cooled, and fractionated. Once the copper and sulfur had been removed from the brine as increasingly sulfur-rich sulfides, then the remaining copper was able to combine with the chloride and precipitate as atacamite $[\text{Cu}_2(\text{OH})_3\text{Cl}]$ or paratacamite $[\text{Cu}_3(\text{Cu,Zn})(\text{OH})_6\text{Cl}_2]$ at temperatures below 29°C . Atacamite appearance is further inferred to reflect the separation of the low temperature, low-density, Na-K-Mg brines that ultimately produced the extensive salines in the upper Zechstein. This process was not a secondary, supergene, oxidation effect. Rather, the process was a very late, primary, brine separation effect that occurred at the top of the plume, where the brines emerged onto the lower temperature paleosurface.

3.2. Kupferschiefer anomalous geochemistry

Compared to average shales, Kupferschiefer samples (especially those near structurally controlled fault 'feeders' beneath the ore deposits) are highly enriched in Ag, Cd, Hg, Mo, Co, Ni,

Cr, V, Sb, U, and Cs. The clay is also enriched in pyrite, Ba, and Sr in more distal settings. The clay of the Kupferschiefer also has strong enrichments in Re, Pb, Zn, Cu, Au, and PGE elements (Figure 7 in [17]). The carbonaceous shales contain an unusual element suite that represents an end member composition for similar, worldwide, metal-bearing, carbonaceous shales (Figure 7 in [17]). The lower 7 cm contains particularly high concentrations of the exotic element chemistry, which has made the formation important for its economic value, as shown in Figure 3 in [18].

Rather than epigenetically introducing these elements into a pre-existing, detrital shale, in the UDH model it is considered more likely that the clay-sized oxides and native metals (Figures 5 and 6 from [18]) were co-formed with carbonaceous, muscovitic, mud slurries resident in high temperature (approximately 350°C), mud chambers that were deep in the Kupferschiefer conduit system. The anomalous element suite in the clays is strongly similar to the element suite in ultramafic rocks that may have participated in the generation of the sulphidic muds.

The gold, PGE, and uranium occur in the Kupferschiefer in the 'transition zone' adjacent to the Rote Fäule. The noble elements and uranium are considered to have fractionated from the Rote Fäule fluids and were deposited in the redox transition (especially the PGE component). Hence, the introduction of the gold, uranium, and PGE are inferred to have been epigenetically introduced and are not syngenetic like the earlier syngenetic, copper-silver-mud slurry mineralization in the Kupferschiefer.

Evidence for a deep-basement source for metals in the Kupferschiefer was also shown by a K-means cluster analysis of trace elements in six samples from the distal pyritic zone in the Kupferschiefer collected for the 247 ± 20 Ma, Re-Os isochron [19]. The cluster analysis showed that the rhenium and osmium are very strongly correlated with elements, such as chromium, vanadium, nickel, cobalt, and iron. These metals are major metallic constituents of peridotites and their serpentized products. The $^{187}\text{Os}/^{188}\text{Os}$ initial ratio of 0.8 ± 1.2 suggests that the serpentization may have been partly induced by deep, crustal, hydrothermal fluids that were integrated with radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios, which had accumulated in the deep Caledonide basement beneath the Kupferschiefer. Mikulski and Stein [43] utilized $^{187}\text{Os}/^{188}\text{Os}$ ratios that are near peridotitic/serpentinic initial ratios of 0.2 and obtained Re-Os dates on individual minerals to obtain ages that spanned the Permo-Triassic boundary. Kerogen hydrocarbon is strongly statistically linked to the abundance of PGE, As, V, Cr, Ni, Cu, Au, and quartz overgrowths in the Polish Kupferschiefer (Figures 5 and 6 from [18]). The positive correlations are consistent with co-eval formation of metals and kerogen and indicate that the metallization has not been randomly superimposed on a pre-existing kerogenous shale.

Evidence for coincident deposition of halogen brines and copper sulfide-illite-kerogen minerals in the Kupferschiefer is shown in Figure 4 of [20]. Copper chlorides are present on diagenetic quartz overgrowths and sylvite crystals are present in inclusions in calcite within co-existing kerogen (Figures 2 and 5 from [20]). Evidence for coincident formation of halogen brines and copper sulfide-illite-kerogen deposition is also shown on Figure 3 of [20]. The identification of sylvite is important because it provides a source of potassium for illite formation. The hypogene texture of these samples allows the interpretation that the copper chloride was directly precipitated from aqueous copper chloride from a high-density, chloride brine that was probably sourced in the basement beneath the Kupferschiefer. According to Michalik

[20], 'Halite cement in the Weisslied sandstones is relatively common, but it occurs as small, often irregular crystals'. Paragenetic determinations by Large and others [21] (in Figures 6 and 7) show that the atacamite is closely associated with late crystallizing, low temperature minerals, such as anilite, djurleite, and yarrowite. This association may represent brine separation from the hydrothermal plume after the copper sulfides finished forming.

The characteristic correlation of kerogen hydrocarbons and metals (many of which are high temperature) in black shale-hosted metal deposits is consistent with a high temperature, hydrothermal origin for the kerogen itself. The high-energy, hydrothermal origin of the kerogen is reinforced by its close, interleaved association with high temperature, crystalline illite (muscovite) that crystallizes at high temperatures and locks in the potassium-argon age clock 350°C. The presence of illite/phengitic muscovite and metals may greatly facilitate (via aluminum-, halogen-, and Lewis acid-mediation) rearrangement of hydrocarbon compounds and alkylation at interfaces between illite and kerogen. The increase in kerogen content may be related to hydrogenization of original kerogen from hydrogen released during metal sulfide deposition from hydrothermal brines and hydrogen sulfide gas.

The deep-source, mud-volcano model offers a novel explanation for the well-known, highly anomalous, hydrocarbon occurrence in the Kupferschiefer black shale. The kerogen component of the black shale may have had a deep source, ultimately in serpentinized peridotites in the lower crust near the continental Moho. A significant component of this kerogen is possibly released into the saline brines during dehydration reactions and is progressively hydrogenated during sulfide formation to point where it may have entered the oil window. The hydrogen provided for this reaction is supplied by hydrogen sulfide with the sulfur going to form sulfides from metal-chloride ions traveling in the high-density brines. The hydrogenation explains progressive changes from PAH-dominated kerogens in the lowest Kupferschiefer to more hydrogen-saturated alkane arrays in chromatograms from the higher parts of the Kupferschiefer and lower Zechstein (Figure 1 in [22]). This chromatogram pattern was originally recognized at the Konrad Mine by Püttmann and others [22] and has since been repeatedly observed at most of the major Kupferschiefer mines from Poland to Germany.

The oil-like, alkane chromatograms of the upper Kupferschiefer indicate that the hydrogenation of the kerogen entered the oil window at the end of Kupferschiefer time. Thus, the hydrothermal mud-volcanic model is also compatible with a hydrothermal oil model. The syngenetic hydrothermal generation of oil does not require conventional maturation from kerogen to oil in a pre-existing black shale. Rather, the hydrothermal oil forms at the same time as the black shale forms. In the UDH model, the carbonaceous, black shale slurries were erupted on the Permo-Triassic paleosurface. The above scenario allows the possibility that this oil and gas generation event may be correlated with the widespread petroleum accumulations that have been developed in the centers of the Rotliegend basin (**Figure 6**) in the immediately underlying Rotliegend unit (especially the Weisslied silica extrudites; see above discussion).

3.3. Unusual textures in the Kupferschiefer

The Kupferschiefer (copper shale) has unique textures that are not like normal, detrital, sedimentary textures that are typically observed in deltaic shales. In many cases, the textures resemble hot slurries that were deposited under high-energy conditions. Thin sections reveal

unusual, non-shale-like, petrographic textures (**Figure 9**). Spheroidal, orbicular particulates are present within the Kupferschiefer. The UDH model agrees with observations by Kucha [23] that are consistent with brine-silicate-flocculate interactions during upward transport from deep brine chambers (Figures 1, 12, and 15 in [23]). The concentrically banded, colloform, spheroidal, ooid-like, chalcopryrite aggregate (shown in Figure 3b in [4]) probably formed as a concentric set of rings accreted around a chalcopryrite microsphere during its upward transport in a heavy metal-rich, brine slurry.

Evidence for high-energy hydrothermalism in the Kupferschiefer is shown by the arrow-like brecciation and deposition of chalcopryrite in veins into the black shale. **Figure 10** shows an immiscible chalcopryrite sulfide slurry/melt that may have injected into the soft, carbonaceous muds of the Kupferschiefer within a high-energy, near-vent, mud-volcanic facies (also see panels A and D in plate 2 of [24]). The chalcopryrite is a matrix-supported breccia with the matrix of chalcopryrite supporting the brecciated mud. The chalcopryrite appears to have been forcefully injected into the shale, brecciating it as the chalcopryrite melt was injected. Hence, textures in the Kupferschiefer resemble hot slurries that were formed under high-energy conditions (**Figure 10**, as modified from [25]) and deposited on a paleosurface under low-energy conditions.

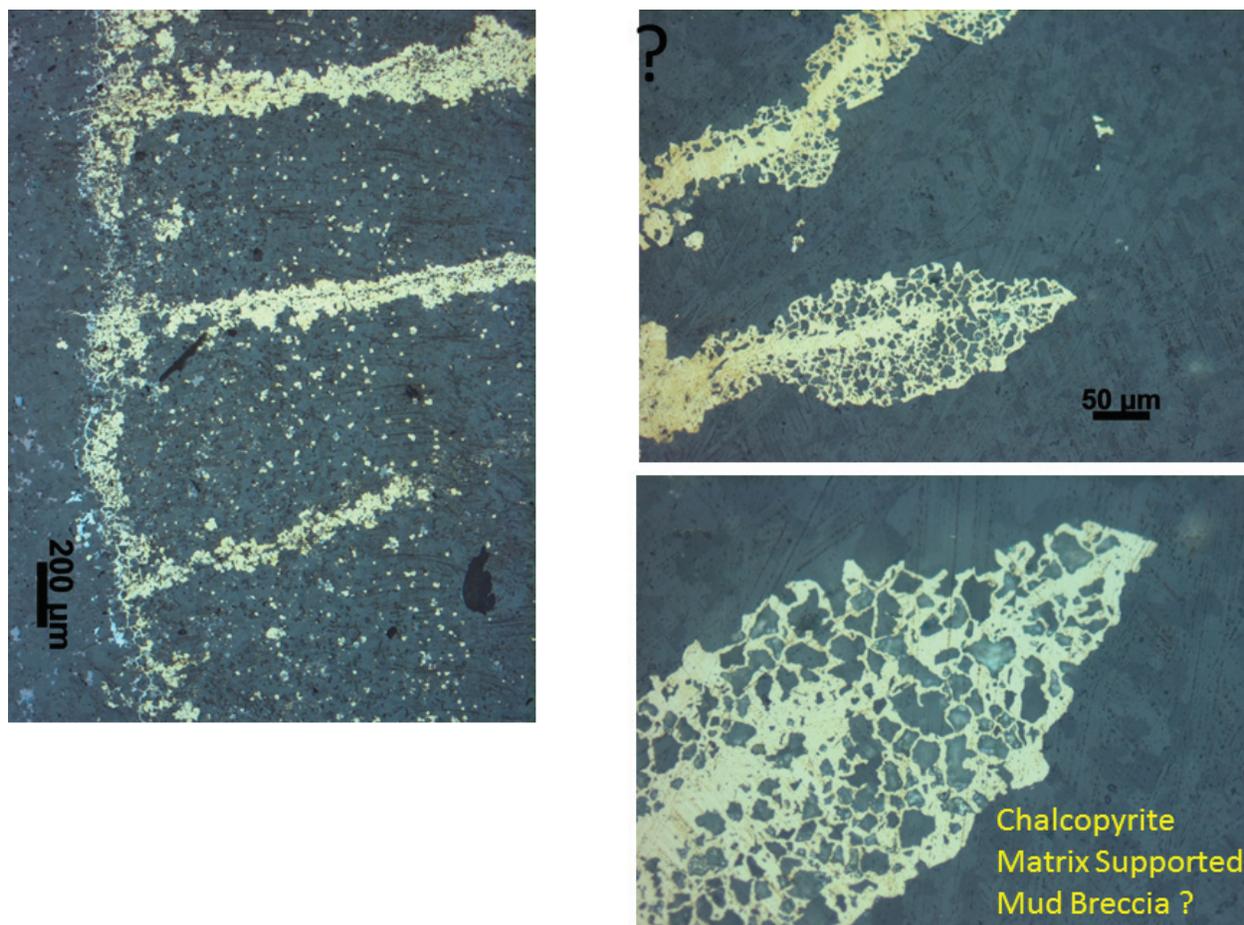


Figure 9. Spear-shaped, immiscible, chalcopryrite injectite into soft, carbonaceous muds of the Kupferschiefer. Sample is from Spremberg drill hole 131, M 734.1, KS T3, // ppl. Nicols.

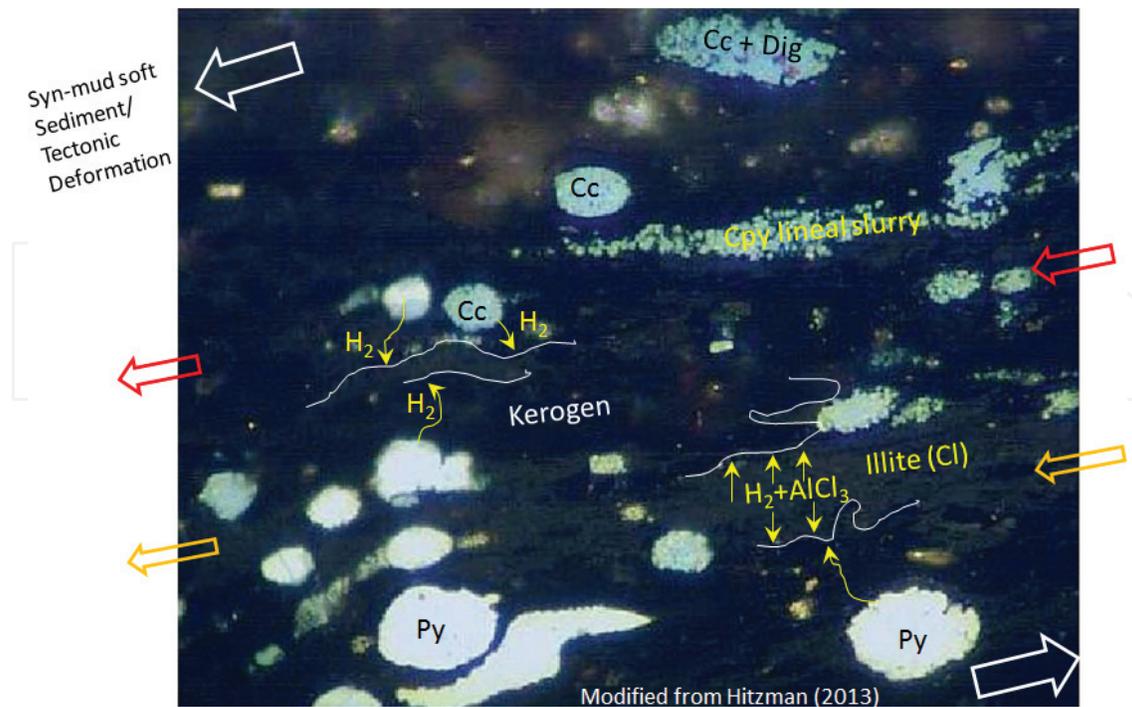


Figure 10. Interlaminated kerogen-illite carbonaceous mud with local sulphidic laminae/lineals and prominent microspherules of pyrite and chalcocite-digenite (some of which coexists with and replaces pyrite). The texture strongly suggests that the sulfides were being carried as particulates interlaminated with kerogen and illite in a sulfide-rich mud slurry.

The sulfide spherules in the copper-rich zone are interpreted as slurry droplets from sulfide suspensate in the overlying heavy brine column. Moreover, the commonly concentric, compositional laminations in the spherules (as shown in Figure 3b of [4]) suggest that the sulfides continued to grow after they were dropped into and carried in the mud-brine slurry. The sulfides are inferred to have formed as a sulphidic mud in a high-energy mud chamber beneath the Kupferschiefer shale horizon and then subsequently were erupted into the water column as high-velocity spherulitic suspensate. The sulfides were carried as lamellar slurry aggregates in soft, warm, kerogen-rich, illite-rich, carbonaceous muds, which co-formed with some of the metal sulfides. The continued growth was enabled by nearby vent-sourced, hydrogen sulfide gas and aqueous, metal-chloride flow through the soft carbonaceous mud. The framboidal (mainly in pyrite) or spherical textures of minerals in the Kupferschiefer (Figure 7) may document de-energization via unmixing during temperature decrease and especially during depressurization of higher energy precursor sulfide melt. The botryoidal textures, which are colloidal-like, indicate that colloidal processes can occur under both high-energy and low-energy conditions.

From the UDH point of view, the entire mud deposit that comprises the Kupferschiefer shale has an exotic character. As the high-density, brine-mud slurry ascended, it evolved from a high-energy environment of mineral stability to a low-energy environment of mineral stability. Hence, the mineralogy reflects a continuum of mineral fractionations that evolved continuously during the ascent of the mud-brine plume. In this manner, high temperature mineral slurry aggregates can reside next to low temperature mineral aggregates within the same

sample at all scales. There is no need to have different high and low temperature brines affecting pre-existing detrital shales. Rather, all of the high- to low- temperature components co-evolved in the same process that began in a high-energy setting and erupted into a low-energy environment.

The previous descriptions refer to slurry textures in hand samples to microscopic samples. There is also an interesting, somewhat anomalous, larger-scale, macro-feature described by Krol and Sawlowicz as a massive sulfide vein in the basal dolomites of the Zechstein in the Lubin mine (Figures 3, 15–17 in [26]). From an ultra-deep mud volcanism approach, the feature can be interpreted as a carbonaceous mud injectite, massive sulfide, slurry sill that was injected into the dolomites of the lower Zechstein at a low angle.

3.4. High temperature to low temperature continuum of hydrothermal minerals

The apparent disparate temperature conditions indicated by various data for the Kupferschiefer can be explained by a UDH process that operated over a decreasing temperature sequence. The UDH process began in the deep crust with extremely high temperatures ranging from sulfide magmas that permissively formed near 1000°C. The UDH material then moved upward in the crust to near-surface environments with low temperature and pressure conditions, shown by the presence of anilite (which is only stable below 29°C). Ultra-deep-sourced, mud-brine, chemical volcanism can explain these disparate temperatures in a process that began in deep, high temperature regions of the lower crust and extended upward to low temperature, near-ambient conditions. At the paleosurface, the brine-mud plume extruded into the hydrosphere during the Permian-Triassic boundary.

3.4.1. High temperature suite

Spieth (in progress) conducted detailed minerographic and microprobe examinations of Kupferschiefer ore samples and prepared compositional phase diagrams. Samples were evaluated from the high-grade Kupferschiefer deposits from the Rhoen Mountains in the west, via Richelsdorf, Mansfeld, Sangerhausen, Wettelrode, Spremberg, and Weisswasser deposits in Germany to the Polish deposits in Konrad, Lubin, Polkowice-Sieroszowice, and Rudna in the east. A clear pattern of a high temperature, hydrothermal origin has emerged, as initially documented at Spremberg, Germany [27].

The high-energy, supercritical, hydrothermal plume can have melt components, such as the gold-bornite exsolution products that were formed from micro-droplets of copper-gold sulfide melt carried as a suspensate in the hydrothermal, volatile plume. **Figure 9** is a labeled photomicrograph of Kupferschiefer ores that shows interlaminated, kerogen-illite, carbonaceous mud with local sulphidic laminae/linears and prominent microspherules of pyrite and chalcocite-digenite, some of which coexist with and replace pyrite spherules.

The presence of copper selenides and high temperature digenite and djurleite in the Spremberg-Graustein deposit in Germany indicate the high temperature of formation (145–557°C) of the Kupferschiefer and associated Rote Fäule deposits [27]. Phase relations in the Cu-S-Se system also indicate the high temperature origin of the copper mineralization and the rapid cooling and exsolution within the copper minerals that also probably include gold exsolutions

in clausthalite (PbSe) (**Figure 11**). Base metal-bearing selenides (klockmannite $[\text{CuSe}]$ and krutaite $[\text{CuSe}_2]$) coexist with covellite and digenite (**Figure 12**). Experimentally determined phase relationships [28], coupled with empirical compositional data obtained by Kopp and Spieth [27] presented on Cu-Se-S ternary diagrams (**Figure 13**) demonstrate that the assemblage of covellite, umangite $[\text{Cu}_3\text{Se}_2]$, klockmannite, and krutaite formed at high temperatures ($384\text{--}343^\circ\text{C}$) [27]. The high temperatures are also indicated by the presence of high digenite $[\text{Cu}_9\text{S}_5]$, together with djurleite. Microprobe evidence showed the copper selenides are associated with high digenite in the Rote Fäule zone of the Spremberg-Graustein deposit. These minerals are equilibrated with high temperature, hydrothermal conditions between 343 and 384°C [27]. Stability fields of sulfide minerals present in the Kupferschiefer range between 72 and 557°C and up to 1120°C for digenite (high) (**Table 1**). Sources of information were included in [29–37].

Microscopic textures and compositions of the sulfides are consistent with the presence of a high digenite-high chalcocite-bornite sulfide melt that existed at temperatures above the supercritical-subcritical boundary for water. These sulfide phases might have unmixed as

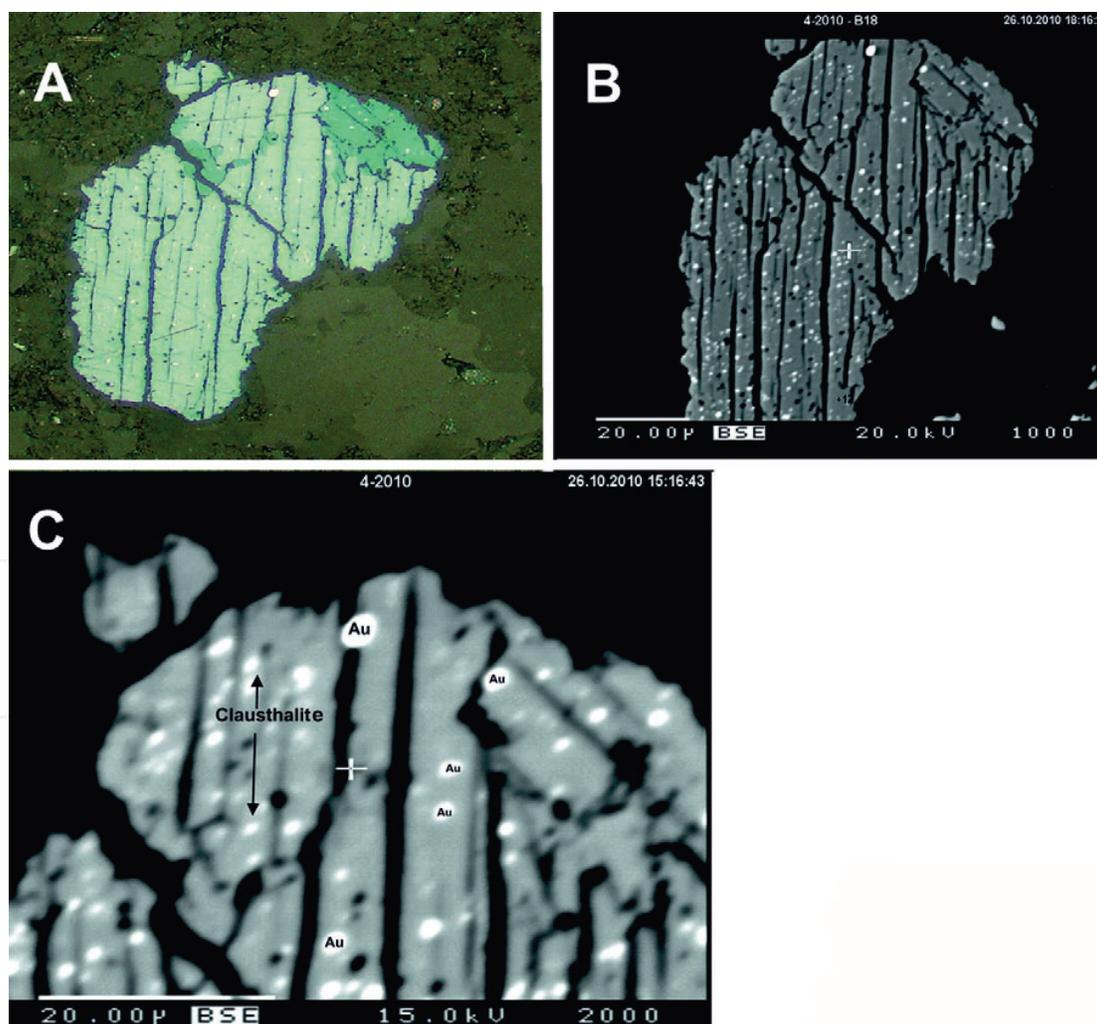


Figure 11. Digenite from the Rote Fäule at Spremberg: A. Reflected light $\times 1000$, // polars. B. The BSE image reveals numerous precipitates of native gold and clausthalite. C. The image shows the enlarged upper part of the image from the top right with rich gold and clausthalite content.

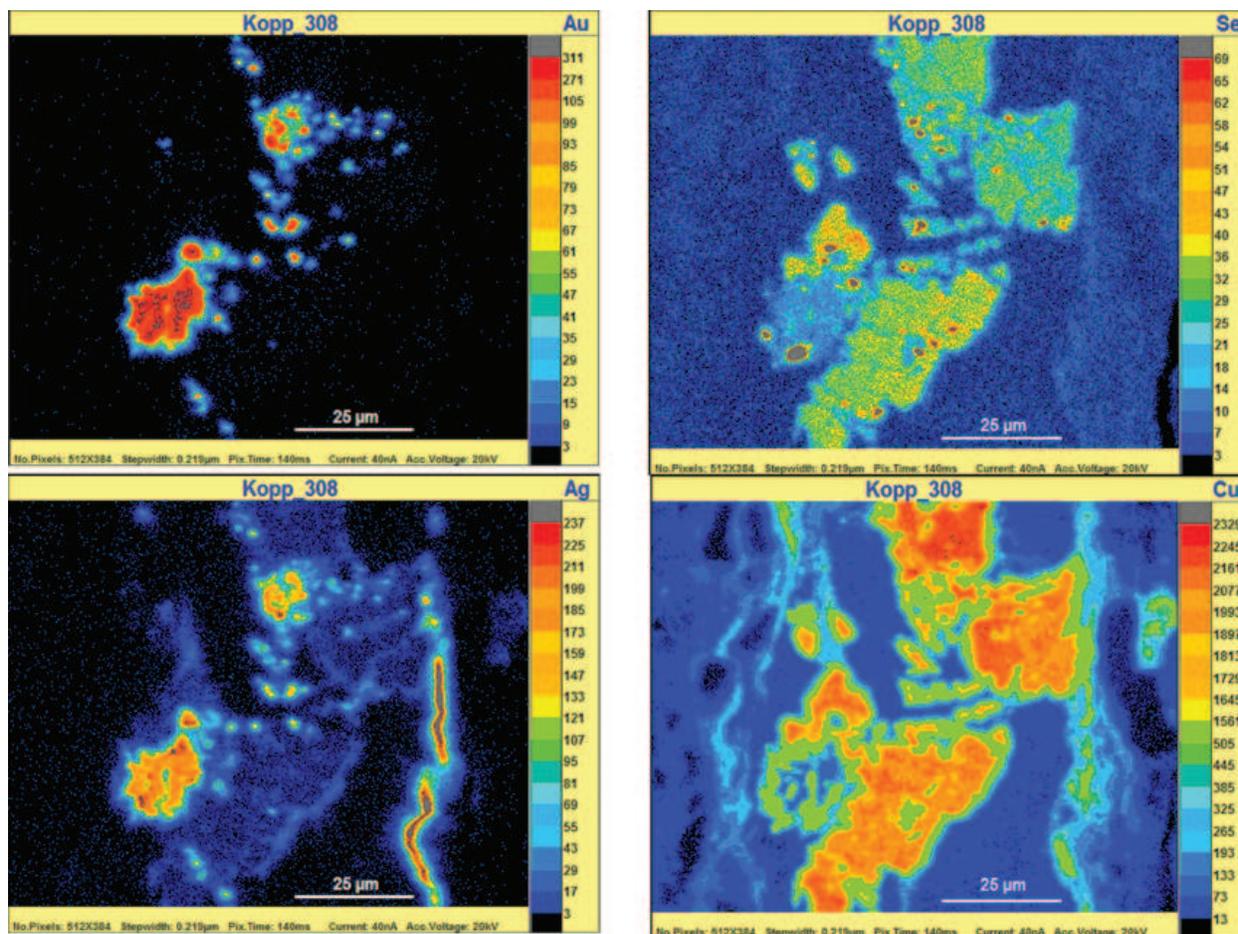


Figure 12. Ag-Au-Se-Cu-S distribution in a copper sulfide grain with electrum and klockmannite included in a chalcocite matrix from the transition zone between Rote Fäule and Kupferschiefer at Spremberg.

immiscible phases of high temperature, copper sulfide melts that initially existed as nano-sized, sulfide droplet emulsates carried in high temperature, supercritical brines. The brine-mud-kerogen mix is inferred to have been partly sourced from deep, steatitic, brine chambers that were derived from the dehydration of serpentinite sources in the deep crust. The brines were then carried upward to the eruptive site at the Kupferschiefer paleosurface. As the brines ascended, droplets of similar composition and density may have aggregated into larger droplets that comprise much of the spherical and orbicular-shaped, sulfide grains. When the brine-sulfide magma crossed into the subcritical phase for saline water below 400°C, the sulfide droplets ionized and crystallized into fibrous forms and other cryptic forms. When temperatures dropped below 500°C (and especially below 400°C) and the brines ionized, covellite began to exsolve from high digenite or high chalcocite and exsolution laminae of covellite formed within chalcocite/digenite. Ionization of the kerogen-bearing brine component below 400°C induced a rapid hydrogenation of the kerogen hydrocarbon component and may have led to the production of a hydrothermal oil component between about 370 and 320°C.

The presence of phengitic muscovite (which is frequently referred to in the literature as illite) can also be used as evidence for high temperatures of formation. The presence of high purity, high crystallinity phengitic muscovite, which texturally coexists with high temperature sulfides, also indicates a temperature of at least 200°C. Even higher temperatures are indicated by

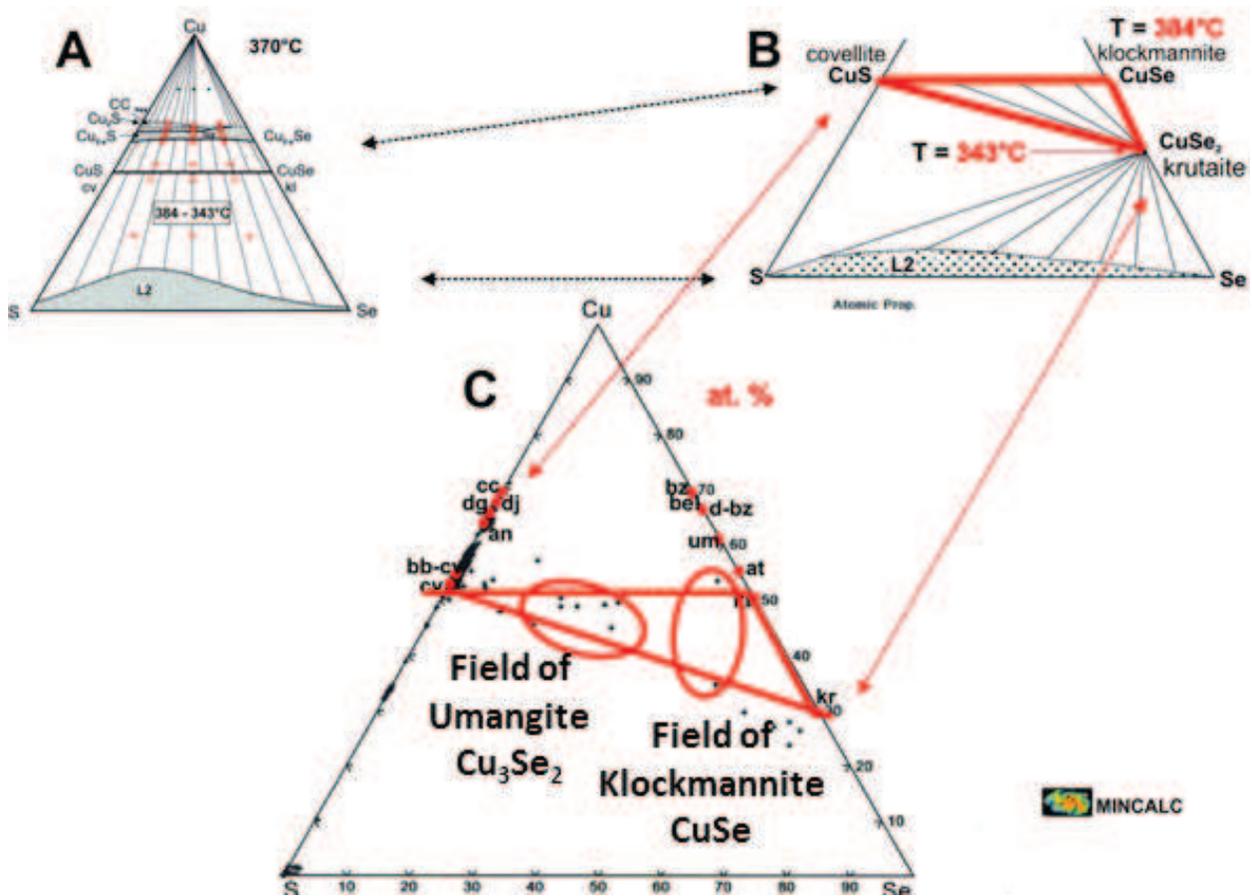


Figure 13. Ternary diagrams showing phase relations in the Cu-S-Se system between ~384 and ~323°C (modified after [28]). Red solid dots in A represent the composition of the Bernardini experiment [28]. Red triangle in B is the compositional field for the krutaite-klockmannite-covellite system. C shows composition of Cu-S-Se analyses of copper-silver deposit at Spremberg (modified from Kopp et al. [27]).

Cu-sulfide	Composition	System	Stability	References
Chalcocite (Low)	$\text{Cu}_{1.99-2}\text{S}$	Monoclinic	$T = 103^\circ\text{C}$	1, 2
Chalcocite (high)	$\text{Cu}_{1.98-2}\text{S}$	Hexagonal	$T = 103-435^\circ\text{C}$	2
Chalcocite (high-P)	Cu_2S	Tetragonal	$P > 1 \text{ kbar}, T = 500^\circ\text{C}$	3, 2
Djurleite	$\text{Cu}_{1.97}\text{S}$	Orthorhombic	$T = 93^\circ\text{C}$	1, 2
Digenite (low)	$\text{Cu}_{1.75-1.8}\text{S}_5$	Cubic	$T = 76-83^\circ\text{C}$	5, 2
Digenite (high)	$\text{Cu}_{1.73-2}\text{S}_5$	Cubic	$T = 83-1129^\circ\text{C}$	6, 2
Anilite	$\text{Cu}_{1.75}\text{S}$	Orthorhombic	$T = 72^\circ\text{C}$	7, 4
Yarrowite	Cu_9S_8	Hexagonal	$T = 157^\circ\text{C}$	2
Bornite	Cu_5FeS_4	Tetragonal	$T = 228^\circ\text{C}$	8, 2
Chalcopyrite	CuFeS_2	Cubic	$T = 557^\circ\text{C}$	8, 2, 9

References: 1. Roseboom [29]; 2. Vaughan [30]; 3. Skinner [31]; 4. Potter II [32]; 5. Morimoto and Koto [33]; 6. Morimoto and Kullerud [34]; 7. Morimoto et al. [35]; 8. Schröcke [36]; 9. Barton [37].

Table 1. Temperature and pressure stabilities of various forms of copper sulfide minerals in the Kupferschiefer [27].

dated, high-quality illite/muscovite separates that probably locked in their K-Ar ages near 350°C, based on temperature-closure data for high-quality muscovite near 252.5 Ma. The 252.5 Ma date probably also marks the changeover from high temperature sulfide deposition to lower temperature, sulfide deposition. Re-Os dates on individual bornite and chalcocite samples (which include the main volume of the high temperature suite) are all older than 252.5 Ma.

The temperatures of selenide formation are in the same temperature range as those in the hydrothermal hydrolysis experiments reported by Lewan and others [10] that created oil from Kupferschiefer rocks. In a 1978 experiment, Lewan [38] created oil in the laboratory by submerging crushed Kupferschiefer rocks in a 1-l container of water and heating it to temperatures between 300 and 360°C (greenschist metamorphic conditions) where after 72 hours it became temperature-equilibrated. At the end of the experiment, oil was floating on top of the water. No oil was formed at temperatures below 300°C or without the presence of water. In effect, Lewan created hydrothermal oil. Most importantly, alkane oils were created in the same high temperature ranges as the stability of the Cu-Se sulfides mentioned above. The Kupferschiefer pyrolysis experiments represent the first pyrolysis experiments done in the presence of a natural hydrothermal metal system. Hence, the Kupferschiefer system represents the first case history where well-constrained temperatures for sulfide formation match temperatures at which Lewan created hydrothermal oil by hydrous pyrolysis. Oil synthesis probably formed in the Kupferschiefer under high temperature conditions at the same time and similar temperatures as were present when the metal sulfides formed.

3.4.2. Low temperature suite

In the near-surface environment of the Weissliegend-Kupferschiefer chemical sand-mud pulse, temperatures in the main Kupferschiefer dropped below 350°C, allowing the low temperature assemblage to precipitate from the metalliferous, K-Mg-Na-chloride brines. At this point, orange bornite (>268°C), spionkopite [$\text{Cu}_{39}\text{S}_{28}$], geerite [Cu_8S_5], yarrowite ($[\text{Cu}_9\text{S}_8]$ also called baubleibender covellite, stable below 157°C), djurleite (stable up to 100°C), and anilite (not stable above 39°C) formed. When temperatures dropped below 100°C, chalcocite may have converted into djurleite (**Figure 14**), which marked the beginning of the end of the sulfide formation process, which was completed when anilite formed below 39°C. At this point, the brines had probably erupted/flowed onto the sea bed, spewing copious amounts of metalliferous muds in low-relief, pancake-shaped, mud volcanoes. When the textural data discussed above are combined with the temperature data and exotic mineral data in the overlying Zechstein salines, they provide powerful evidence for a mud-brine, chemical volcanic model that is deep-sourced.

Under extremely high copper concentrations in the chloride brines, atacamite may have been precipitated as microspheres near covellite-muscovite/phengite interfaces. The appearance of atacamite may have signified the separation of the low-density, K-Mg-Na-Ca-chloride brine at the end of covellite deposition. This low-density brine would then separate from the higher density, sulphidic and carbonate brine components just below the paleosurface and rapidly form the extensive Zechstein brine deposits, which include saline facies. These saline formations would contain inclusions of exotic minerals, such as talc, serpentine, and clinocllore that crystallized deep in the brine system in the lower crust, probably at temperatures well above 350°C.

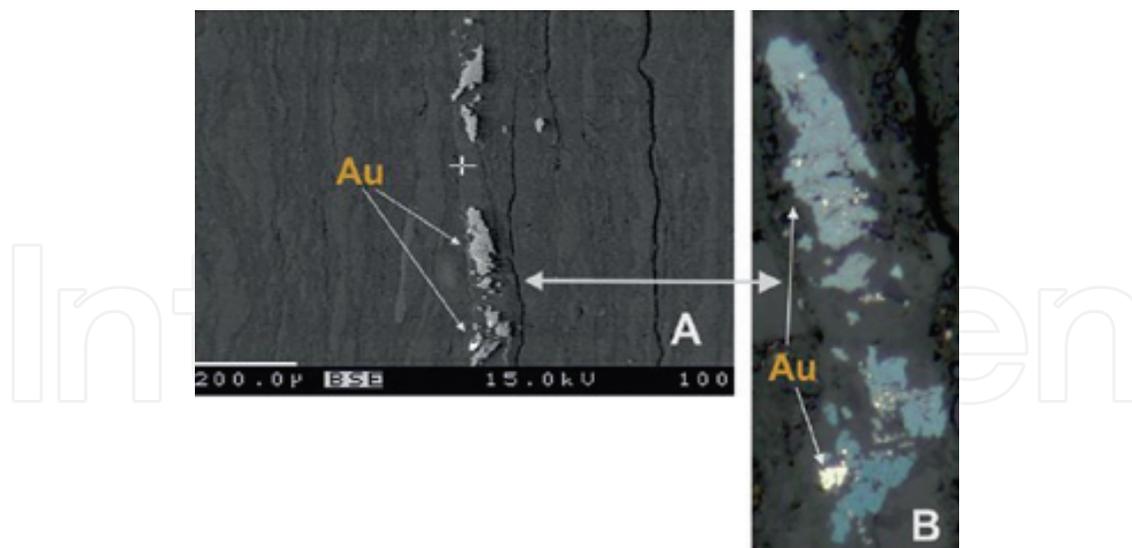


Figure 14. BSE image showing discrete grains of copper sulfides containing native gold inclusions from the lower Kupferschiefer that are interlaminated with kerogen-illite shale; B. Reflected light, X500, plane polars showing chalcocite, light gray djurleite, gold exsolutions, and small grayish inclusions representing native gold, electrum, or clausenthalite from the transition zone between Rote Fäule and Kupferschiefer at Spremberg.

3.5. Zoning in the Kupferschiefer-Zechstein

The Kupferschiefer-Zechstein is a multiply zoned, hydrothermal, brine-mud system. The Kupferschiefer deposits are zoned on small and large scales, both laterally and vertically. On a mine scale, numerous studies have shown the Kupferschiefer shales are zoned vertically within the 1-m thick section. Vertical depositional zoning from the bottom to the top of the Kupferschiefer is: (1) copper sulfides (chalcocite → digenite → chalcocite-digenite-bornite → chalcocite-digenite-covelite → digenite-covelite-chalcopyrite → chalcopyrite-bornite-galena) → (2) upward into the Zechstein carbonate marls of galena with minor chalcopyrite → sphalerite → pyrite.

On a lithostratigraphic basis at the mine to district scale, the Kupferschiefer-Zechstein is characterized by enriched polymetallic mineralization in four zones from top to bottom (**Figure 5**): (1) hanging wall Zechstein carbonate, (2) Kupferschiefer shale carbonaceous main horizon, (3) footwall Weissliegend silica sands, and (4) Rote Fäule, which post-dates the previous three rock types as a typically replacive, hydrothermal alteration. The hanging wall mineralization is in the Werra carbonate rocks of the Zechstein Group dolo-limestone and is 1–10 m thick. The main mineralized horizon is in Kupferschiefer black shale and is less than 0.5–2 m thick. The foot wall mineralization is in the Weissliegend silica sand unit and is 1–15 m thick. The highest copper grades, which strongly focused historical mining activity, occurred at the base of the Kupferschiefer shale. Copper grades typically ranged between 8 and 20% in a carbonaceous layer about 2–6 cm thick.

Within the mine areas, the Rote Fäule independently overprints the above-described mineralization and consistently contains elevated gold, which reaches ore grade in a transition zone between the pre-existing Kupferschiefer-Zechstein mineralization described above. PGE enrichment displays a preference for the transition zone, which indicates their deposition is associated with the shift from the oxidized Rote Fäule source of the PGE-U to the reduced

Cu-Ag (Re) Kupferschiefer shales. The reduction effect is thought to have induced deposition of the PGE suite.

At a regional scale, lateral zoning established mineralization belts are oriented concentrically outward from the Rote Fäule (used a frame of reference only) in the following sequence: hematite → gold → PGE → thucholite → chalcocite → bornite → chalcopyrite → galena → sphalerite → pyrite (**Figure 15**). A general lateral succession (which is sub-horizontal, tabular, and belt-like) of the sulfides begins with copper, which is also rich in silver and which occurs in the transition zone close to the border of the hematitic, Rote Fäule alteration zone. Laterally, farther outward of the copper zone is the lead and zinc zone; even farther outward is the pyrite-rich zinc zone. Lateral zoning occurs over thousands of square km on the scale of the entire Polish Basin. The zonation of hematite and copper in the southwest part to zinc and pyrite in the northeast indicates the direction of paleo-fluid flow. In the mud-volcanic model, the paleo-fluid could include nano- to micro-sized flocculates and suspensates. The high-grade, copper-silver ores of commercial interest are typically located in a sub-horizontal, tabular, belt-like bodies that are 1.5–3.5 km wide and can be more than 10 km in length near the boundary of the Rote Fäule area (e.g. at Spremberg in southeast Brandenburg and Lower Silesia [27]).

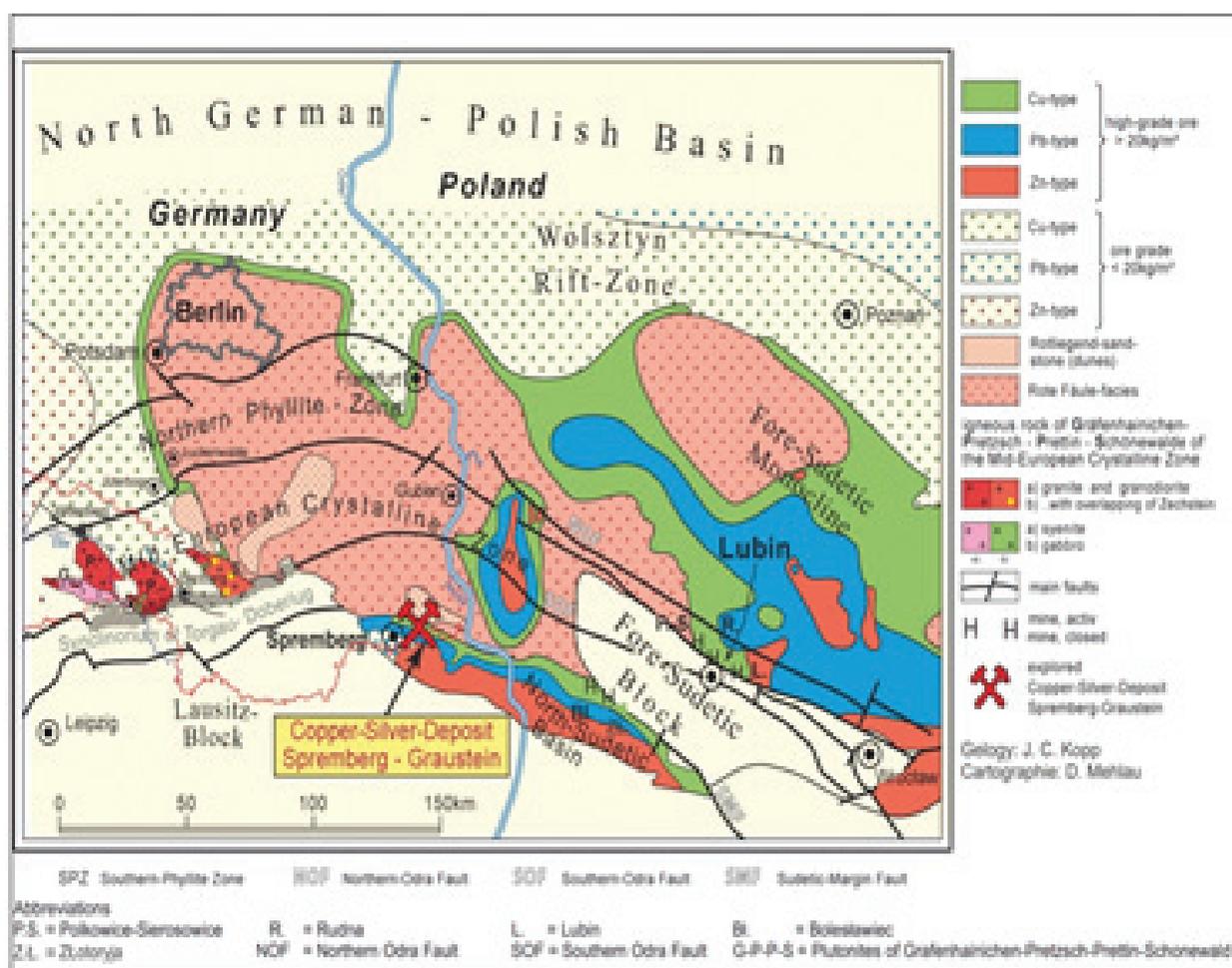


Figure 15. Basin-scale, lateral zoning of Kupferschiefer metallization.

Gas and minor oil fields are hosted in Weissligend sandstones and basal Zechstein carbonates. Gas is locally co-extensive with the copper deposits in the zinc zone at the mine scale. Gas is low in H₂S and high in N₂ and He, which is similar to chemical signatures of kerogen in the mantle. On a basin scale, oil occurs near the centre and north of the gas occurrences (Figure 6). In southern Germany and Poland, an oil generation zone may occur in the outer Zn zone. The regions with gas fields coincide with copper regions. Gas resources are locally world class, as in the Groningen field of northern Netherlands [3].

3.6. Paragenesis and age of the Kupferschiefer minerals

The paragenesis of ore minerals in the Kupferschiefer in 10 metalliferous associations is shown in Figure 16. The sequence of ore minerals in the Kupferschiefer is modified from Jung and Knitzschke [39]. The paragenesis appears laterally and stratigraphically as: the copper-enriched zone at lower stratigraphic levels, with lead and zinc best developed in upper layers, and with pyrite-type metallization appearing in the uppermost or distal facies. Similar sequencing appears in the vein style, cross-cutting metallization.

The Kupferschiefer-Zechstein sequence at Spremberg shows strong chemical and paragenetic relationships between sulfides, kerogenous shales, illite, saline minerals, dolomitic carbonates, silica, and calcite (Figure 16) [27] as modified after [40, 41]. The reaction sequence is: (1) early silica; (2) with copper-silver-rich, illitic, carbonaceous shale becoming more dolomitic and

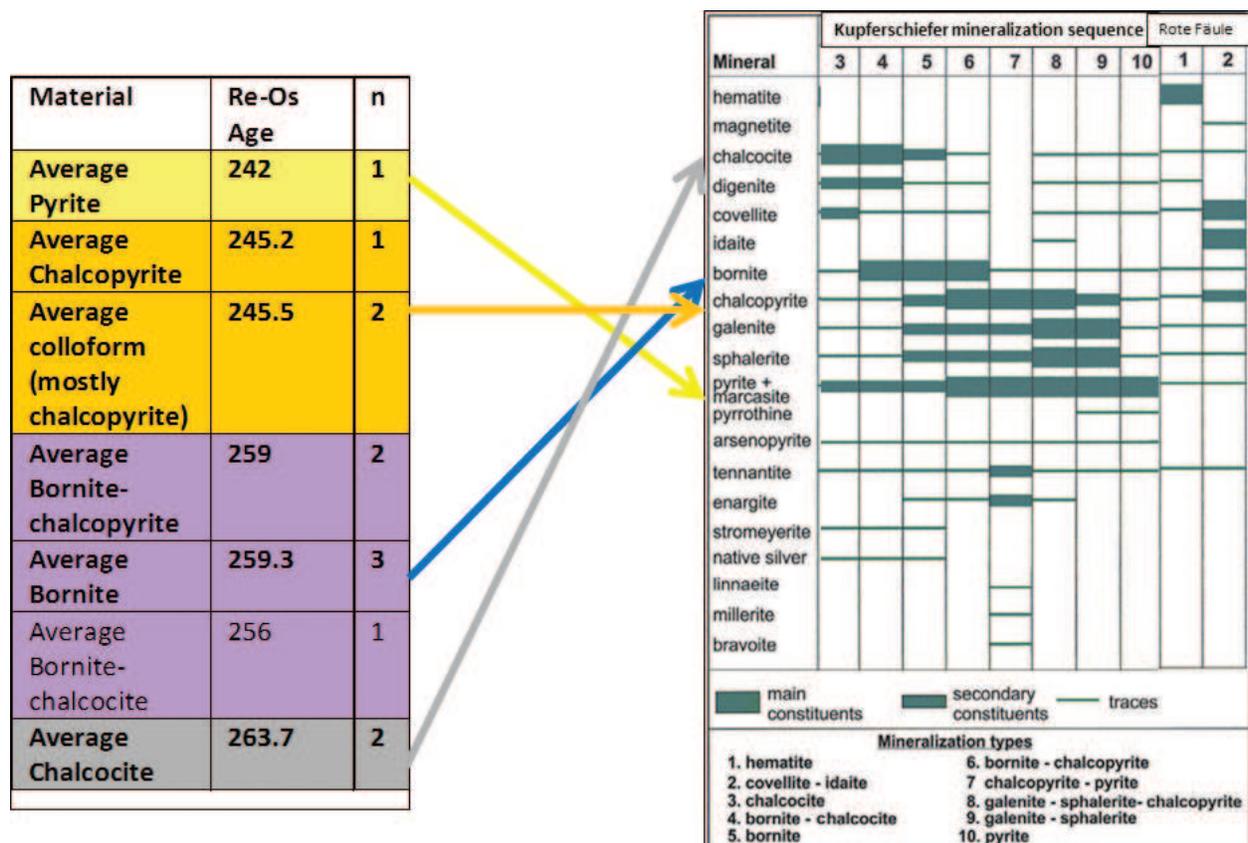


Figure 16. Re-Os ages on sulfides compared with modified paragenetic sequence for the Kupferschiefer (ages from Refs. [4, 43]; modified paragenesis is from Refs. [27, 40, 41]). Stage 2 in the right column also contains major Au-(Pt-Pd-U-Co) and is equivalent to the SOS mineralization (described in Refs. [11, 13]).

bitumen-rich up-section; (3) then an upper, zinc-rich zone associated with dolomitic carbonate; (4) followed by calcitic carbonate; (5) with saline chemical sediments forming a lithocap above the carbonates; and (6) the Rote Fäule representing late stage, oxidized, hematitic alteration that post-dates marly Werra dolomitic carbonate and post-dates underlying Kupferschiefer and Weissliegend silica sand units.

The sequential deposition of silica-rich strata is followed by carbonate-rich strata. Sometimes, biologic activity utilizes the silica-rich effluent in the proximally located flux of hydrocarbons. Oil generation is coincident with steps 8 and 9 in **Figure 16** as the oil is generated and deposited along with the galena-sphalerite-chalcopyrite mineralization.

The paragenesis shown on **Figure 16** is augmented by observations pertaining to the non-sulfide mineralogy, which is also shown as a Kupferschiefer rock section in **Figure 3**. The early chalcocite-digenite mineralization is typically accompanied by silica (which occurs as fragmental, silica, extrudite and injectite bodies) that comprises the Weissliegend beneath the Kupferschiefer. Silica is maximized in unit 3 (the Weissliegend). Silica rapidly decreases upward across a sharp contact with the Kupferschiefer copper shales, where illite/muscovite rapidly increases along with kerogen hydrocarbon, both of which is present in the Weissliegend, but only in minor amounts. The illite and kerogen hydrocarbon are especially abundant in the basal Kupferschiefer, especially in unit 2 and to a lesser extent in unit 3. A rapid gradation occurs upward into the Kupferschiefer, as marked by the appearance of dolomitic marls, which progressively become more abundant than the illite. The dolomitic marly unit coincides with units 6, 7, and 8 in **Figure 16**. The dolomitic marls are succeeded upward by dolomite and subsequently upward by calcitic carbonate. The dolomite coincides with the appearance of abundant sphalerite in unit 8 and especially in unit 9. Pyrite appears in unit 6, but its occurrence as the sole sulfide coincides with the presence of calcitic carbonate in unit 10. The Permo-Triassic boundary approximately corresponds with unit 6.

There is a shift from the chalcocite-digenite-covellite assemblage of stages 3, 4, and 5 to the chalcopyrite-sphalerite-galena-dominated assemblage of stages 7 through 9. A prominent age gap is also present in the Re-Os data (**Figure 17**) that may suggest two stages of Kupferschiefer copper sulfide mineralization: the first being copper-sulfur dominated and the second being copper-iron-sulfur dominated. The ages from the higher quality illite samples taken from **Table 2** in [42] yield an average age of 252.5 ± 4.5 Ma for eight high-quality illite samples. These samples generally were pure (>6.9 wt.% K_2O), were of intermediate grain size (<2 or $2-1$ μm samples that tend to have the purest [highest K_2O contents]), and had high crystallinities ($<48\%$ 2 M disordered component [or more than 52% 1 M ordered component]). There may be a time break of about 10 Ma between the carbonaceous Kupferschiefer and the overlying Zechstein carbonates.

In the UDH mud-volcanic model, the illite ages reported in [42] date primary crystallization of muscovitic mica during the mud-volcanic process. The highly crystalline, high-quality 'illite' samples selected from [42] are inferred to represent primary muscovite that crystallized in mud-volcanic vents, where the potassium-argon was locked in at relatively high temperatures (around $350^\circ C$). The progressively older ages in increasingly more smectitic illitic clays are interpreted to represent the incorporation of extraneous, excess argon in the more distal pyritic zones on the Kupferschiefer shale time line (see **Figure 4** in [42]). Thus, K-Ar dates do not record

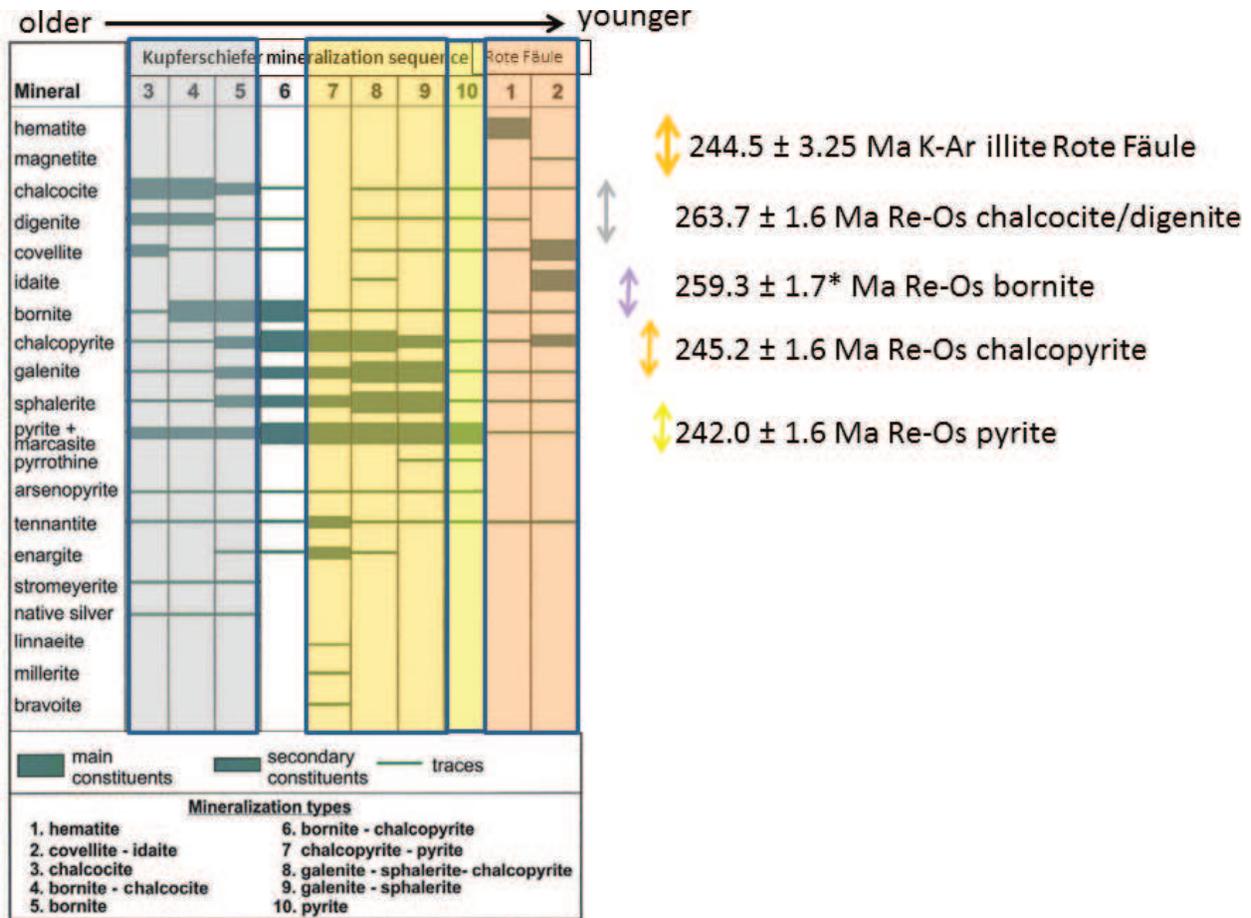


Figure 17. Summary of isotopic age calibration for main stage Kupferschiefer and overprinted Rote Fäule.

diagenetic effects in a pre-existing detrital shale, or do they date secondary, neoformation, or recrystallization of illite by hydrothermalism related to Kupferschiefer mineralization. The 252.5 Ma age is considered an average age for the primary emplacement of the greater, more generic, Zechstein-Kupferschiefer metal system in the Lubin area. The error bars may reflect metal deposition at the early part (circa 257 Ma), which would be the chalcocite-digenite sulfides in the Weissliiegend and basal Kupferschiefer. None of the illite ages come from the underlying Weissliiegend unit. The younger end of the age range may reflect iron-copper sulfide deposition in the upper Kupferschiefer and lower Zechstein Werra dolomite sequence. Three of the ages collected specifically from the Rote Fäule yield an average age of 244.3 ± 3.25 Ma, which is consistent with the observation above that the Rote Fäule is overprinted on the earlier Kupferschiefer rocks.

A second set of 12 rhenium-osmium (Re-Os) ages is available in [4, 43] that more precisely constrain aspects of the metallization in the main Kupferschiefer. These ages were obtained from more targeted, individual, sulfide samples that provide ages for specific sulfide mineralization events. Obtaining Re-Os ages from specific mineral assemblages provide more specificity than Re-Os isochrons, which assume that the samples on a given isochron represent the age of deposition. The high-energy, mud-brine, chemical volcanism model presented here proposes that the sulfide grains are exotic and are not necessarily equilibrated with the same Re-Os reservoir as their contained kerogen matrix.

Thus, the high-quality ages allow a reconstruction of specific events in the sequence of events for deposition of the Zechstein-Kupferschiefer system. The illite ages allow separation of the main Kupferschiefer event at 252.5 Ma from the overprinting Rote Fäule event at 244.5 Ma. The Re-Os data allow a separation of the sulfide deposition events in the Kupferschiefer into two main stages. A copper-sulfur-dominated event (chalcocite-digenite-covellite) affected the Weissliegend and main Kupferschiefer unit from 267.7 to 259.3 Ma (**Figure 17**). A second event of iron-copper-sulfur-dominated metallization mainly affected the carbonate marls of the Lower Zechstein and ranges in age between 245.2 and 240.6 Ma based on averaged data for chalcopyrite and pyrite samples.

The entire Zechstein-Kupferschiefer event from the Weissliegend to the lower carbonate section (Werra) of the Zechstein ranges from 264 to 240 Ma, a time span of about 25 Ma. Late in the sequence, the Rote Fäule appears at approximately 245 Ma. Consideration of the geographic distribution of the illite ages shows that the Zechstein-Kupferschiefer event affected a much larger area than the metal-rich areas around Lubin, Konrad, and other mining areas. The long-lived process affected the entire Zechstein-Kupferschiefer throughout the area that encompasses the Polish Zechstein basin comprising the eastern part of the overall Zechstein basin in north central Europe (**Figure 1**).

Significantly, the age of the Zechstein-Kupferschiefer spans the Permo-Triassic boundary, based on the combined Re-Os and illite ages. The boundary between the Permian and the Triassic can be placed at the top of the black shale of the Kupferschiefer and below the Zechstein carbonates (**Figure 3**). The current Permo-Triassic boundary is radiometrically calibrated at 252.2–252.5 Ma, which is the same as the age of the high-quality illite data for the Kupferschiefer. This boundary also falls near the midpoint of the apparent age gap between 245.5 and 259 Ma in the Re-Os mineral dates (**Figure 16**).

4. Zechstein Group

The Zechstein Group is divided into four cycles (**Figure 2**), each of which consists of marls and limestone at the base, overlain by layers of salines, such as anhydrite and halite [2, 44]. Magnesium and potassium chlorides and sulfates (e.g., sylvite [KCl], polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$], kieserite [$K_2Ca_2Mg(SO_4)_4 \cdot H_2O$], and tachyhydrite [$CaMg_2Cl_6 \cdot 12H_2O$]) are well developed in cycles 3 and 5 of the Zechstein Group.

In addition to the well-known saline minerals above, exotic, highly magnesium minerals (such as talc, clinochlore, and serpentine) typically occur in the lower part of the saline sequence in the Zechstein saline rocks that overlie the Kupferschiefer (**Figure 1** and **Table 2**). The above minerals occur in refractory, shaly interlayers, and residues within saline units. The occurrence of serpentine in insoluble clays in the Emsland occurrence may represent the direct emplacement of serpentine-sourced muds as extrudite slurries into the Lower Zechstein, Werra anhydrites. At Emsland, the serpentine is partly present as ooids, which may have been pelletized during upward transport in a conduit system.

Talc occurrences (which are the most frequent of the unusual mineral occurrences), as well as clinochlore and especially serpentine occurrences, indicate the mud-brines were formed in an

Location	Mineral association	Age	References
Zechstein-Exdale, Yorkshire, England	Mainly halite and anhydrite (85%); magnesite, talc on cleavages in halite, talc in anhydrite-magnesite-halite-talc-rock , halite, minor quartz in seams in anhydrite; halite or sylvinitic mudstone, halite and anhydrite. Boracite, carnallite, hematite, magnesite, rinneite, talc , and euohedral quartz are generally minor constituents	Zechstein (Permian)	[45–47]
Zechstein Salt, Mors dome, Denmark	Euohedral quartz in carnallite-sylvite-halite with fluid inclusion history that ranges from near 300°C to circa 150°C during crystallization and presumed brine ascent	Zechstein (upper Permian)	[48]
Zechstein, in the Frenswegen 3 drillhole, Emsland, Germany	Serpentine (as antigorite) occurs with chlorite (probably clinocllore) and talc interlayered with anhydrite, halite, salts at 1960 and 2035 m depth in the Frenswegen drillhole	Werra Salt unit in the lower Zechstein	[49]
Zechstein-Gorbelen Salt Dome, Germany	Dolomitic carbonates contain hydrocarbons, halite, anhydrite crystals, quartz, pyrite, accessory minerals of quartz, celestine, sphalerite, rare potassium feldspar, fluorite, talc , and galena in a long-mined salt deposit	Zechstein (upper Permian) originally, remobilized in Cretaceous	[50, 51]
Konigshall-Hindenburg salt deposit, Germany	Clinocllore occurs associated with boracite, carnallite, celestine, dolomite, gypsum, halite, hematite, magnesite, magnetite, illite, pyrite, quartz, sylvite, and tachyhydrite in an ancient potash mine closed in 1970	Upper unit in the Zechstein (uppermost Permian)	[52]
Zechstein, West Poland	Talc commonly occurs with celestite in veins in anhydrite; rare quartz, Sr. anomaly in dolomite mounds	Zechstein, Upper Permian	[53]
Zechstein-Kłodawa salt dome, central Poland	Halite, carnallite, kieserite, sylvite, anhydrite, polyhalite, dolomite, chlorite and illite were identified as the main mineral components in the dome, and kainite, langbeinite, picromerite, glauberite, löweite, douglasite, tachyhydrite, bischofite, calcite, magnesite, celestine, gypsum, alunite, boracite, congolite, quartz, talc , pyrite, sulfur, fluorite, glauconite, forsterite , orthoclase and hydrotalcite-like motukoreait e, saponite	Zechstein (Permian)	[54]

Table 2. Locations of talc, serpentine, clinocllore and euohedral quartz associated with saline, potash, K-Na-Mg Cl brine deposits.

ultra-deep environment in an underlying steatitic reaction chamber. These minerals could have been instantaneously erupted as mud slurries into the saline deposits as mud slurries, as they are commonly associated with anhydrite at the halite-anhydrite transition. Polyhalite is also a common associate of talc.

A worldwide survey for these exotic saline components also identified talc, clinocllore, lizardite, serpentinite, and euohedral quartz occurrences from 27 locations, including 11 occurrences of unusual minerals in the Zechstein (**Table 2** and **Figure 1**). These occurrences were documented in [45–54].

4.1. Zechstein saline deposits

The hypersaline Zechstein brines have a unique, nonmarine chemistry. Bodine [55] showed that Zechstein-type salt deposits have a distinct magnesium-potassium geochemistry that shows a composition half way between the aluminum corner (Al_2O_3) and the KAlO_3 corner (Figure 10 in [55]). The main compositional field is completely displaced from the normal marine composition, which is more aluminous [55]. Significantly, the illite clay components in the insoluble compounds are typically much more potassic (>0.85 molar potassium) than in the more detrital marine counterparts.

The illites in the insoluble fraction of the Zechstein-Kupferschiefer are also highly crystalline and contain only very minor smectitic interlayers compared to their detrital counterparts [55]. The high crystallinity characteristics of the Zechstein-Kupferschiefer illite are more typical of hydrothermal illite. Such illites could have been made originally under hydrothermal conditions in a conduit system and later erupted as crystalline illite flocculates into the saline brine, surface environment. In the case of the Zechstein, the setting may have been a playa lake or shallow marine environment, but not a deep sea environment, as suggested by much of the Zechstein-Kupferschiefer literature. Rather than appeal to rapidly changing water depths, it is more likely that the shales were also erupted as carbonaceous extrudite muds erupted into shallow marine waters from high temperature, fissure vents.

The presence of talc, clinocllore, euhedral quartz, and serpentine probably record a higher temperature history resident in deep mud-brines prior to their ascension in hydrothermal mud-brine plumes and prior to their eruption/flow onto the paleosurface into what are construed as shallow lake/marine muds. Serpentine, talc, and clinocllore, generally, form at temperatures above 300°C , which at $25^\circ\text{C}/\text{km}$ indicates a minimum of 11 km depth below the paleosurface. In addition, a euhedral quartz crystal from the Mors Salt dome in northern Denmark studied by Fabricius [56] contains fluid inclusions that equilibrated with polyhalite at homogenization temperatures up to 180°C (Figure 4 in [56]). The crystal nucleated on an early carnallite [$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$] clots at greater than 180°C and trapped 80°C fluid inclusions during its late growth history as it ascended from depths of circa 3 km.

On a global basis, the Zechstein salines are not a unique occurrence [57]. They occur throughout geologic time (Figure 13 in [57]) and seem to be associated with break ups of continental assemblies, especially with the breakup of Pangaea at the end of the Permian. They also are coincident with extinction time lines, such as the major Permian extinction.

4.2. Structural control of Zechstein saline emplacement

A deep-seated origin for Zechstein salines implies that there would be feeder structures that contain salt dikes and other features that demonstrate upward flow from underlying deep sources. The feeder architecture is similar to that proposed by Blundell and others [58], who modeled a deep-seated brine influx into the Zechstein basin.

An example demonstrating the possible, exotic, deep source of the chemical, mud-brine volcanism was observed by one of the authors on a field trip to the Thomas Munzer shaft of the Sangerhausen Mine in Germany in May 1991. **Figure 18** shows steeply inclined and folded, anhydrite laminae superimposed across a relatively flat-lying halite (gray) – sylvite (pink-red)

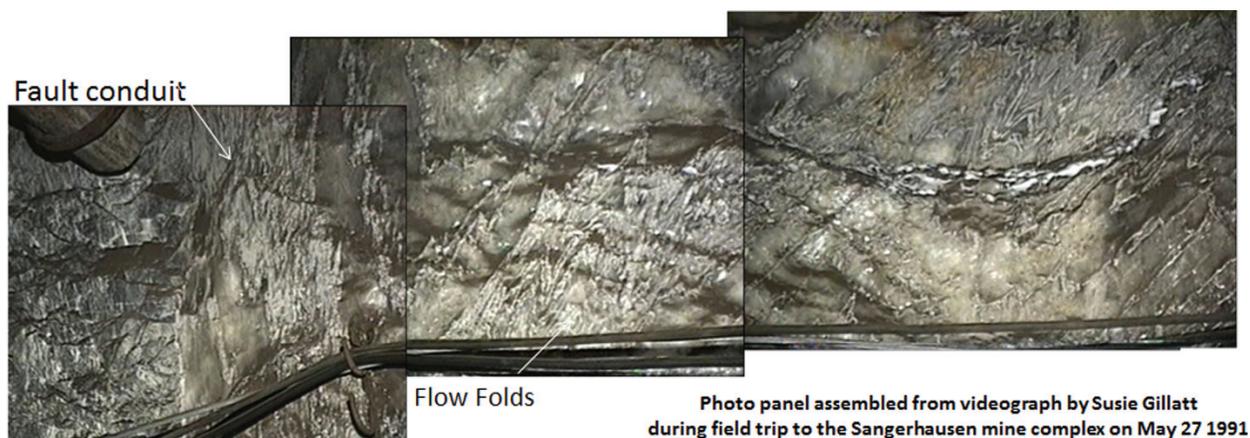


Figure 18. Flow-folded, anhydrite and salt layers exposed in a tunnel face at the Thomas Munzer shaft, Sangerhausen Mine, Germany. The left panel shows a vertical fault with the salt-anhydrite on the right over the Kupferschiefer strata. (Screen shots were assembled by Keith from a video by Susan Gillatt, taken May 27, 1991, on a field trip led by John Guilbert.)

saline deposit that had not experienced the isoclinal folding. In the middle panel, the anhydrite laminae cut a pink sylvitic layer. In the right panel, the pink sylvite layer appears to increasingly cross cut the anhydrite laminae and is intercalated with white anhydrite or gypsum. The folding cannot be tectonic, as both units should be equally affected by the fold deformation.

The folds and mutual cross-cutting relationships of **Figure 18** are consistent with soft, hydrothermal flowage of immiscible, saline brines from an underlying, density-zoned, saline, brine chamber. In this chamber, halite (NaCl specific gravity of 2.16) – sylvite (KCl specific gravity of 1.99) brines are unmixed from anhydrite (CaSO₄ specific gravity of 2.97) brine in a density-stratified brine chamber. The lower density halite-sylvite brine is expelled first and is quickly followed by expulsion of the higher density anhydrite brine, which is injected as cross-cutting laminae into the halite-sylvite brine while it is still a semi-liquid, partially solidified, colloidal gel. Then, both are deformed by flow flowage away from the fault feeder at the left side of **Figure 18**. Both the early halite and the later, isoclinally folded, anhydrite formations display vertical foliation and axial planes within an apparent, fault-related conduit that has a sharp contact on its left side with the Kupferschiefer black shale section, as shown in the left panel of the photo.

Kinematics of the broad folding in the halite and the asymmetric isoclinal folding in the anhydrite in **Figure 18** are consistent with outward flowage to the right into progressively more horizontal flow layering from the fault feeder (conduit) at the left side of the figure. The overall occurrence of the saline brine is consistent with it being a late fractionate of deep-seated, higher density, mud-brine plume that created the high temperature, Kupferschiefer carbonaceous muds. There are exploration possibilities related to the association of fault-controlled brine plumes with veins containing high-grade copper-silver-(PGE-Au)-carbonaceous material.

4.3. Zechstein dolomites as a chemical carbonate mud

Zechstein dolomites occur beneath anhydrite units throughout at least a threefold chemical, sedimentary, cyclothem-like sequence. In the lowest or earliest sequence, the dolomites and calcitic dolomites transition downward into the carbonaceous shales of the Kupferschiefer.

This downward chemical stratigraphy culminates in a very kerogen-rich, copper-rich, illite-rich, shale at its base. The Kupferschiefer itself interfingers laterally with a unit widely referred to as the Boundary Dolomite [9], which rests on the top of Weissliend silica mounds (see Figure 4 in [10]). The Boundary Dolomite is a dolomite-cemented sandstone that rapidly grades downward into the main, structureless sandstone of the Weissliend. Thus, there appears to be a direct chemical and sedimentological connection between the Weissliend chemical extrudites and the Boundary Dolomite, which is a magnesium carbonate fractionate at the top of the Weissliend. In summary, the Zechstein dolomites can be portrayed as chemical sedimentary muds that precipitated above the minimum, dolomite-precipitation threshold of 40°C [59] in the upper portions of fault-controlled, mud conduits.

At the sites where the deep-sourced, mud-brine plumes emerge onto the sea bottom into seawater, sedimentary processes of settling operate. However, the brines themselves are the result of a much deeper chemical process that is not evaporative in nature. This deeper origination process also pertains to the extensive dolomites that typically form the base of a given Zechstein cycle between the anhydrite units and the overlying, sodium-rich, saline deposits. Potassium-rich saline minerals (sylvite) can appear at the end of a given cycle. The chemical fractionation sequence is dolomite, then anhydrite, then halite, and finally sylvite. The exotic magnesium-rich minerals (such as talc and serpentine) typically occur in the early, dolomite to anhydrite part of the sequence, as pointed out by Warren [57].

The above mineral sequence cannot be formed by precipitation through evaporation of normal seawater. The normal precipitation sequence for precipitation from seawater is aragonite, then gypsum, then halite, and then very small amounts of bittern as magnesium and potassium chlorides. Dolomite is conspicuous by its absence. The precipitation or reaction sequence from a deep-sourced, hydrothermal, Mg-K-Cl brine is calcite, then dolomite, then anhydrite, then halite, and finally large amounts of sylvite and MgCl (for example tachyhydrite $[\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}]$ and bischofite $[\text{MgCl}_2 \cdot 6\text{H}_2\text{O}]$). In the UDH perspective, the Mg-K-Cl brine component is a low-density, hypersaline component that separates near the end of a density-driven, brine-mud, fractionation sequence. This Mg-K-Cl brine component would reach the undersea surface and be deposited by settling out of a brine plume.

5. Rote Fäule

The hematite-enriched facies (the Rote Fäule) (**Figure 19**) is wedge-shaped, traverses the stratigraphic sequences of the Zechstein base, and produces a lateral zoning of different ore types (**Figure 5** and the block diagram of Figure 101 in [11]). As a result of the acute-angled dip, economic ore-concentration occurs at the border between Rote Fäule and the underlying sandstones and continues into the Kupferschiefer and Zechstein. The hematitic mineralization is the early stage of Rote Fäule and is described as diagenetic oxidization stage (DOS) by Piestrzyński and Sawłowicz [13]. The DOS is cross cut by a later stage of noble element metallization (Au-Pt-Pd)-U referred to as secondary oxidization stage (SOS) [13].

From the perspective of the UDH model, both DOS and SOS stages are viewed as evolving, strongly oxidized, low-sulfur, chlorine-rich, hydrothermal plume that is superimposed on

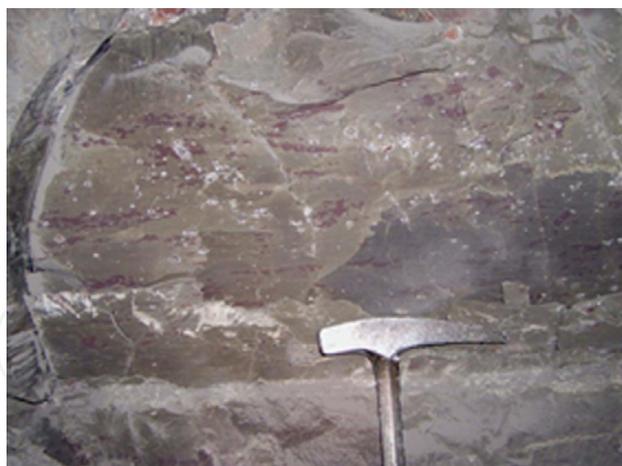


Figure 19. The Rote Fäule, with typical spotted hematite texture overprinting the basal Zechstein dolomite (from Hitzmann [25]).

pre-existing, reduced, Kupferschiefer-Zechstein metallization. In this context, the noble element metallization is viewed as a late, fractionated product that typically forms near the edge of the Rote Fäule plume. The emplacement of the oxidized Rote Fäule plume was independent of the reduced, pre-existing Kupferschiefer Cu-Ag mineralization. Each event represents a separate pulse of an evolving, deep-seated, mud-brine plume system. Each pulse had its own internal evolution that was independent of the other pulses. However, they are broadly connected in space and time at the scale of the entire crust, in the context of a rift system that taps ultramafic sources in the mantle.

In the Polish Kupferschiefer-Zechstein, hematitic and silicic alteration in the footwall sandstone units appears to be spatially associated with the Odra fault system shown in **Figure 15**. This fault system is inferred to have tapped deep-seated, metal and kerogen sources in the underlying basement. As with the Kupferschiefer, the highly anomalous nature of the combined Cu-Ag-Pb-Zn-Mo-Au-PGE-Ni-V-Cr geochemistry strongly suggests a deep-seated, UDH, serpentized source in the basement from which mud-sulfide brines moved to the seafloor interface via a network of deeply penetrating basement cracks. Unlike the Kupferschiefer, the main mineral in the Rote Fäule is hematite, which indicates a much more oxidized oxidation state compared to the reduced Kupferschiefer. A more oxidized character of the Rote Fäule is in accord with the more oxidized nature of the Zechstein carbon-oxygen-rich carbonates.

The Rote Fäule hematitic zone typically occurs in the footwall of the Kupferschiefer, but locally overprints the reduced facies, including the hanging wall Zechstein dolomite marls above the Kupferschiefer shale. The Rote Fäule hematitic overprint shown in **Figure 19** suggests the main Rote Fäule hydrothermal plume was oxidized and its continued 'pumping' resulted in an 'overprint' of the earlier, reduced facies. In some cases, lithic clasts of reduced Kupferschiefer ore appear as included clasts in the Rote Fäule in the northwest part of the Lubin deposit as shown in Figure 3 in [60] and Figure 3b in [61]. These figures show that the reduced Kupferschiefer xenoliths are earlier than and are being consumed by hematitic Rote Fäule mineralization.

An important additional observation is that the gold is spatially associated with Rote Fäule and also cross cuts and replaces earlier, reduced copper sulfides (such as bornite, chalcocite, digenite, and covellite) that are hosted in the kerogenous Kupferschiefer black shale, as shown

in the above cited figures in [60, 61]. The gold is also strongly correlated with other noble elements, such as platinum and palladium. Locally, uranium, as thucholitic kerogen, is also tied to the noble element association (Figures 2, 5, 6 and 9 in [18]). The noble element-uranium association is best developed in what is widely referred to in the above literature as the transition zone between the oxidized Rote Fäule and the reduced Kupferschiefer black shale. From a UDH perspective, the gold-noble element-uranium-Rote Fäule-related mineralization is inferred to be a younger overprint that destroys pre-existing, reduced Kupferschiefer mineralization, and possibly remobilizes it to the margins of the Rote Fäule bodies, where it is co-spatial with the noble element-uranium metallization. As such, the noble element-uranium association is not considered to be directly genetically related to the Kupferschiefer copper-silver metallization, which is earlier.

The previous point has exploration implications in that the margins of Rote Fäule bodies may be prospectable for independent, noble element-uranium accumulations. Potassium-argon dating of high to moderate quality illites, extracted from the Rote Fäule [42], yield four samples that are considered viable indicators of the age of the Rote Fäule. As developed above, the average age of the Rote Fäule as recorded by the more reliable illite ages is 244.5 ± 3.3 Ma (**Figure 17**). These ages are consistent with the observation that the Rote Fäule cross cuts the lower Zechstein Werra anhydrite unit as depicted in **Figure 5**. As such, the Rote Fäule and its attendant noble element-uranium mineralization is inferred to be a late stage, oxidative feature of the Zechstein-Kupferschiefer hydrothermal diapir that is coincident with the early expulsion of salines.

From the perspective of the UDH mud-volcanic model, the Rote Fäule represents an independent hydrothermal event that is not directly related to the earlier Kupferschiefer-Zechstein deposits. Wherever it is observed, the Rote Fäule cross cuts the earlier Kupferschiefer-Zechstein deposits and, so far as we are currently aware, does not exhibit chemical, extrudite facies. It is possible that the Rote Fäule may merge or fractionate into one of the upper Zechstein saline cycles. Nevertheless, its consistent position in the paragenetic sequence and its consistent spatial correspondence with the Kupferschiefer-Zechstein metallization suggests that the Rote Fäule is a late hydrothermal pulse of the broader chemical mud-volcanic process, which ranges in age from about 265 to 235 Ma. More to the point, the Rote Fäule contains its own metallogenic signature that is derived from hydrothermal fractionations within the Rote Fäule event and is not dependent on remobilization of metal sources in earlier formations or pre-existing Kupferschiefer and Zechstein metal deposits.

The three pulses in the broader Kupferschiefer-Zechstein metallization sequence are represented by (1) Weissliegend-Kupferschiefer Cu-Ag (Re, Pb) metallization at ~265–255 Ma, (2) Zechstein Zn-Cu-Pb-Ag metallization at ~250–245 Ma, and (3) Rote Fäule Au-(PGE-U-Co-Se) metallization at ~245–235 Ma. The three heat pulses may represent different stages of dehydration in the underlying ultramafic basement.

6. Later (Rücken) veins

Persistent attempts to determine the age of the Kupferschiefer have resulted in the identification of numerous overprints that are younger than the main Kupferschiefer event that occurred

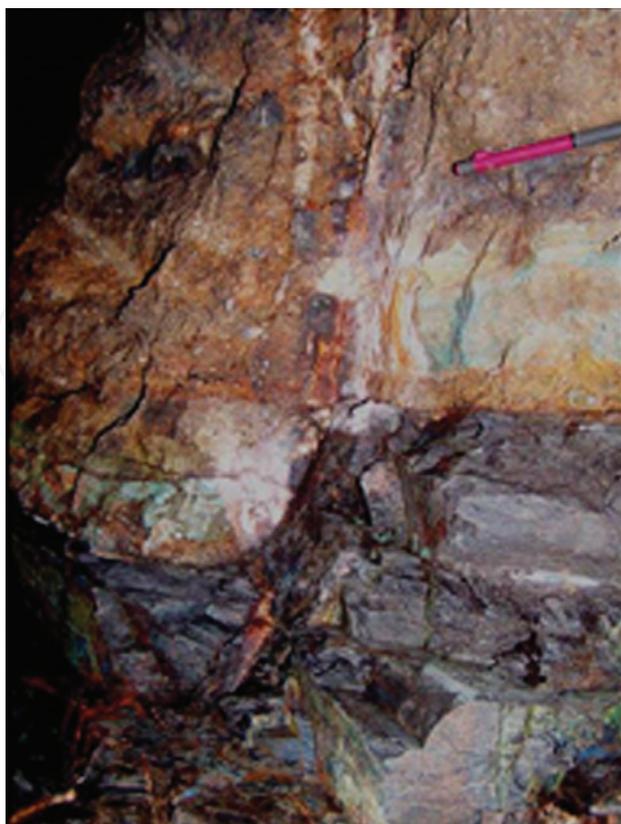


Figure 20. Late siderite-barite-Co-Ni-(Cu, U) veins associated with late faults displacing the Kupferschiefer.

between 265 and 240 Ma. Periodically, the system is re-energized by pulses of new, mantle-sourced, heat flux. One of the more well-known events is the Late 'Alpine age', polymetallic 'Rücken' veins that cross cut the Kupferschiefer-Zechstein metal deposits. **Figure 20** is a photograph of siderite-barite-Co-Ni (Cu, U) vein associated with late faults that displace the bedding of the Kupferschiefer. 'Rücken' veins are especially common in the Mansfeld-Sangerhausen Districts, where paleomagnetic ages on Rote Fäule hematite have yielded a circa 150 Ma paleomagnetic age. This age is inferred to represent heating and resetting of an early Triassic Rote Fäule event by latest Jurassic age, regional heating associated with the 'Rücken' vein event.

The region remains the site of high heat flow, as shown by the geothermal field of the southern Lausitz basement in the Spremberg region (**Figure 21**) and a well-defined, heat flow anomaly and helium anomaly east of Lubin (Figure 4 of [58]). In the tectonic setting of crustal rifting, deep lineaments opened that are part of a global-scale fracturing event whose traces remain to the present. This fracturing opened pathways for brines from very deep-seated mantle locations. Hot, hydrothermal fluids ascended upwards and expelled material with a basic to ultrabasic chemical signature along the fractured, rifting lineaments.

7. Geotectonic setting

The stage for the Zechstein-Kupferschiefer event was set by the assembly of Pangaea, which was mostly complete by the end of the Carboniferous. With this blockage of heat flow from the

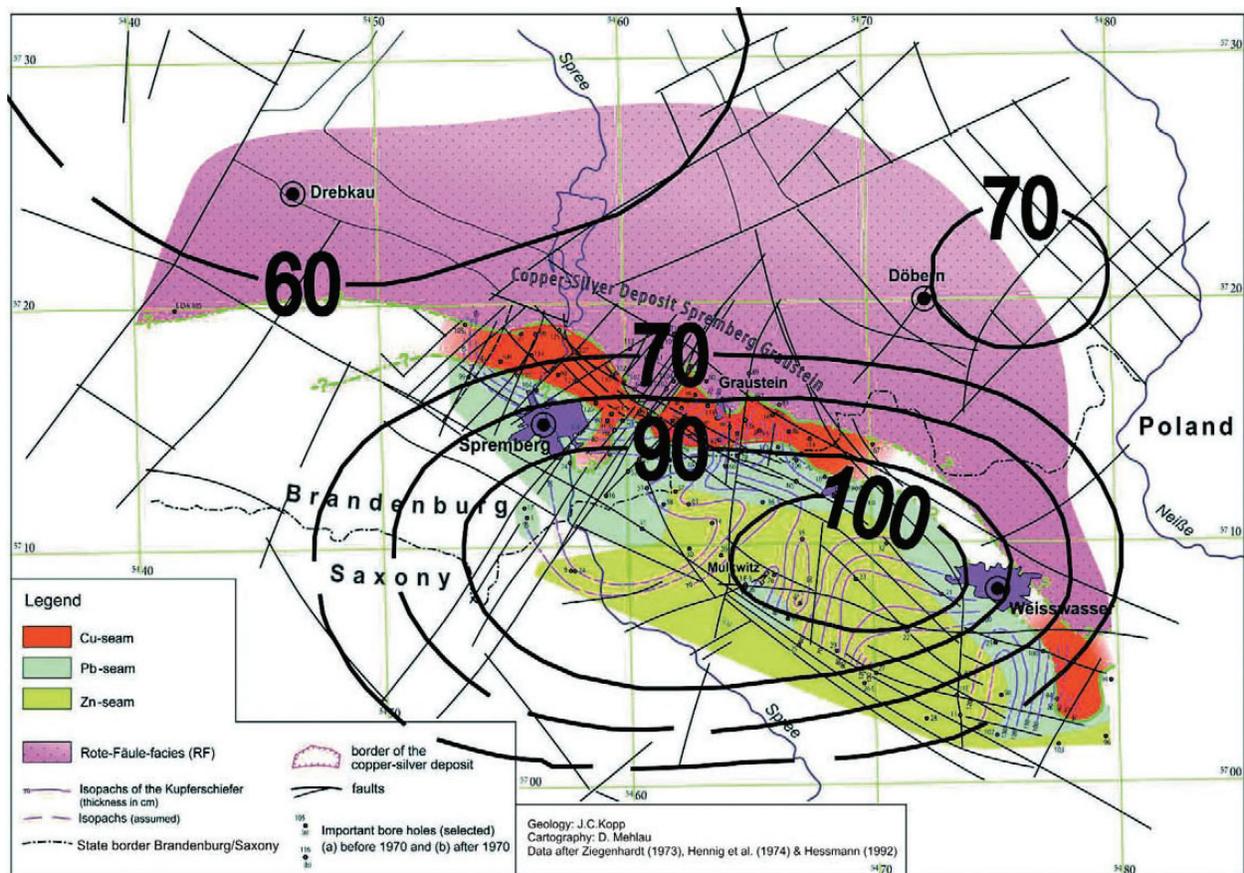


Figure 21. Geothermal field of the southern Lausitz basement showing temperature isoclines and metal zones (from Kopp et al. [27]).

mantle by a large continental mass, hot spots began to develop to destabilize the continental crust and create rifts. The creation of the Zechstein-Kupferschiefer hot spot at the end of Permian time created what amounts to a long-lived zone of weakness that has been periodically active since the main event that formed the Zechstein-Kupferschiefer system. This zone is currently evident as a thermal anomaly centered on the Spremberg area of Germany (**Figure 21**). The presence of the current geothermal anomaly indicates the compliance with a requirement for a massive amount of energy that is needed to drive processes like the one that created the Zechstein-Kupferschiefer system. Smaller scale energy models, such as convection cells, have a problem scavenging the energy required to leach a given source, let alone finding the fracture framework with which to access the leach candidate and remove its chemical contents and then migrate them to a trap site. The deep-sourced, UDH process accesses an endless amount of mantle-derived, conductive heat flow that migrates straight upward along a simple, structurally determined, conduit system.

An elongated intra-continental basin began subsiding in the Late Permian, as marked by the deposition of the Upper Rotliegend at approximately 265 Ma. At this time, the Upper Rotliegend distribution was very similar to the Zechstein-Kupferschiefer distribution (Figure 1 in [5]) and is inferred to be related to the same aulacogenic process. During the rift phase from the latest Early Permian until the mid-Triassic, Zechstein sediments and salines were deposited. Basement fractures are good places for vertically focusing large amounts of deep-sourced materials through

basement-rooted pipes and chimneys. The source of the base metal deposits can be explained by deep-penetrating faults, which opened channel ways for ascending fluids. These structures were active during different stages of the post-Variscan basin evolution. Subsequent phases of localized subsidence continued from the mid-Triassic to Jurassic period of extension [27].

The high-grade copper mineralization of the Zechstein base occurs exclusively in the area of the stratigraphic border between the Saxo-Thuringian and Rheno-Hercynian shear zones of the Variscan orogeny. The so-called European Copper Belt, with its high-grade gold and polymetallic mineralization on the southern rim of the Kupferschiefer Sea (Figure 4 in [62]), may have been fed through a pre-existing suture zone of the Central European Variscides, which is bordered on its southern flank by deep-reaching faults, such as the Odra fault system [27, 63]. These faults form the southern boundary of the Zechstein-Kupferschiefer basin.

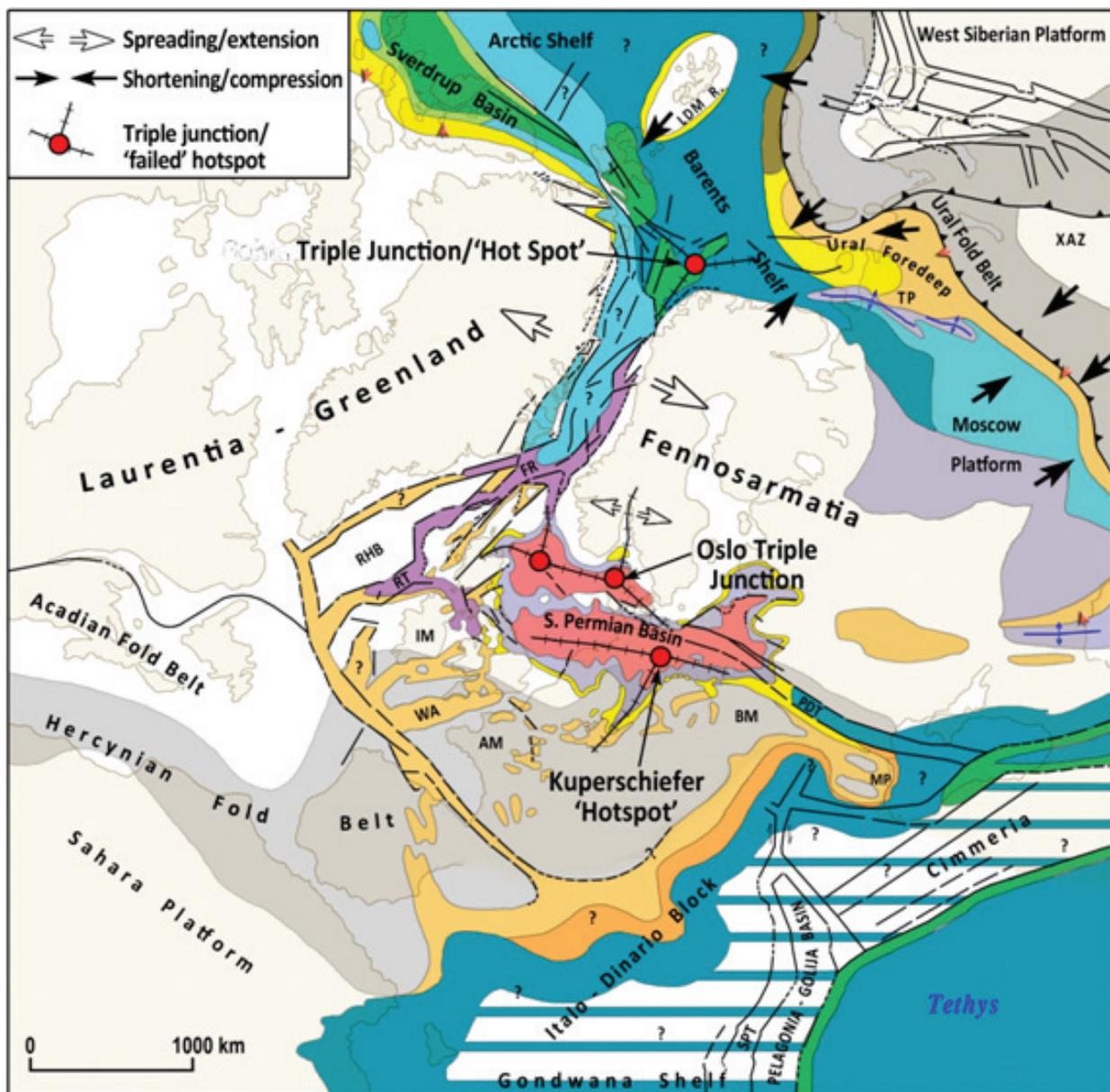


Figure 22. Location of the triple junction/'hot spot' near the Permo-Triassic horizon (255–245 Ma) (modified from Ziegler [65]).

Subsidence within the Zechstein-Kupferschiefer basin (which includes the upper Rotliegend) may have been aided by withdrawal of massive amounts of brine-mud slurries from beneath the current centre of the basin. It is no coincidence that thickness anomalies in the Zechstein coincide with subsidence anomalies on the Zechstein-Kupferschiefer paleosurface (Figure 2 in [64], and Figure 2 in [27]).

The plate tectonic configuration in the Kupferschiefer area at the Permo-Triassic boundary (circa 255–245 Ma) consisted of a triple junction ‘hot spot’ (Figure 22). At that time, Laurentia – Greenland was moving west-northwestward away from Fennosarmatia-Baltica [65] in a rift setting. Also at that time, the Fennosarmatia-Baltica and the Moscow Platform were moving northeastward and colliding with the Ural Fold belt. At the time of the Permian-Triassic boundary, the area of the Zechstein-Kupferschiefer was at a triple junction between a mid-ocean rift and the Ural fold belt. The Zechstein basin was an area of crustal extension. Basement mud-brine slurries migrated upward along subvertical fault zones and were periodically emplaced as the rock series of some of the Upper Rotliegend, Kupferschiefer, and Zechstein carbonates. Not all of the rocks in the Zechstein-Kupferschiefer system are considered to have a deep origin. For example, the red hematitic Rotliegend sandstones described by Glennie [6] are considered to be oxidized eolian sandstones deposited in a desert environment and have undergone normal sedimentary diagenetic processes.

The paleostress regime inferred for the greater Zechstein-Rotliegend region in Permo-Triassic time is shown in Figure 22. The regional stress field inferred from Figure 22 was one of NNE-SSW compression and WNW-ESE extension. In this far-field stress regime, features such as the Oslo graben opened in extension, whereas a number of the WNW features that control reef trends and oil and gas accumulations may have operated as reverse faults. The more northwestern features, which are common features in the Polish part of the Zechstein basins, may have moved in right transpressive slip, whereas less continuous, NE-striking connectors may have operated in left slip.

8. Origin of Zechstein-Kupferschiefer system

The entire Zechstein-Kupferschiefer system can be explained as a product of ultra-deep hydrothermalism that developed during the process of steatization of serpentinite in the lower crust above or near possible mantle hot spots. One such hot spot is posited to have existed beneath the Rote Fäule anomaly in the Berlin area. An interpretive cross-section of the emplacement of a generic ultra-deep hydrothermal (UDH) system is shown on Figure 23, with the uppermost part representing the Kupferschiefer-Zechstein metal and hydrocarbon system. The UDH process that created the Kupferschiefer-Zechstein copper-silver deposit supersystem proceeded in six major steps.

1. The UDH process begins at a zone of depressurization that is tectonically caused by the stress regime shown in Figure 22. The depressurization induces mantle heat flow into zones of weakness, such as the Oslo rift and the north-northeast-trending rift arm that extends south-southwestward from the Kupferschiefer hot spot.
2. Mantle heat flow dehydrates the Serpentsphere [66], at the Mohorovicic discontinuity, where it had accreted at the mantle-crust boundary during numerous, previous, flat

subduction events that range back in time into the Proterozoic. The influx of mantle heat induced dehydration of serpentinite into talc-carbonate rock (steatite). Mass balance of this reaction indicates massive amounts of excess water are created, which combines with other chemicals (such as Na, Cl, K, etc.) to produce high-density mud-brines that are enriched in trace metals typical of serpentinite, such as PGE, Cr, Ni, and Co. The stratigraphy of the combined Weissliegend-Kupferschiefer-Zechstein indicates that three major heat/dehydration pulses might have operated.

3. The chemical and mineralogical reactions in the UDH process take place at high temperatures and pressures that attend the generation of supercritical, non-ionic fluid with a significant component of nano- to micro-sized particulates in the lower crust in the vicinity of the steatite reaction.
4. The brines are expelled due to extremely high fluid overpressures that developed during steatization. This pressure release, along with the exothermic heat generated during the serpentinization reaction, causes upward migration of the buoyant brines toward low pressure anomalies associated with deep-seated basement faults. The dense brine slurries then rise into higher levels in the basement, where they cross the subcritical boundary for brine water at around 400°C and ionize. At this point, mineral compounds start to form from less molecular, flocculate-like particulates. For example, sulfide melt droplets and emulsates may start crystallizing into fibrous, spherulitic minerals (such as shown in **Figure 7**).
5. The high-density brines then emerge onto the paleosurface (inland seabed or paleotopographic surface), forming extensive, saline playa pans and pancake-like mud volcanoes near where the conduits intersect the paleosurface. Basin subsidence may be aided by the withdrawal of massive amounts of mud-brine from chambers deep in the crust near the steatization reaction chambers.
6. The brines included a primary kerogen component that was inherited from the serpentinite source. This kerogen was progressively hydrogenated by the hydrothermal process until it entered the oil generation window near the Permian-Triassic boundary circa 252 Ma. A considerable amount of petroleum may have accompanied the emplacement of the greater Kupferschiefer-Zechstein mineralization. Hydrothermal oil generation accompanied precipitation or deposition of metal sulfides from H₂S-rich brines, which released large amounts of hydrogen. The hydrogen immediately hydrogenates the adjacent kerogen hydrocarbon, especially at illite-phengitic muscovite interfaces. Continued hydrogenation under such a process led to hydrothermal oil generation.

The above-described emplacement process is associated with several associated process-related phenomena.

The rising mud-brine plume fractionates along reaction paths governed by density, composition, decreasing temperature, and decreasing pressure. The density and composition determine the order in which the products are created in a given reaction. The result is a systematic, paragenetic sequence with the sequential, but overlapping, formation of by-product non-metallic minerals (dolomite, then quartz and illite and oil, then later dolomite, then calcite). The sequential expulsion of these by-product minerals is vertically and horizontally zoned. The metallic mineral

Schematic Model of Serpentinite Diapirs in Faulted Rifts of Passive Margins

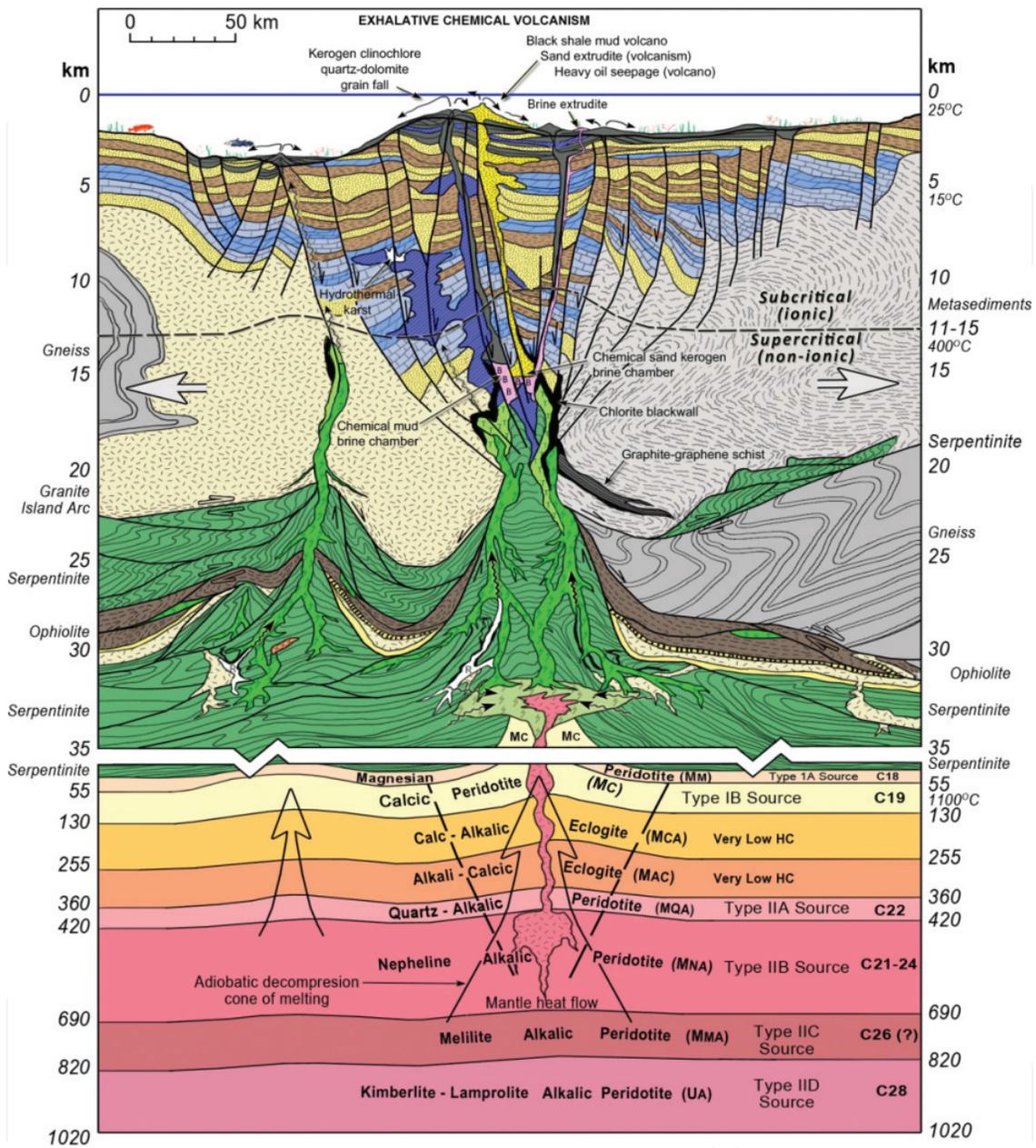


Figure 23. Schematic model of serpentinite diapirs in faulted rifts of passive margins. The model is generic and does not apply to the Zechstein-Kupferschiefer stratigraphy in detail. The part that pertains to the Zechstein-Kupferschiefer system is outlined in red and applies to deposition of the main Kupferschiefer just prior to the Zechstein chemical mud-volcanic event that formed the anhydrite-halite-potash lithocap over the Kupferschiefer.

sequence is generally high digenite, high chalcocite, bornite, covellite, orange bornite, yarrowite, low chalcocite, low digenite, djurleite, and anilite. Temperature ranges of these sequences are from 600°C to less than 40°C. Pyrite can form variously through the sequence, but is especially well developed late in the sequence. Sulfur isotopes generally indicate that the sulfide sequence becomes progressively oxidized during its ongoing pulsed emplacement over the 30 million year interval.

The emplacement of the Zechstein-Kupferschiefer chemical system produced regional scale, proximal to distal, compositional patterns (**Figure 15**). The resulting pattern left systematic mineral and petroleum signatures in the strata surrounding the fractures that can be used to vector toward a probably deep-sourced, mud vent that comprises the central energy and metal anomaly.

The massive amounts of brines and acids would have been toxic to any life immediately above the eruption site and would have entombed any swimming animals above it, such as the pickled, metallized herring fossil in **Figure 24**. The gigantic mud-brine plumes created a massive chemical imbalance in the Earth's ecosystems that induced the well-known Permian extinction event. The toxicity would have been maximized near the tops of the reductive black shales. The black shales mark the extinction event below the Zechstein at the top of the Kupferschiefer black shale (**Figure 3**). The toxicity would have continued into the saline intervals that mark the upper part of the Zechstein sequence. However, the global ecosystem rapidly recovered in the Triassic immediately after the reduction event and salinity crisis ended.

Hence, the Kupferschiefer and its larger Zechstein-Rotliegend system provide clues, not only into metallogenic processes, but also into the entire geologic process that operated at the end of Permian time during the breakup of Pangaea and the great extinction event.

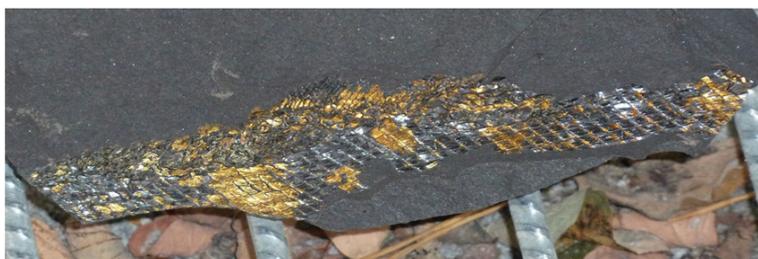


Figure 24. Fish fossil (*Palaeniscum Freiesiebeni*) in the Kupferschiefer replaced by chalcopyrite and chalcocite, Lubin, Poland. Photo by Volker Spieth.

9. Summary

From a UDH, chemical mud volcanism point of view, the following major points are critical to the reconsideration of Zechstein-Kupferschiefer mineralization:

1. The black shale component of the Kupferschiefer is a small part of the co-genetic, mud-chemical, volcanic system that began with the Weissliegend silica extrudite complex circa 265 Ma and ended with the Rote Fäule oxidative event circa 235 Ma. As such, the Weissliegend to Kupferschiefer-Zechstein sequence was long-lived and represents a phased/pulsed, high-energy to low-energy continuum that is punctuated by quiescent periods.
2. The deep-seated nature of the generic Zechstein-Kupferschiefer-Weissliegend system is manifested by exotic element chemistry (PGE, Co, Ni, Cr, and V) that indicates a deep, ultimately serpentinitized, peridotite source in the lower crustal Serpentsphere (Moho).
3. The exotic nature of the chemical constituents allows a much more flexible explanation of genetic issues, such as disparate age dates. In the case of the age dates, a given sulfide

mineral might equilibrate at different depths and temperatures with different isotopic signatures that would lock in different ages. Similarly, a given mineral, such as high digenite, might crystallize at 600°C deep in the vent complex, whereas a nearby mineral, such as anilite, would stabilize at very shallow levels in the complex at below 40°C. Phengitic, highly crystalline pure muscovite would lock in its K-Ar clock at 350°C, whereas cooler, more smectitic, illitic muscovite would be much less Ar-retentive and indicate temperatures below 200°C.

4. The Zechstein-Kupferschiefer, hydrothermal, chemical mud-brine, mud-volcanic system represents a continuum process that operates from high-energy to low-energy. The various exotic minerals within this system capture different parts of the process. As such, the mud-brine volcanic system requires modeling as an open, dynamic, non-equilibrium system, not a closed, static, equilibrium system, as is tacitly assumed by many other models.
5. Most of the Cu-Ag resource is now established to be hosted in the Weissliegend unit and not in the traditional Kupferschiefer black shales. As such, exploration should focus on silica-mud mounds that may represent energy centers for the Weissliegend, silica-Cu-Ag-related, mud volcanism.
6. Reconsideration of the textural features of the Kupferschiefer shale indicate that the entire unit contains exotic clasts and matrix and that the unit includes a high temperature stage that formed at least 10 km beneath the paleosurface. The Kupferschiefer-Zechstein mud slurries flowed onto the paleosurface into low-relief depressions adjacent to Weissliegend, silica extrudite, mud volcanoes. The Kupferschiefer is also a dense, reduced, carbonaceous slurry that separated from a dolomite-cemented, silica extrudite (the Boundary Dolomite) that formed on the top of the silica mounds (especially in the Lubin district of southwest Poland).
7. The presence of exotic minerals (such as talc, serpentine, and clinochlore) in the overlying Zechstein salines, indicate these minerals were derived from a deep, steatized, serpentinite source beneath the Zechstein basin.
8. Zechstein basin subsidence may have been aided by withdrawal of massive amounts of chemical, high-density brines from steatitic reaction chambers in the lower crust.
9. The kerogen in the Kupferschiefer black shales is also considered exotic and was hydrogenated and augmented during its upward ascent and was reacted into hydrogen-rich alkane oils and low C-number alkane gases (especially methane).
10. Based on reconsideration of available illite K-Ar data and Re-Os isotope data, the main Kupferschiefer-Zechstein mineralization is inferred to have occurred between 265 Ma and 235 Ma. The Permian-Triassic boundary is located at the top of the Kupferschiefer shale at its rapid transition to Zechstein carbonates at circa 252 Ma.
11. The oxidized, hematitic, Rote Fäule unit represents a younger hydrothermal plume that was superimposed on all of the earlier chemical exhalatives and that has yet to have a recognized, mud-volcanic component. Gold (PGE, Co, U, and Se) characterize the metallogeny of this later event and were deposited as a secondary, oxidized fractionate (SOS) that is indigenous to the Rote Fäule.

12. The geotectonic setting for the Kupferschiefer was emplacement into an aulacogen, failed rift along deep-seated, west-northwest-trending faults, for example the Odra fault system. The overall shape of the Zechstein basin suggests a Kupferschiefer hot spot was associated with a major anomaly in the Rote Fäule in the vicinity of Berlin.
13. Toxicity related to the emplacement of the reduced black shale of the Kupferschiefer was focused at the Permo-Triassic boundary. The toxic, brine plumes of the Kupferschiefer contributed to the great Permian extinction event that attended the beginnings of the breakup of the Pangaea supercontinent.

The Zechstein-Kupferschiefer super system is considered to be an archetypal example of regional scale, mud volcanism related to hydrothermalism that was sourced in serpentinized peridotite and that was triggered by mantle heat flow. Other examples of known or possible, regional scale, mud volcanism include the Permian basin of northern Texas, USA; the Green River basins of Eocene age in central Colorado, USA; the current Mariana serpentine mud-volcanic system in the 700 km long, 60 km wide forearc of the Marianas; and the current hydrocarbon-related, mud volcanism in the Caspian Sea region and the Salton Sea in southern California, USA.

The Kupferschiefer-Zechstein and its analogues point to the importance of an Earth-scale process of hydrothermalism that has largely been underestimated in the geologic literature. In its own right, hydrothermal, chemical mud volcanism may be as important a geologic process as metamorphism, magmatism, and sedimentation.

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