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MASS BALANCE EVALUATION OF THE LATE DIAGENETIC HYPOTHESIS FOR KUPFERSCHIEFER CU MINERALIZATION IN THE LUBIN BASIN OF SOUTHWESTERN POLAND°

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Introduction

The Kupferschiefer pyritic black shale is the lowermost unit of the Late Permian Zechstein marine evaporite sequence that extends throughout central Europe from England to southern Poland (Fig. 1A). It unconformably overlies a basin and range topography in which basins such as the Lubin basin are filled with the brine-saturated oxidized volcanics and sediments of the Early Permian Rotliegende sequence (Fig. 1B and C). The Kupferschiefer shale hosts base and precious metal mines that have been important in the development of mining technology and the European mining industry. Whether the Kupferschiefer and adjacent strata were mineralized during their deposition (syngenetic-early diagenetic hypothesis) or later by brines expelled from the red-bed-filled basins (late diagenetic hypothesis) has been a matter of continuing debate (see Jowett, 1991).

A data set derived from over 400 cored drill holes covering a broad area around the strata-bound Lubin Kupferschiefer Cu-Ag deposits in southwestern Poland has been recently published in a series of maps by the State Geological Institute of Poland. This data set, possibly unique in scope and quality, allows the late diagenetic hypothesis to be quantitatively assessed by simple mass balance calculations. We use these data to determine the total oxidation and Cu mineralization of the Kupferschiefer and adjacent strata, to calculate the amount of Rotliegende brine required to produce this oxidation and Cu mineralization, and to compare this quantity of brine to that which could be expelled from the Lubin basin by Zechstein and Triassic loading. The comparison poses the late diagenetic hypothesis in more quantitative terms than has been previously possible, indicates the importance of accurately determining the present-day in situ Cu content of Rotliegende brines, and suggests that brines may have been expelled in southeastern Poland from a much larger distribution of Rotliegende than is represented by the Lubin subbasin.

Geology of the Lubin District

Carboniferous molasse sediments accumulated in southwestern Poland in the foreland depression of the Hercynian orogeny. The border faults of this depression were later reactivated by early Permian rifting. Extensional basins formed as half-grabens bounded by faults on their southern borders and were filled by oxidized Rotliegende sediments and volcanics (Wagner et al., 1980; Jowett and Jarvis, 1984). Metamorphosed and deformed pre-Carboniferous Paleozoic sediments and undeformed Carboniferous granites and sediments were exposed as highlands (such as the Fore-Sudetic block and the Wolsztyn highland) between the Rotliegende basins such as the Lubin (Fig. 1B).

The Permian Rotliegende sediments are subdivided into Autunian-age siliciclastic sediments, interbedded and overlain by basalt flows and high-level rhyolite intrusions; and into overlying Saxonian-age siliciclastic sediments (Pokorski, 1978, 1988; Ryka and Pokorski, 1978; Hryniewiecka, 1988; Ryka, 1989). The Saxonian sediments change from alluvial fan and braided stream sandstones and conglomerates in the lower and marginal areas, to meandering stream and saline lake siltstones and mudstones higher in the section and toward the basin centers. The upper section of the Saxonian is dominated by very permeable eolian Weissliegendes sandstones.

A regional Late Permian transgression deposited up to 800 m of Zechstein shallow-marine sediments in four to five carbonate-anhydrite-salt cycles (Peryt, 1989). The pyritic and organic carbon-rich Kupferschiefer (Oszczepalski, 1989) forms a ubiquitous ba-

° A contribution to IGCP Project 254 "Metalliferous Black Shales."

sal unit of the Zechstein and presents itself in strong chemical contrast to the oxidized Rotliegende beneath. The Kupferschiefer grades upward into the shallow-marine Zechstein Limestone (Zechsteinkalk) and the Werra anhydrite and salt horizons. The Zechstein is thickest at the basin centers but covered the entire region at the time of mineralization, although it has since been eroded in some areas of Cretaceous Alpine uplift such as the Fore-Sudetic block (Fig. 1C).

Renewed rifting in the Triassic associated with the opening of the Tethys ocean to the south led to the rapid sedimentation of 600 to 800 m of continental Buntsandstein sandstone and mudstone in the Fore-Sudetic monocline. The Buntsandstein sandstones mark synextensional subsidence, wheres the Muschelkalk (200–250 m) and Keuper marine carbonates and shales (~300 m) reflect the tectonically quieter, thermal subsidence that followed active extension (Jowett, 1986).

The Carboniferous coal-bearing sediments were matured by the increased heat flow and burial depth during the Triassic extension. They are considered the source rock for CH_4 trapped today in the Weissliegendes and other units below the Zechstein cap rock (Glogoczowski et al., 1977; Peryt, 1989). The oxidized Rotliegende sediments and volcanics are considered the likely ultimate source of metals precipitated in and near the Kupferschiefer shale (e.g., Wedepohl, 1964; Rentzsch et al., 1976; Jowett, 1986; Oszczepalski, 1989).

The Zechstein shales, limestones, and evaporites completely capped the Rotliegende basin and provided a strong barrier to upwelling ore fluids. Subsequent sedimentation probably produced fluid overpressures approaching lithostatic within and immediately below the Kupferschiefer. Slight movements along this maximum overpressure horizon as well as organic maturation reactions in the Kupferschiefer fractured and increased its permeability (Fig. 1; e.g., Jowett, 1987).

Ore Fluid Movement

Metal zoning evidence

Mineralization and oxidation related to mineralization are observed in the lower Zechstein sediments in the Lubin area (Rydzewski, 1978; Oszczepalski and Rydzewski, 1983, 1991; Jowett, 1986; Oszczepalski, 1989). The Kupferschiefer is oxidized to "Rote Fäule" (a mining term meaning red "fooling", in the sense of being barren, rock) at the northern end of the Fore-Sudetic block. The sulfide content increases to ore grade (generally) radially from the Rote Fäule, passing through zones where the sulfide mineralization is dominated by copper, then lead, and then zinc. Unaltered pyritic Kupferschiefer is encountered in still more distal areas. The oxidation and base metal zoning clearly indicates that the fluids moved through the Kupferschiefer and adjacent units from the southern boundary fault zone on the northeastern margin of the Fore-Sudetic block toward the center of the Lubin basin. Rote Fäule and high copper grades associated with the Dolsk fault that forms the northern boundary of the Lubin basin suggest that brines moved toward the center of the Lubin basin from the north as well as the south (Figs. 1B and 2).

Compactive expulsion hypothesis

A simple hypothesis is that the capping of the oxidized basin sediments with the Kupferschiefer shale and the subsequent loading by Zechstein evaporites and Triassic sediments caused the compactive expulsion of fluids up the boundary faults. Overpressuring of the pore fluids beneath the Zechstein cap reached close to lithostatic levels and hydraulically jacked up the overburden, greatly increasing the permeability of the Kupferschiefer shale. The expelled fluids then moved across the Weissliegendes and Kupferschiefer in order to leak out (with least resistance) through as broad an area of the impermeable Zechstein cap as possible. Metals were deposited as the oxidized Rotliegende brines reacted with pyrite and organic carbon as they moved horizontally (and vertically) through the Kupferschiefer. In the areas most intensely affected, the fluids completely oxidized the Kupferschiefer, producing the hematitic Rote Fäule which is devoid of metals, pyrite, and organic carbon (Oszczepalski, 1986).

Critical issues remaining

The issues that must be addressed in evaluating the late diagenetic hypothesis are straightforward: (1) how permeable must the Kupferschiefer have been to allow the horizontal fluid flow required to produce the observed oxidation and metal deposition, (2) how much Rotliegende brine must have passed through the Kupferschiefer to oxidize it and convert it to Rote Fäule, (3) how much fluid must have passed in order to deposit the known inventories of base and precious metals, and (4) could compaction of the Rotliegende-Carboniferous basin sediments by deposition of the Zechstein and Triassic strata have expelled the required fluid volumes?

We address the last three of these questions in this communication by computing the total mineralization, the total oxidation, and the total sediment volume in a process-representative portion of the Lubin basin. Simple mass balance analyses then show the conditions under which compactive expulsion of Rotliegende brines could have led to the observed oxidation and copper mineralization.

A Representative Basin

A mineralization-representative portion of the Lubin basin was selected on the basis of the present-day distribution of copper mineralization shown in Figure 2. The southern boundary of the representative source volume area was determined by bisecting the basement highland to the south of the Lubin basin (the Fore-Sudetic block) by a northwest-southeast line. To the northeast a parallel line was drawn to bisect the weak copper mineralization that lies between the intense copper mineralization along the southern and northern boundaries of the Lubin basin. Finally, northwestern and southeastern terminations were selected at either end of the Fore-Sudetic block. The representative area is about 70 by 190 km or 13,000 km^2 in area and covers much more than half of the Lubin basin. The northern boundary of the area roughly bisects the Wolsztyn highlands that run within the northern third of the Lubin basin (Fig. 1B).

Volumes

Within the process-representative portion of the Lubin basin identified in Figure 2 we computed the volume of Saxonian and Autunian sediments, and the volume of Autunian volcanics from sediment contour maps (Pokorski, 1978; Ryka and Pokorski, 1978; Hryniewiecka, 1988). The volumes were computed by polygon interpolation using an arc-information workstation and are shown in perspective view in Figure 3.

The Autunian sediments thicken toward the northwest (Fig. 3A) and have a calculated volume of 1,059 km^3. The Autunian volcanics are concentrated almost entirely in the northwest sector (Fig. 3B), have a maximum thickness of >1,500 m, and a total volume in the representative area of 3,050 km^3. The Saxonian sediments also thicken to the northwest and have a volume of 3,000 km^3 in the representative area (Fig. 3C). The total volume of sediments and volcanics in the representative area is thus about 7,109 km^3. Combined with an estimated equivalent volume of Carboniferous sediments below these Rotliegende sediments (Fig. 1C), there is approximately 14,000 km^3 of sediment available as a source of fluid for compactive expulsion from the representative area.

Rote Fäule

Similar calculations were made using the arc-information workstation for the amount of altered rock which reacted with fluids from the underlying basins. The volume of Kupferschiefer horizon oxidized to Rote Fäule within the representative Lubin basin area is 0.89 km^3 (Fig. 4A; Oszczepalski, 1989).

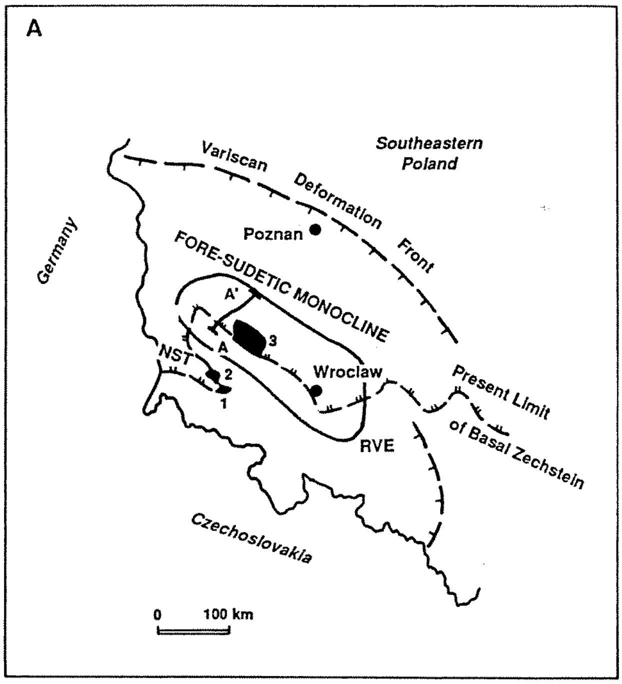

FIG. 1. A. Location map of the portion of the Lubin basin that is most likely to have contributed mineralizing brines to the Lubin-Polkowice mining district (3) is outlined and labeled "RVE" (representative source volume area). The North Sudetic trough (NST) and the Fore-Sudetic block immediately to the northeast (Fig. 1B), and the Lena (1) and Konrad (2) mining districts are also indicated.

Copper metal

The amount of copper introduced by the ore fluids was calculated using contour maps of copper content within the ore series (Weissliegendes, Kupferschiefer, and Zechsteinkalk in Figure 2). There is a sharp cutoff at copper grades of ~0.1 percent. Copper concentration in the Kupferschiefer, for example, tends to be either >0.1 percent Cu or at the 20 to 200 ppm Cu levels typical of unmineralized black shales (Wedepohl, 1964; Wazny, 1967). For this reason it is Polish practice to compute surface copper densities by summing the product of copper grades in composited samples greater than 0.1 wt percent Cu and the sample interval (typically 0.5–1 m) over the depth of the drill holes. When copper is inventoried in this way, the average copper introduced in the representative Lubin basin is 38.2 kg/m^2, and the total Cu content is 350 million metric tons of copper metal (Fig. 4B).

The Kupferschiefer

The Kupferschiefer is a 50- to 80-cm-thick black shale that grades upward and landward (south) into a shaley carbonate. The average organic carbon content of the Kupferschiefer is 6.13 wt percent (range 2.4–16 wt %). Where the Kupferschiefer is oxidized,

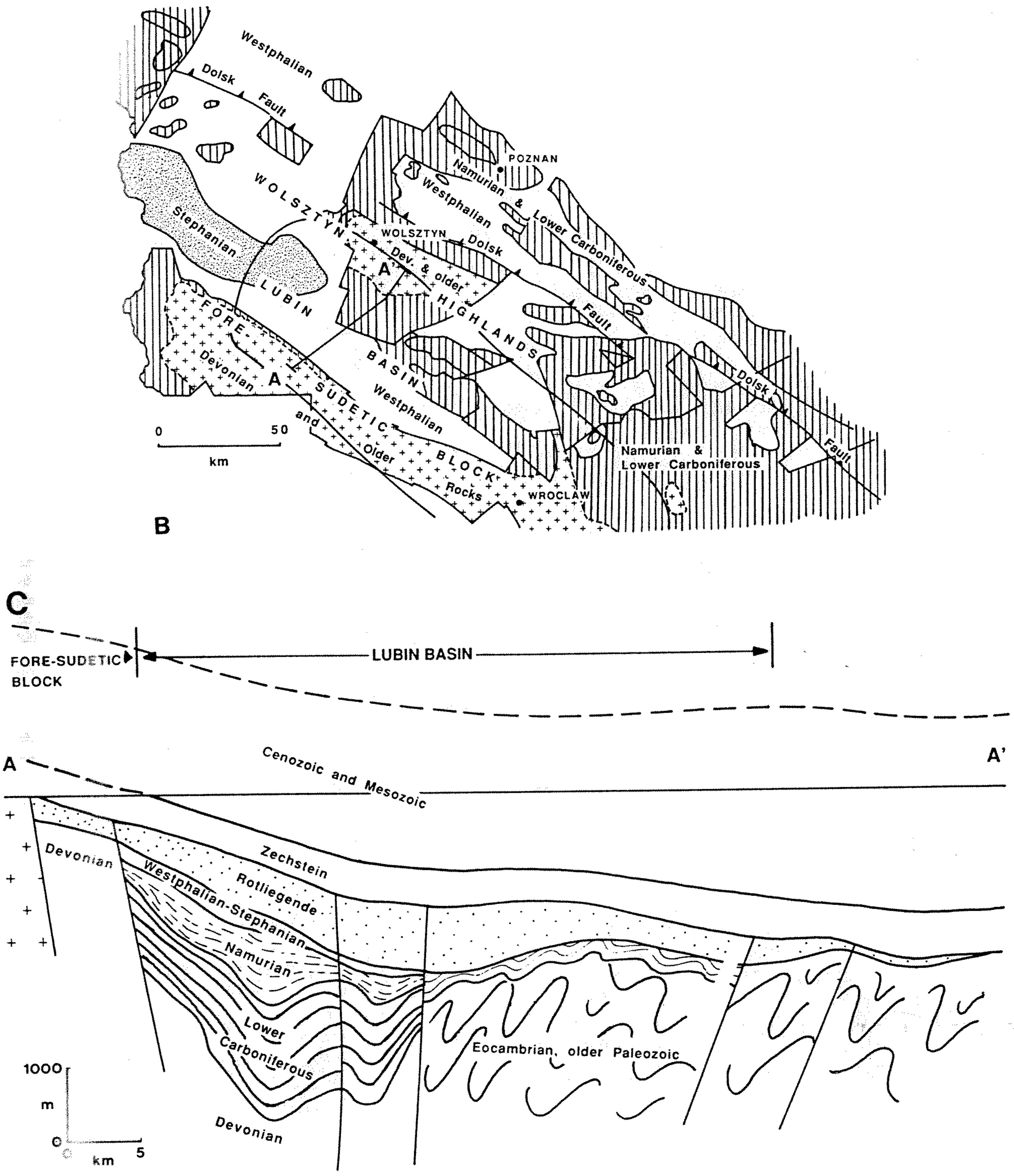

FIG. 1. (*cont.*) B. Plan view of a portion of A showing the northern (Dolsk) and southern bordering faults of the Lubin basin, the Wolsztyn highlands that lie within it, the location of section A-A', and the outline of the representative source volume area. C. Cross section A-A' across the Lubin basin showing the block-faulted basement topography, the Rotliegende through lower Carboniferous sediments that contributed mineralizing brines, and the Zechstein shale-carbonate-evaporite sequences and Triassic and later sediments that capped and loaded the Lubin and other subbasins in the region. The present surface is indicated by the solid line A-A'; sediments since eroded are bounded by dashed lines.

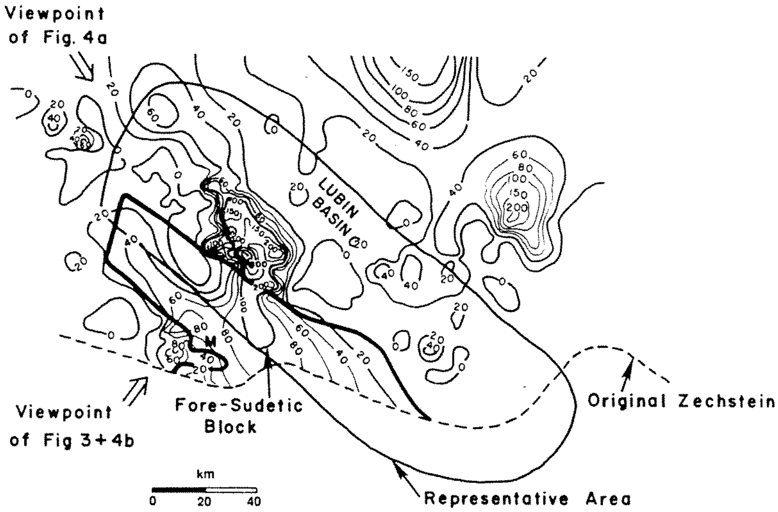

FIG. 2. Contours of copper surface density (kg Cu/m^2), determined from analysis of over 400 drill holes, and the location of the Fore-Sudetic block were used to select the process-representative portion of the Lubin basin as described in the text. Also shown (heavy solid line) is the southern limit of Zechstein shales and evaporites. The southern border of the Triassic sedimentary basins was nearly in the same location, on the foothills of the Sudetic Mountains to the south. Viewpoints for the perspective illustrations shown in Figures 3 and 4 are indicated. "M" marks the maximum thickness of oxidized Kupferschiefer (see Fig. 4a).

the organic carbon content is ~0.21 wt percent (range 0.07–0.85 wt %; Oszczepalski, 1986). The average pyrite content of the unaltered Kupferschiefer is 3 wt percent whereas in the oxidized Kupferschiefer hematite averages 4 wt percent (Oszczepalski, 1986; Oszczepalski and Rydzewski, 1991). The density of the Kupferschiefer averages 2.7 g/cc. Converting the 6.13 wt percent organic carbon and 3 wt percent pyrite to moles per kilogram, the Kupferschiefer contains about 0.25 moles pyrite/kg and 5 m organic carbon/kg.

The Rotliegende waters

Present-day Rotliegende pore fluids have been sampled and chemically analyzed and provide an indication of what the fluids expelled through the Kupferschiefer in former times might have been like (Bojarska et al., 1981; Laszcz-Filakowa, 1981; Downorowicz, 1983). The Rotliegende fluids that are not affected by more recent surface flow from the Odra or other faults have SO_4^{-2} concentrations of about 1,000 ppm or 10.4 mmoles/kg (Laszcz-Filakowa, 1981). There are only a few published analyses of copper concentration in Rotliegende fluids. These show less than 1 ppm Cu and typically 50 to 60 ppm Pb and Zn (e.g., Downorowicz, 1983). Hallager et al. (1991) report brines produced from the Akkrum field in the Rotliegendes in the Netherlands containing up to 475 ppm Fe, 108 ppm Pb, and 147 ppm Zn, but <0.5 ppm Cu. The low copper concentration might be due to copper precipitation in the well bore.

Mass Balance Calculations

Fluid volumes available

Klemme (1972) has shown that the porosity of sandstones typically decreases linearly with burial temperature at a rate of 0.32 percent/°C. The porosity of gas-bearing Rotliegende sediments in the southern Fore-Sudetic monocline is 12.1 ± 4.2 percent (89 measurements; Slupczynski, 1979; Hryniewiecka, 1988). Although some of the porosity reduction from the depositional value of ~45 percent is due to cementation, much is undoubtedly due to compaction. The >2-km Zechstein and post-Zechstein sedimentation (Fig. 1C) could therefore have compacted the underlying Rotliegende sediments by 20 percent if the geothermal gradient at the time were 32°C/km. Volcanics and other sediment types may not compact exactly as sandstones, but their compactions should be similar enough that, under the conditions of elevated heat flow that pertained during the post-Zechstein Triassic rifting, 20 percent can be considered a reasonable estimate of the maximum average compaction of the entire sediment package. A 20 percent compaction of the 14,000 km^3 of sediments in the representative Lubin basin volume element would expel 2,800 km^3 of Rotliegende plus Carboniferous brine.

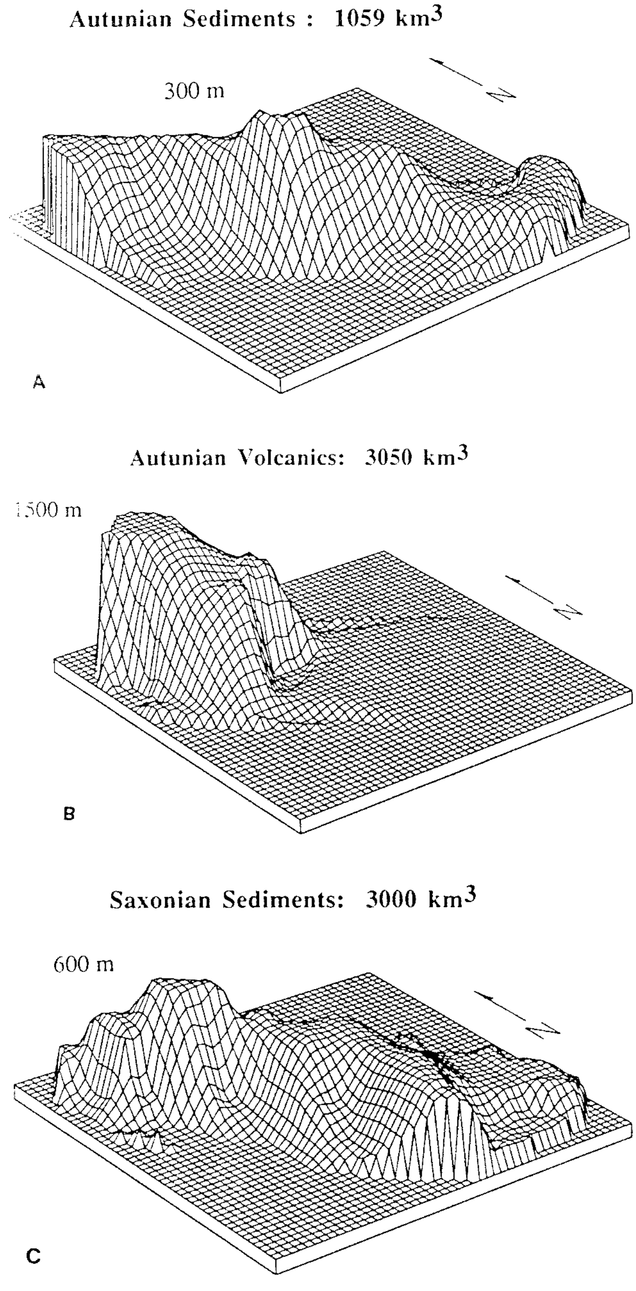

FIG. 3. The volumes of the Rotliegende sediments and volcanics are shown for the representative Lubin basin from a southwestern perspective on the south side of the Fore-Sudetic block (see Fig. 2). Maximum thicknesses are indicated. Autunian sediments (A) occupy the western two-thirds of the representative area; Autunian volcanics (B) the western half of the area. Saxonian sediments (C) cover the entire representative area.

Oxidation of the Kupferschiefer

Sulfate is the most significant oxidant in the Rotliegende fluids. Isotopic evidence suggests that sulfur from the Rotliegende sediments, probably as SO_4^{-2}, was added to the Kupferschiefer shale and that the fluids used a network of hydrofractures to penetrate the Kupferschiefer shale (Jowett et al., 1991). About a mole of SO_4^{-2} is required to oxidize a mole of organic carbon (e.g., Anderson and Garven, 1987) and about 2 moles of SO_4^{-2} are required to oxidize a mole of pyrite. Thus the oxidation of 5 moles of $C_{organic}$/kg Kupferschiefer requires about 5 moles of SO_4^{-2}, and the oxidation of 0.25 moles/kg of pyrite requires about 0.5 moles of SO_4^{-2}. At 10 mmoles SO_4^{-2}/kg, each kilogram of Kupferschiefer requires 550 kg of Rotliegende pore fluid to oxidize. The 0.89 km^3 (2.4 $\times$ 10^{12} kg) of oxidized Kupferschiefer in the represen-

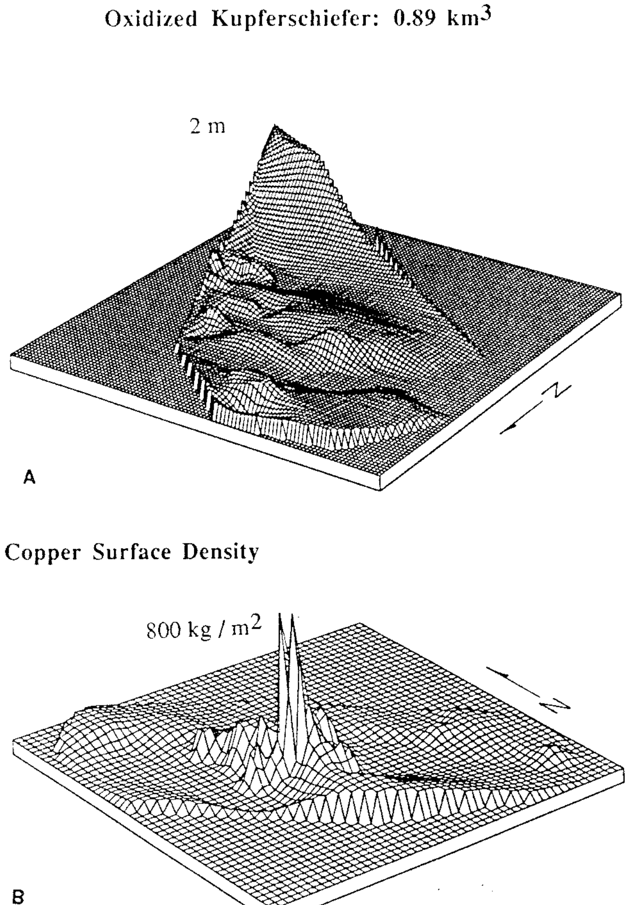

FIG. 4. A. The Kupferschiefer is oxidized only in the northwest third of the Lubin basin outlined in Figure 2. The thickness of the oxidized Kupferschiefer is shown looking southeast from the viewpoint shown in Figure 2. This viewpoint is required to illustrate the increased thickness in oxidized Kupferschiefer to the southeast. The thickness of the oxidized Kupferschiefer increases across the Fore-Sudetic block and reaches a maximum in the North Sudetic trough. This maximum thickness is marked by "M" in Figure 2. Note that the perspective view ends at the margin of the representative area before point M is reached. B. The surface density of copper for the Lubin basin is shown in perspective from the same viewpoint as the sediment thicknesses in Figure 3. The peaks indicate the Lubin-Polkowice mining district.

tative Lubin basin thus requires a total of 1.32×10^{15} kg or 1,320 km^3 of Rotliegende fluid.

The oxidized Kupferschiefer probably records less than half the total oxidized brine expelled from the basin. Brines were reduced by CH_4 to precipitate the sandstone-hosted copper which equals the Kupferschiefer copper in total mass (Jowett, 1992). Some brine was undoubtedly expelled through already oxidized areas of Kupferschiefer and thus was not recorded by the oxidation. The largest volumes of Rote Fäule near the Fore-Sudetic block are not included in our representative source volume area. The total expulsion of oxidized brine was thus probably at least twice that directly indicated by Rote Fäule, or ~2,640 km^3 of brine. This brine volume could have been supplied by compaction of the sediments in the Lubin representative source volume area.

Copper influx

If the copper concentration in Rotliegende pore fluids was ~127 ppm Cu, the 2,800 km^3 of compactively expelled Rotliegende brine could also account for the copper mineralization of the Kupferschiefer and associated sediments. For example, total copper equals 350×10^{12} g which equals 127×10^{-6}g Cu/g brine $\times$ 2,800 $\times 10^{15}$ cm^3 brine $\times$ 1 g/cm^3 brine. A copper concentration of 127 ppm is considerably above the ~1 ppm observed in present-day Rotliegende pore waters and greater than has been observed in moderate temperature brines in other areas (e.g., the Cheleken brines contain 0.9–15 ppm Cu at 50°–80°C, and the Atlantis II 56°C brines contain 0.3 ppm Cu; Tooms, 1970), but it is similar to the 50 ppm copper concentrations White (1971) found just barely adequate to produce the White Pine copper mineralization by the compactive expulsion of brine.

Discussion and Analysis

A number of assumptions have been made in the above analysis. For example, we assumed that a volume of brine equal to that expelled from the Rotliegende sediments was expelled from deep Carboniferous sediments and that this brine either had or achieved a similar chemistry. A simple compaction relation was used to estimate expulsion. These both are uncertain so we conclude only that if the total dissolved copper content of the Rotliegende brine was within a factor of 2 of ~137 ppm, the volume of brines required to mineralize the margins of the Fore-Sudetic block could have been derived locally from a 70 $\times$ 190-km portion of the Lubin basin (our representative source volume area). It is possible that the copper concentrations in the Rotliegende brines were this high if copper precipitated in the well bore during sampling.

If the Cu concentrations that typified the Rotliegende pore waters at the time of Kupferschiefer mineralization were significantly less than 127 ppm, expulsion of brine from the representative source volume area in Figures 1 and 2 could not have precipitated the known copper inventory. To precipitate the known mineralization in this case, (1) copper-bearing brines must have convectively recirculated within the Lubin representative source volume area dissolving additional copper at each cycle, (2) such brines must have been drawn from outside the Lubin area, or (3) syngenetic to early diagenetic metal precipitation must have contributed to the copper grade.

Convection within the representative source volume area could have increased the flow of brine through the mineralized parts of our study area. Simultaneous convection and compactive expulsion through the Kupferschiefer (a possibility suggested by Jowett, 1986) may at first seem a strange combination. However, overpressuring of the Rotliegende brines must have increased the permeability of the Kupferschiefer to allow passage of the compactively expelled brines. Unless the Kupferschiefer permeability was comparable to the darcy permeability of the underlying eolian Weissliegendes sands, lateral brine flow would have been entirely through the Weissliegendes and the Kupferschiefer would not have been mineralized. Because the present-day permeability of the Rotliegende sediments is high (mean of 91 measurements is 26.1 mD with a range from 0.4–187 mD and a standard deviation of 35.6 mD; Slupczynski, 1979; Hryniewiecka, 1988), convection in the basin is expected. The Raleigh number is four times critical for a 10-mD basin 2.5 km deep with a thermal gradient of 55°C/km. Convection in the Lubin basin through a very permeable Kupferschiefer that was hydraulically jacked open by lithostatic fluid pressures could significantly increase fluid transport through the Kupferschiefer and adjacent strata and contribute significantly to the mineralization and oxidation. This possibility can be addressed by modeling and will be discussed in a later communication. Perhaps the most important point here is that overpressuring is required to make the Kupferschiefer shale permeable enough to allow the late diagenetic mineralizing brines to convect or be compactively expelled through it.

The Zechstein basin thickens significantly to the northeast. In the Lubin basin area the base of the Zechstein lies at a ~2-km depth, but it is at a ~7-km depth in central Poland (Oszczepalski and Rydzewski, 1991). The deeper burial of roughly the same thickness of Rotliegende sediments in central Poland (e.g., Pokorski, 1978) by greater thicknesses of impermeable Zechstein strata (Wagner et al., 1980) would produce greater compaction and also encourage escape through the shallower cover to the south. Thus it seems quite likely that Rotliegende brines could have been contributed to the Lubin deposits from outside the Lubin basin. Copper was still probably provided by the Autunian volcanics (Jowett et al., 1987), but the greater flux of brine could significantly reduce the concentration of copper in the brine required to precipitate the observed mineralization.

Syngenetic or very early diagenetic copper precipitation could have contributed to the mineralization. Significant redistribution of metals may still have attended from the expulsion of basin brines. Syngenetic mineralization is treated here as a last resort—a possibility to be appealed to only if adequate late diagenetic mineral deposition can be ruled out.

Figure 5 summarizes our analysis of the late diagenetic copper mineralization hypothesis. Data from over 400 scientific core holes in the area surrounding the Lubin basin strata-bound Cu-Ag deposits collected by the State Geological Institute of Poland allows evaluation of the hypothesis that mineralization resulted from the reduction of oxidized brine expelled from Rotliegende strata during Zechstein and Triassic loading. A process-representative portion of the Lubin basin was selected from the pattern of copper mineralization. Over 2,800 km^3 of fluid could have been expelled by Zechstein and Triassic loading from this portion of the Lubin basin. At 10 m*m* SO_4^{-2} (the present-day sulfate concentration in Rotliegende pore waters), this brine volume could have oxidized the observed volumes of Kupferschiefer in the process-representative portion of the Lubin basin even assuming that half the brines were reduced by CH_4 or pyrite in strata below the Kupferschiefer or escaped through Rote Fäule (already oxidized Kupferschiefer). If the expelled brines contained 127 ppm Cu, they could also have produced the observed copper mineralization. If the copper concentration in the brine was less, a greater brine source volume, brine recirculation, or sygenetic to early diagenetic mineralization must be appealed to in order to account for the observed mineralization.

The copper content of brines at the time of sedimentary copper mineralization is critically important to evaluating the late diagenetic mineralization hypothesis in Poland and elsewhere. Measurement of the in situ copper content of undiluted present-day Rotliegende brines at a number of locations by means that avoid Cu precipitation in or near the well bore, and extrapolation of these concentrations to the higher temperature conditions that pertained in Triassic time, could determine the need for brine contributions from outside the Lubin basin or convective brine recirculation within the basin. The cop-

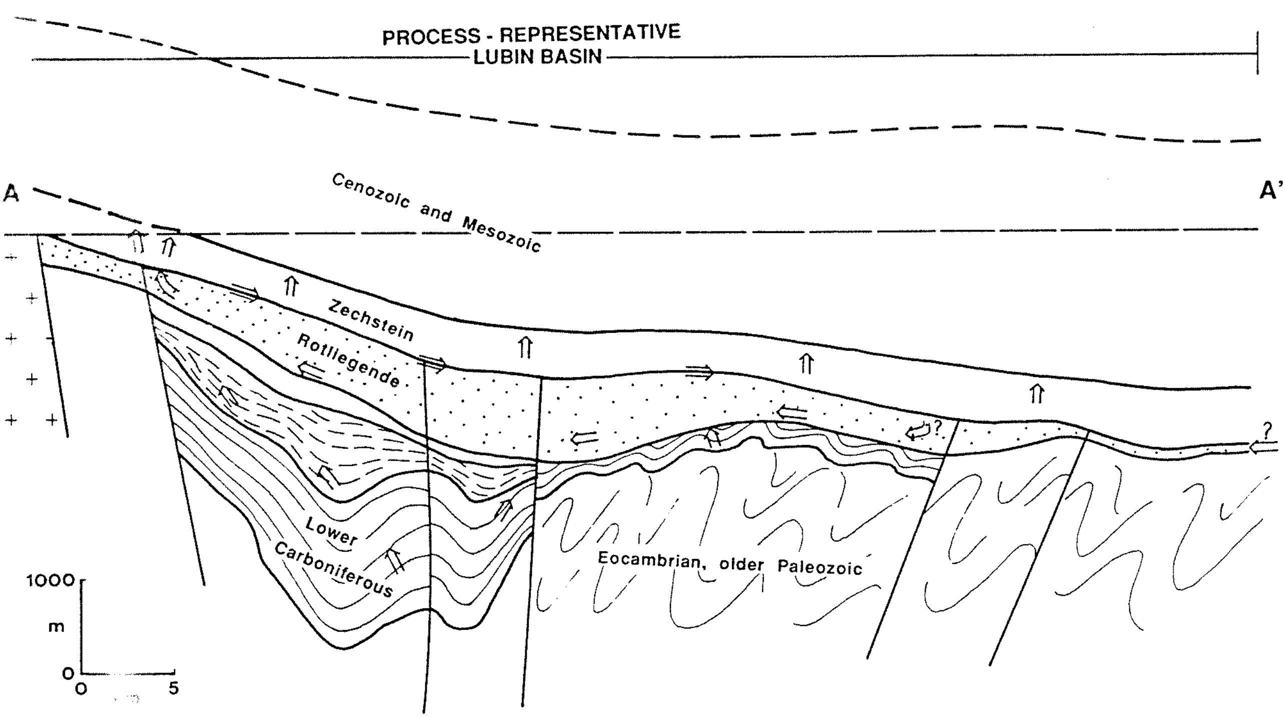

FIG. 5. Summary diagram showing that 20 percent compaction of the Rotliegende and Paleozoic sediments in the process-representative Lubin basin could precipitate the Cu mineralization found in the Kupferschiefer and Weissliegendes sediments if the brines contained 127 ppm Cu. Lower concentrations would require convective recirculation or brine contributions from outside the Lubin basin, as indicated by the arrows with adjacent question marks on the left of the diagram.

per measurements would also be useful in assessing the viability of hydrologic models that have been proposed for White Pine.

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