Pristane/phytane ratios in the mineralized Kupferschiefer of the Fore-Sudetic Monocline, southwest Poland

D.J. Large, A.P. Gize

Department of Geology, University of Manchester, Oxford Road, Manchester, M13 9PL, UK

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Abstract

The interaction of organic matter with fluids is important in geochemical processes in surface and diagenetic environments. In the Kupferschiefer copper deposits of southwestern Poland organic-fluid interactions are inferred to have been important in the genesis of the ore deposits. Previous organic geochemical studies of the Kupferschiefer report evidence of a late diagenetic oxidation event that altered the organic geochemistry. This study uses the saturated hydrocarbons as indicators of the biological input and the earliest diagenetic processes to affect the organic geochemistry of the Kupferschiefer. The normal alkane distributions are lithofacies controlled indicating that they reflect biological input. The ratio of the saturated isoprenoids pristane/phytane are potential indicators of the redox conditions during sedimentation and diagenesis. Very low Pr/Ph ratios are associated with lithofacies that were deposited in hypersaline environments. Increases in the Pr/Ph ratio within individual traverses are interpreted as indicating increasing oxidation of organic matter during deposition and early diagenesis. Trends of increasing pristane/phytane ratios are observed at the base of the Kupferschiefer and at the transition, within the Kupferschiefer, from the clay-rich to the carbonate-rich Kupferschiefer which corresponds approximately to the transition from Cu-zone to the Pb-zone. Early diagenetic, copper-depleted Cu- and Cu-Fe-sulfides have also been reported form the top of the Weissliegendes and the Cu-zone/Pb-zone transition, and it is conceivable that both could be related to the same processes.

1. Introduction

The interaction of fluids with organic matter is an important geochemical process in oceanic, sedimentary and diagenetic environments. In these processes organic matter has the potential not only to act as a transfer medium, elemental reservoir and reductant, but also to provide molecular information on the environments in terms of biological inputs, thermal history, and the physico-chemical conditions under which diagenesis occurred. One such process in which organic matter has the potential to play a variety of roles is the genesis of sediment-hosted base metal deposits.

Organic matter has been reported in close association with a variety of sediment-hosted ore deposits including the "Carbon Leader" in the Witwatersrand, some Carlin type disseminated gold deposits, Mississippi Valley-type deposits and pertinent to this study, polymetallic mineralization in organic-rich shale. The geochemistry of organic matter in ore deposits can be viewed in one of two endmember ways. Either the organic matter is chemically isolated from the ore-forming process or it in some way reflects the ore-forming process. Should the organic matter reflect the ore forming process then its role can also considered in two ways (Gize, 1993). The first is that the organic matter was directly involved.
in ore precipitation by, for example, increasing metal and sulfur solubilities in the ore solutions, providing sulfur at the site of precipitation or acting as a reductant. The second is that the organic matter, although not an active participant, still records the ore formation. This could be recorded for example by thermal anomalies, or hydrolysis of the organic matter in the presence of hydrothermal solutions (Gize, 1993).

A major difficulty in understanding organo-metallic inter-relationships is the compositional variability of the organic matter, which depends on a variety of factors including biological source, thermal history and depositional environment. A typical geochemical extract will contain saturated hydrocarbons, unsaturated hydrocarbons, aromatics, metallo-porphyrins, carboxylic acids, alcohols and organo-sulfur compounds. Each fraction can provide a different answer to the inter-relationship question. For example, if the role of organic matter is considered in terms of complexing and chelation, then the saturated hydrocarbons play no role. The unsaturated hydrocarbons have the potential to form weak interaction (π-bonding) at low temperature only. The aromatics can form very stable “sandwich” compounds with selected metals only, and the reversibility of the aromatic metal interaction may be questionable; the porphyrins can similarly chelate a restricted range of metals (Ni, V=O, Fe). Both alcohols and carboxylic acids can provide functional groups for complexing and chelation, provided the pH of the solutions are correct for deprotonation. In this study, the saturated hydrocarbons alone will be examined to test if these compounds reflect conditions during ore precipitation. The general lack of reactivity of saturated hydrocarbons with metals means that direct relationships, with the exception of reduction, can be eliminated.

To investigate whether the saturated hydrocarbons can reflect ore genesis the Kupferschiefer deposits of southern Poland have been targeted for the following reasons. First, the deposit is actively mined enabling access to fresh samples and thus minimising the effects of recent atmospheric and microbial oxidation. Second, the ores are zoned with respect to copper, lead and zinc, permitting potential resolution of the organic–metal relationships. Third, previous work has established that the thermal maturity is relatively low, at the threshold of the oil window. Consequently the organic compounds of interest are available for study. Fourth, the mineralization is restricted to a relatively narrow stratigraphic horizon and, therefore, age differences in the organic matter can be ignored in the assessment of maturity. Last, it has been found that zones can be constrained in which Cu–Fe–S minerals display mineralogical changes which may result from early diagenetic alteration (Large et al., 1995).

This final point is significant, because in the case of the Kupferschiefer, there are currently two schools of thought concerning ore genesis: early diagenetic (microbial processes) and late diagenetic (thermo-chemical processes). Rather than use the organic matter to verify one and eliminate the other, the evidence for both schools is taken as an indication that perhaps there were two events. The first early diagenetic and superimposed on this a later diagenetic event. Care has to be taken in deciding which compounds amongst the saturated hydrocarbons reflect the earliest event. In this study, variations in the ratio of the isoprenoids pristane/phytane, a potential indicator of the redox conditions in the water column and sediments during early diagenesis, is compared to changes in the ore mineralogy. In effect, the pristane to phytane ratio should not have been masked by later epigenetic events, thus providing a window into the earliest sedimentation conditions in the Kupferschiefer. If a correlation exists between mineralogy and pristane/phytane ratios, then the organic geochemistry of the Kupferschiefer can be considered to have been influenced by the same processes which produced the sulfide mineralogy. The implications will be that both the organic geochemistry and the ore mineralization were affected by the same processes and, therefore, a component of the Kupferschiefer mineralization may also have been syngenetic or early diagenetic. If there is no correlation then the early diagenetic organic geochemistry of the Kupferschiefer was either an isolated system, or the mineralization occurred later, or evidence of a link was obscured during later diagenetic processes.

2. Sample localities and geological setting

Samples were collected, in February 1993, from selected areas in the Rudna and Lubin Mines in the
Lubin Copper Mining district of southwestern Poland (Fig. 1). The ore-bearing horizon in these mines is at the base of the Permian Zechstein Formation where Cu–Pb–Zn ores are hosted in the Weissliegendes, Boundary Dolomite, Kupferschiefer and Zechstein Limestone of the Z1 cyclotherm. The regional setting of the Lubin Copper mining district is on the north side of the Fore-Sudetic Block, in the Fore-Sudetic Monocline and details of the regional geological setting of these copper deposits have been given by Oberc and Serkies (1968), Speczik (1993) and Oszczepalski (1986), Oszczepalski (1989). Fifty samples were collected from seven traverses, two from the Lubin Mine and five from the Rudna Mine (Figs. 1 and 2), covering the sequence from the Weissliegendes 1 m below the base of the Kupferschiefer to the dolomite 2 m above. These samples are representative of the upper part of the mineralized zone.

The Lubin Mine is closer to the Fore Sudetic Block than the Rudna Mine. The two sample traverses selected from this mine are characteristic of the shallower water Lower Zechstein sequence (Oszczepalski, 1989). The basal Weissliegendes, a fine-grained white sandstone, is overlain by the fossiliferous Boundary Dolomite. Overlying the dolomite is the Kupferschiefer, which in this locality is a sandy and silty laminated shale unit (30–50 cm thick). This is overlain by the fossiliferous microcrystalline Werra Dolomite. The ore mineralogy at the Lubin Mine is dominated by the Cu–Fe–S system.

The Rudna Mine is located north of the Lubin Mine and the samples collected from here are representative of the deeper basin (Oszczepalski, 1989). At the sampling locations, the fine-grained Weissliegendes is directly overlain by the Kupferschiefer which may be up to 60 cm thick. The top 10 cm of the Weissliegendes is often fossiliferous. In this mine the Kupferschiefer can be split into two distinct units: (1) a lower clastic mud unit characterized by abundant thin silty laminae alternating with clay- and organic-rich laminae and; (2) an upper carbonate-cemented unit characterized by thin organic and clay laminae that enclose lenses of dolomite cement. The sedimentary facies at the Rudna Mine are highly variable due to local elevations in the Weissliegendes, which have been interpreted as submerged aeolian dunes (Oszczepalski, 1989). In sequences overlying the Weissliegendes, the equivalent of the Boundary Dolomite is present, and the Kupferschiefer may be thin or absent (Mayer and Piestrzynski, 1985).

The ore mineralogy in the traverses studied is strongly zoned. The lowermost Cu-zone that extends from the white sandstone into the basal 17 cm of the Kupferschiefer is dominated by Cu and Cu–Fe sulfides (mainly bornite and chalcocite). Minor, but locally significant, concentrations of Ag, Mo, Co, Ni and Pb sulfides and arsenides also are present within this zone (Mayer and Piestrzynski, 1985). Overlying the Cu-zone is a Pb-zone (at least 10 cm thick) where galena is the dominant sulfide with minor amounts of sphalerite, chalcopyrite and bornite. The transition from the Cu-zone to the Pb-zone is sharp and, in our samples, is in the bottom 20 cm of the Kupferschiefer. The Pb-zone grades upwards into a third Zn-zone dominated by sphalerite, with minor galena and chalcopyrite. The Zn-zone extends upwards into the Zechstein Limestone, but its upper boundary, estimated to be up to 2 m above the top of the Kupferschiefer (Mayer and Piestrzynski, 1985), was not sampled. Framboidal pyrite is abundant and occurs throughout the ore zones studied.

3. The Kupferschiefer

Models for the genesis of the Kupferschiefer deposits have been developed (e.g., Jowett, 1986;
Kucha and Pawlikowski, 1986; Oszczepalski and Rydzewski, 1991; Wodzicki and Piestrzynski, 1994) in which ascending oxidizing fluids formed these zones during the main mineralizing event, resulting in the sequence (from most oxidized to most reduced) hematite–chalcolite–bornite–chalcopyrite–galena–sphalerite. Based on textures, mineral distribution and geochemical data, two hypotheses have been proposed regarding the timing of this main mineralizing event. One hypothesis infers that the main mineralizing event occurred during early diagenesis and the other hypothesis infers that the main mineralising event occurred during late diagenesis. The main characteristic of the early diagenetic models is that reduced sulfur is supplied by bacterial sulfate reduction during the mineralizing event, whereas, in the late diagenetic models reduced sulfur has either been pre-concentrated in the Kupferschiefer (in pyrite or organo–sulfur compounds) or is supplied by thermochemical sulfate reduction. Estimated temperatures of ore deposition in these models range from 25 to 100°C.

Proponents of an early diagenetic model (Oberc and Serkies, 1968; Oszczepalski, 1980, Oszczepalski, 1989; Sawlowicz, 1990; Oszczepalski and Rydzewski, 1991) cite textures (e.g., framboidal base-metal sulfides (Sawlowicz, 1990) and the compaction of organic laminae around base-metal sulfide cements (Oszczepalski, 1989)) combined with sulfur isotope evidence for bacterial sulfate reduction ($\delta^{34}\text{S} = -44\%$ to $-35\%$, Sawlowicz, 1989; Sawlowicz and Wedepohl, 1992) as evidence of an early diagenetic mineralizing event. Furthermore these models consider that thermochemical sulfate reduction at temperatures of 100°C or less is unreasonable due to unfavourable reaction kinetics. Mineralization in the adjacent limestones and sandstones resulted from the diffusion and/or advection of hydrogen sulfide from the Kupferschiefer. Hydrogen sulfide transport is invoked to explain the presence of base metal sulfides in rocks which are devoid of organic matter and, hence, assumed to be incapable of reducing sulfur in-situ (Oberc and Serkies, 1968; Sawlowicz and Wedepohl, 1992). A major problem with the early diagenetic models is clarification of the depth range associated with the term “early diagenetic”. Recent evidence indicates that dissolved sulfide concentrations approach zero at depths ranging from 80 cm to 80 m; below these depths sulfate is still bacterially reduced but at such slow rates that sulfide production is counter-balanced by dissolution of the least reactive silicates (Raiswell et al., 1993). It therefore seems unlikely that bacterial sulfate reduction could have made a significant contribution to the ore-forming process at depths greater than 100 m unless sulfate was supplied in the fluid that transported the metals or supplied locally near areas of gypsum or anhydrite cement.

Proponents of a late diagenetic mineralizing event (e.g., Kucha and Pawlikowski, 1986; Jowett, 1987; Jowett et al., 1987; Wodzicki and Piestrzynski, 1994) argue that the apparent replacement of carbonate cements and detrital silicates by sulfides and the formation of coarse lenses of sulfide, rhythmic sulfide bands and sulfide veins are indicative of late diagenetic mineralization. The reasons for unequivocally attributing these textures to a late diagenetic origin are unclear. The possibility that many of these textures, assigned to deep processes could originate in an early diagenetic environment are not evaluated by these authors. Arguments that the ore mineral zones (hematite (Rote Fäule), chalcocite, bornite, chalcopyrite, galena and sphalerite) which dip away from the Rote Fäule and cross-cut lithology boundaries at a low angle (Jowett et al., 1987) must have had a late diagenetic origin are equivocal. Textures which are indicative of early diagenetic or syn-depositional base metal sulfide formation result from relatively minor base metal accumulation in the organic-rich shales, prior to the main ore forming event. The exact depth range over which late diagenetic thermochemical mineralization is inferred to have occurred ranges from an unspecified minimum depth up to depths greater than 1 km (Jowett, 1987).

4. Previous organic geochemical studies

Using gas chromatography–mass spectrometry (GC–MS) Puttmann et al. (1987) reported increased concentrations of aromatics (especially dibenzothiophene) and interpreted this as evidence for oxidation of the organic matter and showed that it is most intense at the base of the Kupferschiefer. These authors also noted enhanced concentrations of poly-
cyclic aromatic hydrocarbons (naphthalenes, phenanthrenes) and heterocyclic-aromatics (dibenzo furans, dibenzo thiophene) at the base of the Kupferschiefer. They also correlated the distribution of copper and silver to the concentration of aromatics and recorded an inverse relationship with the organic oxidation parameter, the ratio phenanthrene/methylphenanthrenes. Additional evidence for oxidation is provided by fluorescence studies of the liptinite macerals. Puttmann et al. (1989) further attributed decreased yields in saturated hydrocarbons and porphyrins to oxidation. A terrestrial input to the Kupferschiefer in the Lower Rhine Basin was deduced from the presence of A-ring degraded pentacyclic triterpenes (Schwark and Puttmann, 1989).

Vitrinite reflectance measurements indicate the thermal maturity of the organic matter is low, at the onset of the oil window (Sawlowicz, 1991). In a detailed geochemical investigation of organic extracts from a large area of the Polish section of the Kupferschiefer, Sawlowicz (1989) showed that the organic matter in richly mineralized shales had a high degree of aromatization and low H content. In contrast, organic extracts from the “Rote Faule” zones (a hematite-cemented zone underlying the Kupferschiefer) were intensely oxidized. Sawlowicz (1991) complemented this earlier study with isotopic and elemental analyses of kerogens and, the organic composition in the Kupferschiefer was suggested to reflect some form of degradation, possibly reflecting low temperature microbially mediated metal and sulfate reduction. A noteworthy observation was the presence of localized organic extracts with high yields of saturated hydrocarbons. This feature has been interpreted (Gize, 1993) as hydrocarbon anomalies resulting from water interactions with the kerogen.

These organic studies have been used to support ore genetic models. Sawlowicz (1991) limited organic interpretations to support of intense microbial activity during early diagenesis. Puttmann et al. (1987), Puttmann et al. (1989) used evidence of organic matter oxidation to support models which invoke mineralization by ascending oxidising solutions. In this scenario, metal precipitation and organic matter oxidation is proposed to have been caused by thermochemical sulfate reduction, with the organic matter acting both as a reductant and hydrogen source (Bechtel and Puttmann, 1991).

It is clear from the above discussion that recent studies are polarized in genetic models for the Kupferschiefer, and it may be that both are correct to some extent. It is conceivable that an early sulfide ore was formed syndepositionally and remobilized later. Remobilization of ores as a result of oxidation is a common process and the organic geochemical studies of Puttmann and co-workers provide excellent evidence for an oxidative event superimposed on the organic matter. To address the earliest stages in the history of the Kupferschiefer, organic studies need to focus on organic transformations that are known to occur in the water column and earliest stages of diagenesis, but are not likely to have been severely affected by later events. The pristane to phytane ratio (Pr/Ph), is advocated as such an indicator of the redox conditions in the water column and earliest sediments. These saturated hydrocarbons, not having reactive functional groups, are relatively refractory to later events. Potential also exists for the input of isoprenoids, in particular phytane, from organosulfur compounds (Kohnen et al., 1993) but this could not be evaluated.

If variations in redox conditions are recorded by the Pr/Ph ratio and these variations are consistent with changes in the ore mineralogy, then good evidence will have been gained for mineralization having occurred syndepositionally or during early diagenesis of the Kupferschiefer. Later changes, such as remobilization or hypogene oxidation cannot be eliminated, but they will have been shown to be superimposed on a very early mineralization stage.

5. Analytical procedures

Samples were collected from fresh mine faces, wrapped in aluminium foil and packaged in paper bags to avoid plasticizer contamination. Prior to analysis a representative sample was taken for petrographic studies. Petrographic blocks were prepared by setting in a cold resin (Metset, Buehler) overnight, to ensure no thermal effects were induced in the mineralogy. The blocks were then cut with a wafer saw, using water only as the lubricant. The samples were then polished manually (alumina grades: 200, 600 grit, 1 mm, 0.3 mm, 0.05 mm; Buehler) with a minimum of pressure.
Prior to organic analysis, the exteriors of samples were removed in order to eliminate potential contamination from mine machinery (e.g., diesel exhausts, generators). The samples were then cut to centimeter-sized blocks using a water only cooled saw and powdered in a tungsten carbide ring mill. All glassware and extraction thimbles were pre-cleaned prior to Soxhlet extraction. In the course of the study, the extraction thimbles (cellulose, 123 x 41 mm, Whatman) were found to be a source of phthalate ester contamination. This contamination was reduced by pre-cleaning the thimbles with two extraction. The weighed powdered sample was then extracted for 24 h using a negative azeotropic mixture of toluene:methanol (27:73, Fisons Distol Grade). The solvent was evaporated under low pressure using a rotary evaporator, the extract dissolved in a minimum of dichloromethane (Fisons Distol Grade), and transferred to a pre-cleaned glass vial. After solvent evaporation, each vial was stored in darkness, at 1 °C, in order to minimize sample degradation by photodegradation and microbial oxidation before analysis by GC–MS.

GC–MS analyses was performed using a Hewlett-Packard 5890 gas chromatograph, coupled to a VG Trio-1 quadrupole mass spectrometer. Gas chromatographic conditions were: helium carrier gas, splitless injection with a 5 s purge after 20 s, injector at 250°C, oven initially held at 50°C for 1 min before ramping at 4°C min⁻¹ to 300°C and being held isothermally at 300°C for 20 min. Columns were either 12 m BP1 or BP5 (J&W). The GC–MS interface was set at 300°C. Mass spectrometer conditions were: source temperature 230°C, ionization energy 70 eV, scan range 40–550 amu, 0.9 s scan time and 0.1 s interscan time. The Pr/Ph ratio was calculated using integrated peak areas.

6. Organic geochemistry results

6.1. Yields

Fig. 2 shows the total extractable hydrocarbon yields (mg/g powdered sample, Table 1) for the traverses from the Rudna and Lubin Mines. High concentrations of sulfides throughout the sample profiles increase the sample densities and, therefore, the yields are low compared to sulfide-free oil shales. An immediate difference is evident between the two mines. In the Lubin traverses the yields are relatively uniform (1–2 mg/g) with a possible decrease towards the top of the section in the overlying dolomite. In marked contrast the traverses from the Rudna Mine show enhanced yields (up to approx. 6 mg/g) from the clay-rich and carbonate-rich Kupferschiefer. In the Weissliegendes and Zechstein Limestone (Werra Dolomite) of the Rudna traverses the yields are comparable to those from the Lubin Mine. No correlation with sulfide composition is observed in any of the traverses.

7. Hydrocarbon distributions

Total ion current chromatograms (TICCs) of two representative vertical traverses from the Rudna and Lubin mines are shown in Fig. 3 and a close up one chromatogram is displayed in Fig. 4. The predominant compounds in the total hydrocarbon extracts are a homologous series of normal alkanes and isoprenoids. Consistent lithology-controlled shifts in hydrocarbon distributions are evident.

In traverses from both mines, the Weissliegendes sandstone is characterized by low yields, which, in some samples are sufficiently low to result in trace phthalate ester contaminant peaks becoming evident. In the stratigraphically lowest samples, the overall hydrocarbon distribution is bimodal with the main distribution centered around n-C_{15-17}, with a second hump corresponding to an unresolved complex mixture (UCM) in the region of n-C_{30}. Towards the upper 20 cm the TICCs show a shift towards a more unimodal distribution centered around n-C_{18-19}. The Boundary Dolomite, which is present in only one of the Lubin traverses, displays a bimodal distribution centered at n-C_{16-17} and a UCM in the region of n-C_{30}. Thin dolomite layers in the Weissliegendes below the Boundary Dolomite display both slightly bimodal (centered on n-C_{17-19} and an UCM in the region of n-C_{30}) and unimodal (centered on n-C_{16-17}) distributions.

TICCs from the Kupferschiefer in the Rudna Mine generally show a unimodal hydrocarbon distribution centered around n-C_{13-15} except towards the top of the Kupferschiefer and at the base of the Zechstein Limestone (Werra Dolomite) where the dominant
hydrocarbon is pristane. In the Lubin Mine, some Kupferschiefer samples show a bimodal distribution with the main concentration centered on n-C\textsubscript{15} and a UCM in the n-C\textsubscript{30} region. In the Rudna Mine the uppermost samples of the Zechstein Limestone have a hydrocarbon distribution characterized by the presence of elemental sulfur and by an irresolvable baseline hump in the n-C\textsubscript{15-19} range. In the Lubin Mine elemental sulfur is not observed in the Zechstein Limestone and the distribution is bimodal centered at n-C\textsubscript{17} and a UCM in the n-C\textsubscript{30} region.

8. Pristane / phytane

The pristane/phytane (Pr/Ph) ratio measured in the traverses (Fig. 5, Table 1) varies from 0.7 to 6.7 and in both mines the ratio displays similar trends. Relatively low Pr/Ph ratios occur close to the contact between the Weissliegendes and the Kupferschiefer and in the Zechstein Limestone. Pr/Ph ratios in the Kupferschiefer are variable but relatively high compared to values in the adjacent sandstone or dolomite. In the Rudna Mine, the maximum Pr/Ph

Fig. 2. Yields in mg/g plotted against their stratigraphic positions in the seven sample traverses (5 from Rudna, 2 from Lubin). Sample numbers are given down the left hand side of each column. Sample R1A4B was split into three pieces 5 cm apart. Where constrained, the position of the boundary between the zones dominated by Cu-sulfide and Pb-sulfide mineralization is shown (only in the traverses from the Rudna Mine).
Table 1
Tabulated yields, pristane/phytane ratios (Pr/Ph), depth and lithology. The depth of a sample is given relative to the base of the Kupferschiefer.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Depth (m)</th>
<th>Lithology</th>
<th>Yield (mg/g)</th>
<th>Pr/Ph</th>
<th>Sample code</th>
<th>Depth (m)</th>
<th>Lithology</th>
<th>Yield (mg/g)</th>
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The ratio is generally within or close to the upper carbonate-rich Kupferschiefer in the Pb-zone. A distinct trend of increasing Pr/Ph ratio is found within 10 cm of the base of the Kupferschiefer. At this boundary, the minimum Pr/Ph ratio is generally in the top 10 cm of the Weissliegendes or Boundary Dolomite and increases upwards, towards, and into the Kupferschiefer. This increase is best constrained in Rudna traverse 4 where Pr/Ph ratios were measured at 5 cm intervals, from 15 cm below the Kupferschiefer to 5 cm into the Kupferschiefer. These values all show a steady upward increase in Pr/Ph ratio. Where constrained (Rudna Traverses 1–3), another trend is the increase in Pr/Ph ratio that occurs going from the Cu-zone to the Pb-zone. Bearing in mind the stratigraphic thickness covered by each sample (5–10 cm), this increase is best constrained in Rudna traverse 4.
cm) then this increase lies within sampling error (±5 cm) of the transition from the clay-rich Kupferschiefer to the carbonate-rich Kupferschiefer.

9. Discussion

9.1. Hydrocarbon distribution

Before considering the implications of variations in the Pr/Ph ratio we must first consider the variations in the general hydrocarbon distribution. TICCs from both mines display hydrocarbon distributions characterized by two components; normal alkanes in the range n-C_{13-19} and an UCM in the region of n-C_{30}. The hydrocarbon distributions reflect directly the stratigraphy, with bimodal distributions (two maxima one at n-C_{13-19} and another at the UCM) characteristic of the Weissliegendes and dolomites contrasting with the unimodal distributions (one maximum at n-C_{13-19}) in the Kupferschiefer. Changes in the hydrocarbon distribution can result from variations in biological sources, thermal maturity, host rock mineralogy and as a consequence of hydrothermal alteration (Powell and McKirdy, 1973; Tissot and Welte, 1984; Gize, 1993).

Variation in biological sources is the most likely cause of the varied normal alkane distributions. The normal alkanes n-C_{13-19} are typical of a source rock derived from marine plankton and algae (Tissot and Welte, 1984). This biological source is consistent with the marine depositional environment of the Kupferschiefer and the organic petrography which indicates a predominance of alginite and detroliptinite. If the proportion of algal matter determines the degree to which the n-alkanes dominate then the difference between the Kupferschiefer and adjacent lithofacies can be considered as representing the proportion of algal matter. Furthermore, the general observation that the higher the total extractable hydrocarbon yield the more alginite there is in the sample can account for why the UCM is prominent in some of the low yield Kupferschiefer samples from the Lubin Mine. The origin of the UCM in the region of n-C_{30} is less well understood in terms of biological source, but has been noted in other carbonates (Gize and Barnes, 1987).

Another possibility is that the hydrocarbon distribution reflects hydrothermal alteration. Gize (1993) inferred that alteration of kerogen to lower molecular weight normal alkanes occurred in Mississippi Valley-type deposits as a result of hydrous pyrolysis during mineralization. Application of this interpretation requires that the Kupferschiefer has experienced more hydrothermal alteration than the adjacent sandstones and dolomites. There is no evidence of local faults which could have focused the hydrothermal fluids in the sampled areas. It is also unlikely that the least permeable unit should be the most hydrothermally altered. Lastly, if the change in hydrocarbon distributions reflect the mineralization process, then there should be a correlation between the distribution...
of base metal sulfides and the unimodal hydrocarbon distributions. Similar amounts of sulfide mineralizations occur in all the lithofacies and no such correlation is observed.

If the alkanes n-C_{13-19} are derived from the thermal breakdown of higher molecular weight hydrocarbons, then a significant thermal gradient would need to be inferred to have existed between the Kupferschiefer and adjacent sandstones and dolomites. This gradient seems improbable on a centimeter to meter scale. Mineralogical catalysis of decarboxylation reactions (e.g., α-decarboxylation of fatty acids by aluminosilicates and β-decarboxylation by carbonates: Tissot and Welte (1984)) could also enhance the breakdown of higher molecular weight hydrocarbons, but this seems unlikely as no clear correlation occurs between the hydrocarbon distribution and the distribution of aluminosilicates or carbonate.

If it is accepted that variations in biological input are the most satisfactory reason for the normal alkane distributions and that these distributions vary with the stratigraphy, then irrespective of later oxidative events recorded by the aromatic hydrocarbons, a part

Fig. 5. Pristane/phytane ratios plotted against their stratigraphic positions in the seven sample traverses (5 from Rudna, 2 from Lubin). Sample numbers are given down the left hand side of each column. Sample R1A4B was split into three parts 5 cm apart. Where constrained, the position of the boundary between the zones dominated by Cu sulfide and Pb sulfide mineralization is shown (only in the traverses from the Rudna Mine).
of the refractory saturated hydrocarbons has been shown to reflect the biological input associated with the earliest stages in the development of the Kupferschiefer. Consequently it is feasible to examine the saturated hydrocarbon parameter, the pristane/phytane ratio, as a potential record of the redox conditions in the water column and near-surface sediments at the time of deposition.

9.2. Pristane/phytane ratio

The potential use of the Pr/Ph ratio as an indicator of the redox conditions in early diagenesis was emphasised by Didyk et al. (1978). In this hypothesis Didyk et al. (1978) propose that the precursor molecule of pristane and phytane is the chlorophyll side chain, phytol. Under relatively oxidising conditions, phytol is converted to phytenic acid, followed by decarboxylation and hydrogenation to pristane. Under relatively reducing conditions, phytol is hydrogenated to dihydrophytol before transformation to phytane. Later workers have since reported situations where the ratio cannot sensibly be ascribed to redox conditions, thus requiring other factors need to be considered, such as potential co-elution, salinity, biological source and thermal maturity (Ten Haven et al., 1987; Ten Haven et al., 1988; Powell, 1988). These other effects must be evaluated before using the Pr/Ph ratio as an indicator of early diagenetic redox conditions.

Erroneous concentrations of pristane have been reported to be caused by the co-elution of a branched hydrocarbon 2, 6, 10 trimethyl-7-(3-methylbutyl)-dodecane (Ten Haven et al., 1987). Using the diagnostic ions m/z 168/169 (Yon et al., 1982) this compound does not appear to be present in our samples. The effect of burial and thermal maturation is to increase the Pr/Ph ratio (Powell and McKirdy, 1973) but variations within sample traverses are unlikely to be due to differing degrees of thermal maturity. The maximum Pr/Ph ratios are within the Kupferschiefer and increases in the ratio occur at the Weissliegendes–Kupferschiefer boundary and at the transition from carbonate-poor to carbonate-rich Kupferschiefer.

With respect to biological source, organic material derived from higher plants produces on maturation a high Pr/Ph ratio (in the range 5–10: Powell, 1988), whereas, organic matter derived from marine algal sources produces a low Pr/Ph ratio (in the range < 1–3: Powell, 1988). The maximum Pr/Ph ratios recorded in the Kupferschiefer (in the range 4–6.7) are, therefore, more typical of organic matter derived from higher plants. A higher plant input into the Kupferschiefer is not, however, supported by the normal alkane distribution or the organic petrography which indicate a predominantly algal input. Compounds other than phytol have been proposed as an alternate source of pristane, particularly tocopherols (Goossens et al., 1984). Tocopherols are associated with photosynthetic organisms and are relatively resistant to early diagenetic degradation, hence, they could account for the locally enhanced Pr/Ph ratios. Very low (< 1) Pr/Ph ratios have been associated with hypersalinity (Ten Haven et al., 1987) and this could potentially be the cause of some of the very low ratios recorded in the Boundary and Werra Dolomites, for which high salinity syn-depositional conditions have been inferred (Oszczepalski, 1980).

Based on the Didyk et al. (1978) hypothesis, the high Pr/Ph ratios in the Kupferschiefer indicate relatively oxidising conditions (or zooplankton predation or recycling associated with such conditions) in the overlying water column or early sediments, or both. This interpretation initially appears contrary to the euxinic environment proposed for the Kupferschiefer (e.g., Oszczepalski, 1989). Organic matter, however, becomes oxidized under both aerobic and anaerobic conditions; the extent to which it is oxidized depends on the a variety of factors including, sedimentation rate and organic productivity (Pedersen and Calvert, 1990). The presence of early diagenetic carbonate concretions in mudstone is associated with enhanced anaerobic oxidation of organic matter during periods of very low sedimentation rate (Raiswell, 1988; Bottrell and Raiswell, 1990). The carbonate-rich Kupferschiefer sampled in this study contains variable amounts of early diagenetic, concretionary, calcite cements. In view of this, the increase in the Pr/Ph ratio and the particularly high ratios could reflect enhanced, early diagenetic, anaerobic oxidation of the organic matter associated with very low sedimentation rates. Whether or not the high Pr/Ph ratio is due to the oxidation of phytol or the selective preservation of tocopherols or other
compounds cannot be ascertained but local oxidation related to the formation of early diagenetic calcite is a reasonable hypothesis. The lack of correlation between the Pr/Ph ratio and the abundance of authigenic dolomite is not surprising as the concretionary calcite cements and the dolomites could have formed as a result of quite different processes.

The increase in the Pr/Ph ratio at the transition from the Kupferschiefer to the Weissliegendes is not marked by an increase in the abundance of authigenic carbonate in the Kupferschiefer. The increase at this boundary could in part be due to the especially low Pr/Ph ratios encountered near the top of the Weissliegendes, which may reflect the same high salinities recorded by the Boundary Dolomite in shallower water sequences. Enhanced early diagenetic, bacterial oxidation of organic matter on this boundary could also have occurred as a result of sulfate being supplied from porewater in the Weissliegendes.

Several authors (Kucha and Pawlikowski, 1986; Jowett, 1987; Jowett et al., 1987; Wodzicki and Piestrzynski, 1994) have inferred that the mineralization in the Kupferschiefer occurred in response to the post-depositional reduction of ascending fluids. These models propose a redox gradient across the Kupferschiefer from most oxidized at its base to most reduced at its top, with the degree of oxidation decreasing from the Cu-zone to the Pb-zone. The pristane/phytane trends reported in this detailed study indicate the opposite trend, therefore, if a redox gradient did exist across the Kupferschiefer it occurred after the Pr/Ph ratios were developed in the host rocks.

Comparing trends in the Pr/Ph ratio with the sulfide mineralogy also reveals a distinct positive correlation. In the Rudna Mine, at the top of the Weissliegendes and base of the Kupferschiefer and at the contact between the Cu-zone and the Pb-zone, Large et al. (1995) report Cu and Cu–Fe sulfides becoming less copper rich. On both these horizons, they observe upward gradations from chalcocite to more copper-poor Cu–S sulfides and from bornite to copper-depleted bornite. Anilite associated with the other copper-depleted Cu–S minerals on these horizons is not a stable phase above 39°C (Gronvold et al., 1987) and indicates a low temperature alteration event which Large et al. (1995) interpreted as early diagenetic. Changes in the Pr/Ph ratios across these boundaries also record evidence of increased oxidation of organic matter during early diagenesis. Possible correlations between the organic geochemistry and sulfide petrology should however be considered cautiously as petrological observations made on a centimeter scale record smaller scale changes than the organic extracts which represent the average organic chemistry from samples 5–10 cm thick. If, however, both the Pr/Ph ratios and the sulfide mineralogy were established during early diagenesis then it is conceivable that both are related to the same change in redox conditions.

10. Conclusions

The history of an ore deposit, from precipitation to the present day can be a complex series of events. Previous studies, including organic geochemical work, have described a redox boundary across the Kupferschiefer, with the most oxidized conditions in the lowermost section of the Kupferschiefer. In order to investigate processes which pre-date this oxidation event, the saturated hydrocarbons have been used because of their relative unreactivity. The normal alkane distributions are stratigraphically controlled and were, therefore, formed during the deposition of the Kupferschiefer and associated sediments, before any later oxidation. The Pr/Ph ratio has previously been shown to be a potential indicator of the redox conditions in the water column and earliest sediments. In this study, anomalously high Pr/Ph ratios are reported from the Kupferschiefer. Furthermore, consistent increases in the Pr/Ph ratio occur at the transition from the Weissliegendes to the Kupferschiefer and at the transition from the clay-rich to the carbonate-rich Kupferschiefer. These increases suggest an upward change to relatively more oxidized conditions. Both the trends of increasing Pr/Ph ratio and the anomalously high ratios are probably the result of enhanced, early diagenetic, anaerobic oxidation. Early diagenetic copper-depletion has also been reported from these horizons and may be related to the same processes which produced the trends in Pr/Ph ratio.
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References


