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## Origin of Kupferschiefer mineralization as suggested by coal petrology and organic geochemical studies

**ABSTRACT:** The Kupferschiefer base metal occurrences of Central Europe have been investigated by a variety of organic geochemical and coal petrology methods to clarify their genesis. Low rank vitrinite anomalies were encountered in the paleogeothermal field of the Kupferschiefer horizon in close proximity to Variscan paleohighs and tectonically severely disturbed basement. Spatially, they are related to the position of well-known base metal occurrences of the Kupferschiefer type. In the areas of ore grade mineralization an inorganic oxidation effect of soluble organic material has been recognized. Base metal content and degree of oxidation expressed by a ratio of phenanthrene to the sum of methylphenanthrene ( $Ph/\Sigma MePh$ ) increases and then decreases towards the epigenetic Rote Fäule facies. This suggests that ascending, low-temperature and oxidized ore-bearing solutions were responsible for the enrichment of the Kupferschiefer bed. The Kupferschiefer, acting as a geochemical hydrogen-sulphide screen, was a site of the redox type reactions that resulted in base metal reduction (precipitation) and hydrocarbon oxidation within this Upper Permian (Zechstein) bed.

### INTRODUCTION

The problem of the origin of the Kupferschiefer mineralization in Central Europe has lately received little attention. Nevertheless, some new concepts that link this mineralization and the source of base metals with the plate tectonics model and oxidized epigenetic solutions have been proposed (SPECZIK 1985, EUGSTER 1985, JOWETT 1986). These concepts, however, mainly utilize the previously known data and correlations between mineralization, the location of the Rote Fäule horizon, the Zechstein shoreline and the structural development of the spatially associated basement.

Recently, it was found that the high-temperature geothermal field of the Fore-Sudetic Monocline basement in southwestern Poland shows various heat anomalies related to paleohighs and the tectonically distur-

bed basement (SPECZIK 1987, SPECZIK & KOZŁOWSKI 1987). These anomalies are also related to areas of the base metal occurrences of the Kupferschiefer type. Hence, it was suggested that one of the factors controlling the formation of the Kupferschiefer mineralization was the supply of thermal energy.

To reevaluate this thermal energy factor with respect to the Kupferschiefer bed vitrinite and liptinite rank studies and organic geochemical investigations were conducted. This appears important since the temperature seems to be critical for interpretations based on changes in degree of maturity of the organic material.

The Kupferschiefer is generally described as a thin, marly, and bituminous bed formed in a euxinic and sapropelitic environment, which in places is mineralized. Our results do not suggest such a simplistic picture. The most plentiful component of organic macerals is the variously bituminous and oxidized vitrinite. Liptinite (alginate) forms notable accumulations only in places that have a high soluble organic material content, while allochthonous inertinite dominates in near-shore environments.

Because of these factors the vitrinite reflectance determinations were the most commonly used. Fluorometric, liptinite investigations were conducted only for comparative studies. The aim of organic geochemical studies was twofold: (i) an assessment of calculated vitrinite rank using compounds termed chemical fossils (= chemofossils) or geolipids (DIDYK & *al.* 1978, MACKENZIE & *al.* 1982), and (ii) detailed geochemical characteristics of soluble organic material.

Organic geochemical parameters that indicate the paleoenvironmental conditions during sedimentation have subjected to numerous studies (BROOKS & *al.* 1967, ALBRECHT & *al.* 1976, LOUDA & BAKER 1984). Organic matter and its chemofossils could also record secondary alteration processes that occur during or after diagenetic processes, and which could be induced by microbial activity, water washing and weathering effects (LEYTHAEUSER 1973, CONNAN & ORGEVALL 1976, PALMER 1984).

Biodegradation of crude oils under aerobic conditions is indicated by a significant decrease in n-alkanes followed by a degradation of isoprenoid hydrocarbons. When biodegradation is accompanied by water washing effects, besides the primary loss of selected compounds, *i. e.* dibenzothiophenes, a general loss of aromatic hydrocarbons is observed. Weathering is mainly manifested by a decrease in organic matter content and it has a less drastical influence on the composition of saturated hydrocarbons than the biodegradation has. Recently, examples of secondary alteration of hydrocarbons connected with processes of mineralization were reported from the Lodève Basin in France (CONNAN & ORGE-

VALL 1976) and from the Pine Point Pb-Zn deposits in Canada (MACQUEEN & POWELL 1983). As concluded in these two studies, loss of saturated hydrocarbons is attributed to biodegradation of sedimentary organic material.

The samples used in this investigation were collected in Poland (Fore-Sudetic Monocline, North-Sudetic Syncline) and the Federal Republic of Germany (Richelsdorf, Spessart-Rhön Highs and Lower Rhine Basin); they come either from cores, mine profiles or surface exposures.

#### ORGANIC GEOCHEMICAL STUDIES

In the study more than 100 Kupferschiefer samples from various locations in the Kupferschiefer horizon in Central Europe were analyzed. Finely ground rock-samples were subjected to a Soxhlet-extraction process of dichloromethane (24 hours) in preextracted timbles. Organic carbon contents ( $C_{org}$ ) were determined using a Leco WR-12 Carbon determinator; GC analyses were carried out on a Carlo Erba 5160 gas chromatograph; GC-MS analyses of aromatic and polar compounds were performed on a Varian 3700 GC coupled to a Finningan MAT 8200 mass spectrometer (electron energy 70 eV). The same type of column, and temperature program was used both for GC and GC-MS analyses. All these detailed analytical procedures are recently described by PÜTTMANN, MARZ & SPECZIK (1987a).

Results obtained from samples collected in areas of ore grade mineralization differ greatly from those collected elsewhere throughout the Kupferschiefer basin (i.e. regions of primary-syndiagenetic, mainly pyritic mineralization). In the former (southwestern Poland), the fraction of saturated hydrocarbons shows a significant low intensity of long chain n-alkanes in the gas chromatogram. The maximum of the n-alkane distribution is around n-C<sub>14</sub>. The decrease of relative intensities of high-molecular weight alkanes is so strong that n-C<sub>28</sub> is present only in traces. The late eluting compound series is represented only by hopanes and moretanes. Pentacyclic triterpenoids are distinctly separated from all the other hydrocarbons. The aromatic hydrocarbon fraction shows an uncommon composition, with very high intensities of some single compounds. The GC-MS analyses revealed that the four main compounds of this fraction are biphenyl, dibenzofuran, dibenzothiophene, and phenanthrene (see Text-fig. 1). Polar heteroaromatic compounds are represented by benzophenone, fluorenone, xanthone, and acridinone (see Text-fig. 2); MOJELSKY & STRAUZ (1986) suggest that fluorenones are products of geochemical oxidation of fluorene.

The above composition is quite different from the previously known effects of meteoritic weathering, microbial or diagenetic degradation, and water washing of organic material. To the contrary, it shows some analogy to the *in vitro* synthetic oxidation products of coal extracts with sodium dichromate, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (HAYATSU & *al.* 1978). The most significant difference between the extracts of synthetic oxidized coals and extracts of ore grade Kupferschiefer samples is the occurrence of dibenzothiophene as one of the main compounds of the aromatic fraction.

This has been attributed to the genetic conditions during the Kupferschiefer deposition and diagenesis (PÜTTMANN, MARZ & SPECZIK 1987b). The redox

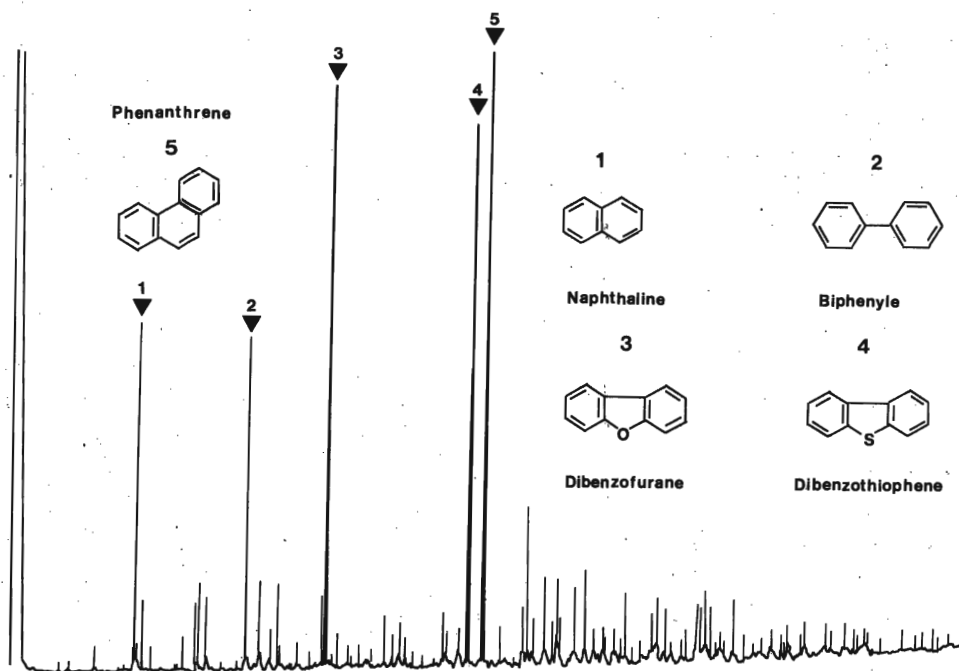


Fig. 1. Gas chromatogram of the aromatic fraction of the Kupferschiefer sample from the Konrad mine (depth 695.0 m), North-Sudetic Syncline

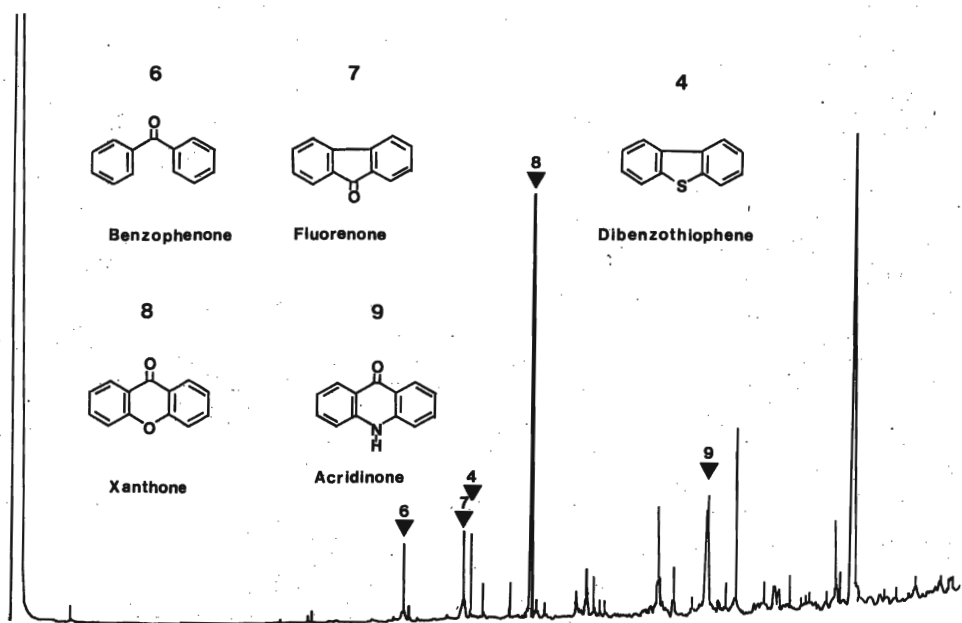
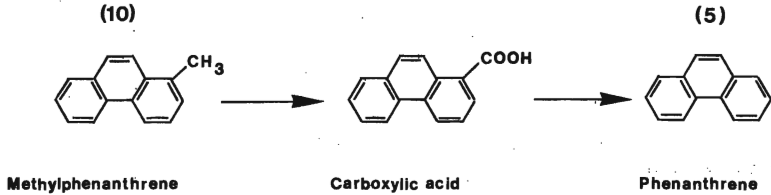


Fig. 2. Gas chromatogram of the polar heterocompounds fraction of the Kupferschiefer sample from the Konrad mine (depth 695.0 m), North-Sudetic Syncline

reactions in the Kupferschiefer sediments presumably provided elemental sulphur. This sulphur reacted with either aromatic hydrocarbons or isoprenoid hydrocarbons under cyclisation and aromatization. The occurrence of dibenzotiofene in coals is unlikely because of relatively low sulphur content.

The relative amount of single aromatic compounds is changed by the assumed oxidation reactions. Oxygen is incorporated in aromatic frame systems and carbonyl compounds become important constituents of the bitumen. The decomposi-



tion of alkylphenanthrenes (methylphenanthrene) to phenanthrene seems to be one of the controlling organic geochemical reaction in the sediments. This type of reaction is well established in the field of organic synthesis (see equation).

The concentration of phenanthrene relative to methylphenanthrenes and the ratio of Ph/ $\Sigma$ MePh increases from 0.41 to 5.03. Hence, the ratio of phenanthrene

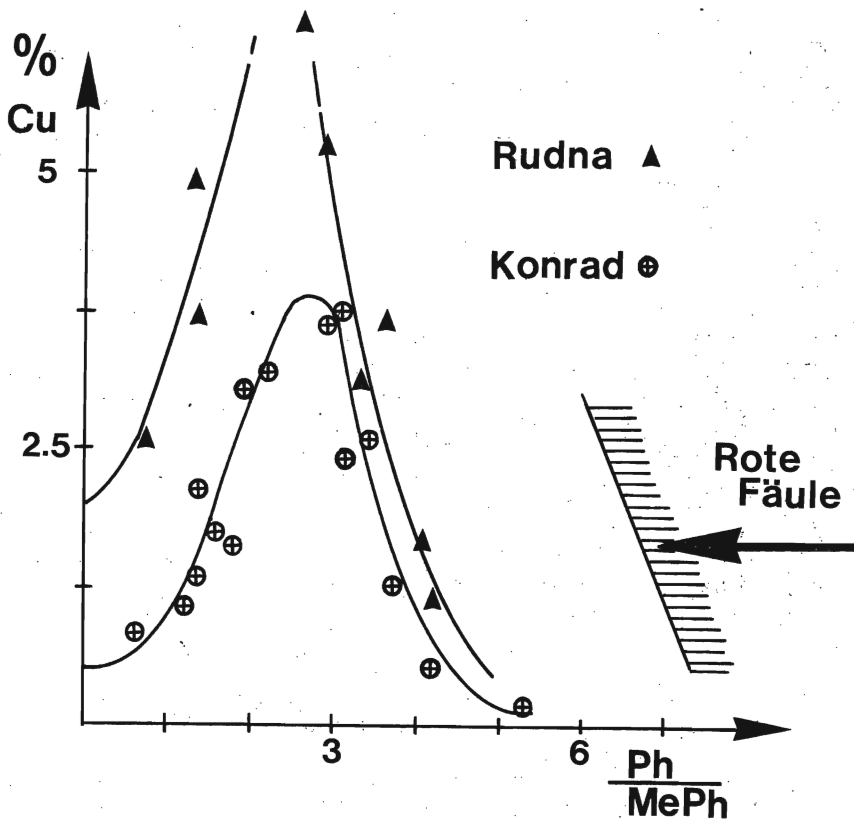


Fig. 3. Correlation between the Cu content, intensity of oxidation of soluble organic material (Ph/ $\Sigma$ MePh ratio) and position of the Rote Fäule horizon; chosen profiles from Rudna and Konrad mines, Fore-Sudetic region

versus the sum of methylphenantrenes provides a measure for the intensity of oxidation. Also the methylphenanthrene index MPI-1 (RADTKE & al. 1982) correlates with the degree of inorganic oxidation of soluble organic material. The intensity of these effects increases towards the oxidized epigenetic Rote Fäule zone, while the base metal content decreases in the same direction (Text-fig. 3).

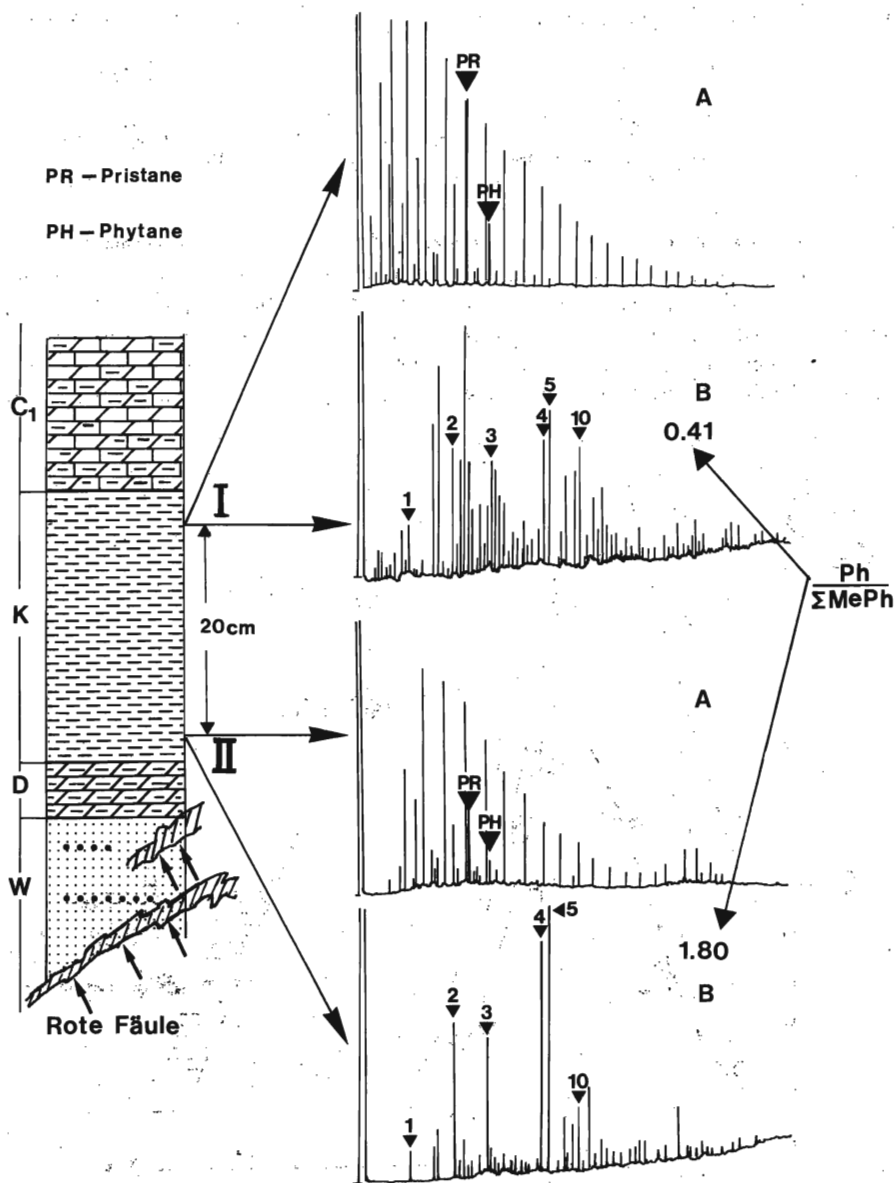


Fig. 4. Representative geological profile of the Rudna mine (Fore-Sudetic Monocline) and gas chromatograms of saturated hydrocarbons (A) and aromatic (B) fractions: the samples II and I (depth 918.9 m and 919.1 m respectively) characterized by increasing distance from the Rote Fäule horizon

W — Weissliegendes, D — basal dolomite, K — Kupferschiefer, C<sub>1</sub> — dolomitic limestone of Zechstein Ca<sub>1</sub>

In addition, analyses of certain profiles show that the content of oxidation indicating compounds increases from the top to the bottom part of the Kupferschiefer (Kupfermergel) bed, while the content of saturated hydrocarbons decreases (Text-fig. 4). Consequently, the most oxidized horizon is at the base of the Kupferschiefer.

A number of studies have tried to show a link between organic geochemical parameters and rank of vitrinite (*i.e.* pristane/phytane, hopane/moretane ratios, CPI index: see MACKENZIE & *al.* 1982). Because the majority of these chemofossils in investigated samples are affected by secondary oxidation, no exact statement about their maturation is possible (Text-fig. 4A). The pristane/phytane ratios vary within a narrow range from 1.92 to 3.3. All samples that show distinct differences in the aromatics composition reveal similar pristane/phytane ratios. This seems to indicate that pristane and phytane are affected equally by secondary oxidation during the later stages of alteration. Hence, these compounds contribute no information about the intensity of the secondary oxidation processes.

In most cases the R-S isomerization at C-22 homohopane has already reached equilibrium value. Therefore, the hopane distribution provides little information about maturation of the organic material. In some samples moretanes can be recognized. The C<sub>30</sub> moretane/C<sub>30</sub> hopane ratio of 0.35 to 0.45 indicates that the maturation of the organic material is not fully completed (SEIFERT & MOLDOVAN 1980).

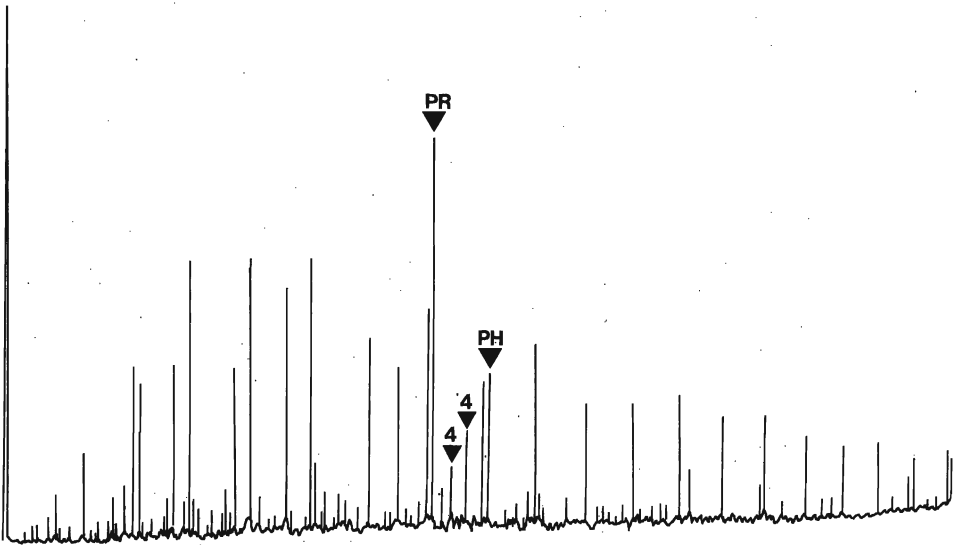


Fig. 5. Gas chromatogram of total extract, sample from North-Sudetic Syncline

In regions of low (primary-syngenetic) Kupferschiefer mineralization oxidation effects are not detected (Text-fig. 5). The composition and distribution of saturated hydrocarbons in samples derived from these regions are generally typical of common diagenetic processes (PÜTTMANN, MARZ & SPECZIK 1987b). The vitrinite reflectance values for these samples calculated on the basis of pristane/phytane or moretane/hopane ratios generally agree with earlier measured values.

## VITRINITE MEASUREMENTS

The dominant maceral of the vitrinite group found is collinite accompanied by a lesser amount of vitrodetrinite and minor telinite. In most cases vitrinite (collinite) is structureless. Minor cell structures (telinite) are filled with collinite or liptinite group macerals. The original cell structure is presumably masked by infilling with colloidal humic gel precipitated from humic solutions.

Vitrinite of the more distant facies is variously cemented and impregnated, with liptinite macerals, predominantly along fissures and cleats. Vitrinite of the Kupferschiefer constitutes the main part of complicated and partly dense network of horizontal and vertical stringers as well as thin layers or pseudoveinlets of solid organic material. Grains or layers of entirely homogenous collinite have not been detected. Collinite gel was also found as infillings of some sporinite tetrads. Some cell cavities of vitrinite are filled or intergrown with clay, but some empty cell lumens are also present. This vitrinite is generally dark with a glassy or pitchy luster and its reflectance is higher for telinite cells than for collinite infillings.

Vitrinite in near-shore environments (Kupfermergel) is rather rare. However, when present it occurs in distinct layers or as irregular grains, often with sharp borders. In some locations roots (up to 10 cm long), bark and leaf fragments were noticed. Smaller grains of vitrinite often exhibit granular pattern and this may be interpreted as "mixinites" (AMMOSOV 1956), i.e. a mixture of micrinite and collinite.

Vitrinites of both locations are variously altered (oxidized). In vitrinite from the Kupferschiefer horizon its inner structure becomes more pronounced, and it shows patchy textures having differences in refractive index and color. Vitrinite from the Kupfermergel shows more pronounced symptoms of oxidation with even oxidation rims along its edges, and along fissures and fractures. The edges of some larger grains show microfissures, and are comparatively darker or lighter than the inner portions of the grains.

Vitrinite reflectance in over 200 polished sections from borehole profiles and some outcrops were determined. The measurements were performed on Zeiss MPV II Microscope-Photomultiplier coupled with Commodore computer. The data were recorded and analyzed with the aid of a modified Leitz Cospec-4 program. Because the anisotropy of the macerals was very small a mean reflectance was determined. To assure a representative mean reflectance, a minimum of 100 individual measurements were performed on each preparation. They were conducted in immersion oil in a one-beam light, using a synthetic YAG 0.88% R<sub>r</sub> standard and a 40 × immersion oil objective lens. The aperture diaphragm limited the area of measurement to less than 5 mm in diameter.

The random (mean) vitrinite reflectance of the Kupferschiefer horizon in southwestern Poland (and partly in the Federal Republic of Germany) was found to be generally low, which is in contrast to the high geothermal gradient recognized in the underlying basement (SPECZIK 1985, WOLF & STELLMACHER 1984). More than 80% of the results fall in a narrow range between 0.5 to 0.9% R<sub>oil</sub> (Text-fig. 6).

Two prevailing types of reflectograms are recognized in southwestern Poland. The first type, having a regular distribution pattern is characteristic of areas of low reflectance that lack or have only a slightly pronounced oxidation of the soluble organic material (Text-fig. 7A). The second type having an irregular di-



stribution pattern reflects the variable oxidation of soluble organic material as well as vitrinite (Text-fig. 7B). This process, and to some extent its temperature, evidently elevates the rank of vitrinite. The latter observation does not quite agree with prevailing views that pore fluid chemistry does not appear to have an effect on coal rank (STACH 1982).

There is a general correlation between the depth of sample collection and random reflectance, except for samples which either have a high content of organic material or reveal pronounced oxidation of soluble organic matter and samples collected close to paleohighs and near shoreline (Text-fig. 8). In fact, there is an increase of the extent of maturation towards the Middle Odra Crystalline Zone, which is well illustrated by the schematic cross-section through the ore fields of Polkowice and Rudna mines (Text-fig. 9). The second type of reflectograms is more characteristic of areas of elevated reflectance, where the maximum peak of vitrinite gradually passes to a maximum peak of allochthonous vitrinite or inertinite. This change is caused both by the presence of vitrinite and inertinite of different origin, as well as variously oxidized vitrinite ("vitroinertinite") that resulted partly from oxidation processes.

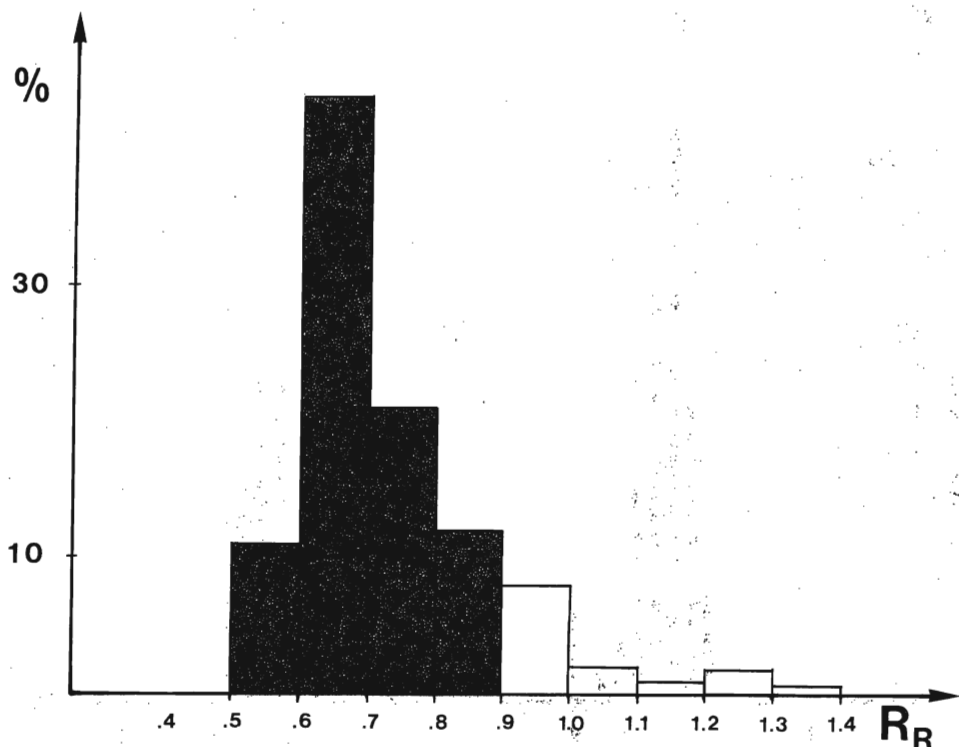


Fig. 6. Frequency *versus* vitrinite random reflectance histogram for all reflectance determinations.

It was difficult to recognize whether the vitrinite particles bear indices of either secondary oxidation by oxidized solutions or natural oxidation (*i. e.* weathering, transport, redeposition). For this determination reflectograms of all coal macerals were very helpful. They often display in this case a clear bimodal character of the vitrinite peaks (Text-fig. 7B). Low vitrinite rank anomalies are encountered in the paleogeothermal field of the Kupferschiefer horizon. In the southern part of the Fore-Sudetic Monocline these anomalies correlate well with the high temperature geothermal field anomalies recognized in the Carboniferous basement (SPECZIK 1987). In a northerly direction the correlation is not so clear, and this may be attributed to the extension of the lower crust during the formation of the Mid-Polish Aulacogen ("Danish — Polish Trough"). The location of the base metal occurrences correlates with low rank anomalies in the geothermal field of the Kupferschiefer horizon as well as with the position of shoreline and paleohighs in the Zechstein basin (Text-fig. 10). A similar vitrinite rank pattern was observed in the North-Sudetic Syncline and in Richelsdorf.

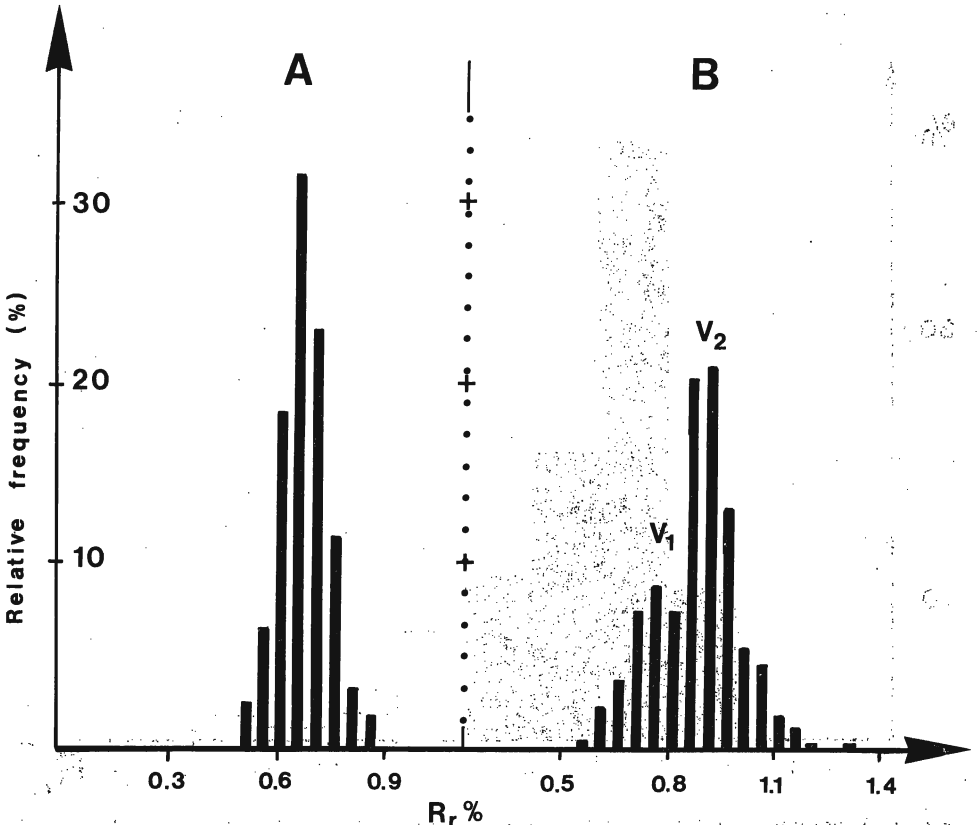


Fig. 7. Two prevailing types of reflectograms

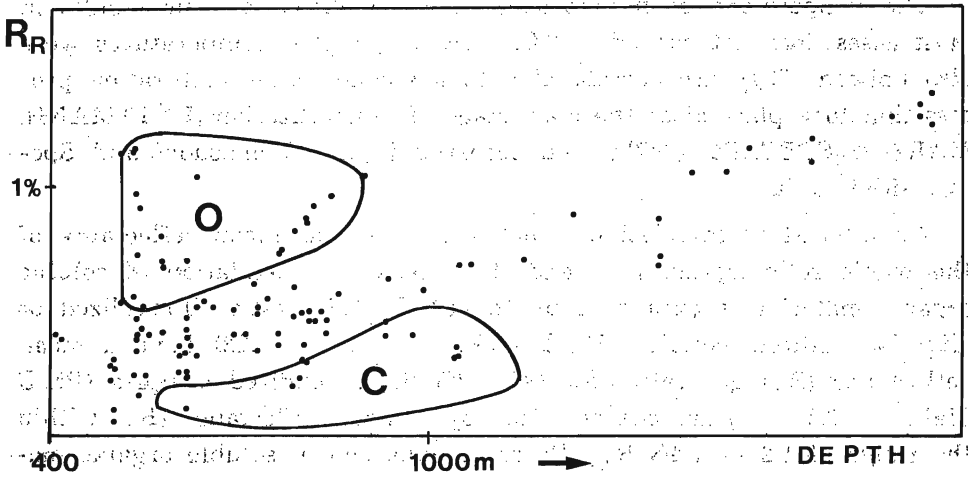


Fig. 8. Scatterogram illustrating a positive correlation between the depth of sample collection and random reflectance: C — samples with high content of soluble organic material, O — samples that reveal pronounced oxidation

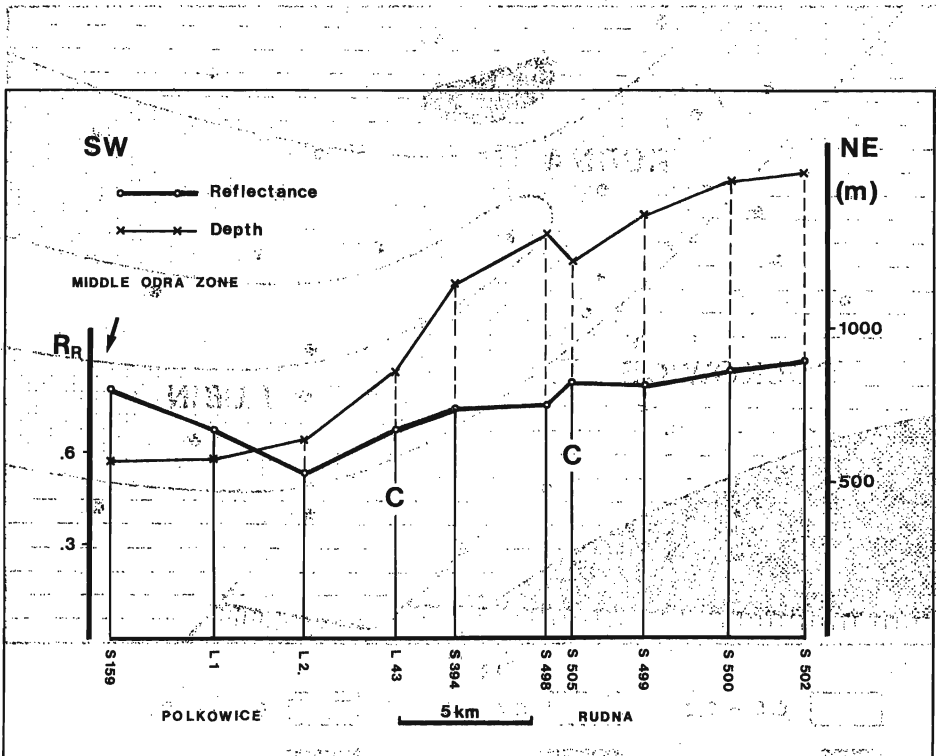


Fig. 9. Random vitrinite reflectance versus the depth of the Kupferschiefer samples plotted on the schematic cross-section through the ore fields of Polkowice and Rudna mines, Fore-Sudetic Monocline

The temperature of mineralizing fluids indicated by our results in most cases does not exceed 100°C. However, higher temperatures were also noticed. They are correlated with a second major maturation process that took place after the main stage of mineralization (PÜTTMANN, MARZ & SPECZIK 1987b), and occurred in the Richelsdorf and Spessart-Rhön areas.

An interesting correlation is noted between the mean reflectance of the whole reflectogram ( $R_w$ ) and the intensity of oxidation of soluble organic material as expressed by the  $Ph/\Sigma MePh$  ratio. Unoxidized or slightly oxidized samples ( $Ph/\Sigma MePh = 0.59 - 1.22$ ) have a mean reflectance ( $R_w$ ) generally low ( $< 1.2\% R_{oit}$ ). Oxidized samples ( $Ph/\Sigma MePh = 1.5 - 3$ ) are characterized by a mean reflectance ( $R_w$ ) within the range of 1.2 - 1.4%  $R_{oit}$ . Extreme oxidation of soluble organic material is manifested by a simultaneous increase of  $R_w$  up to 1.3 - 1.6%

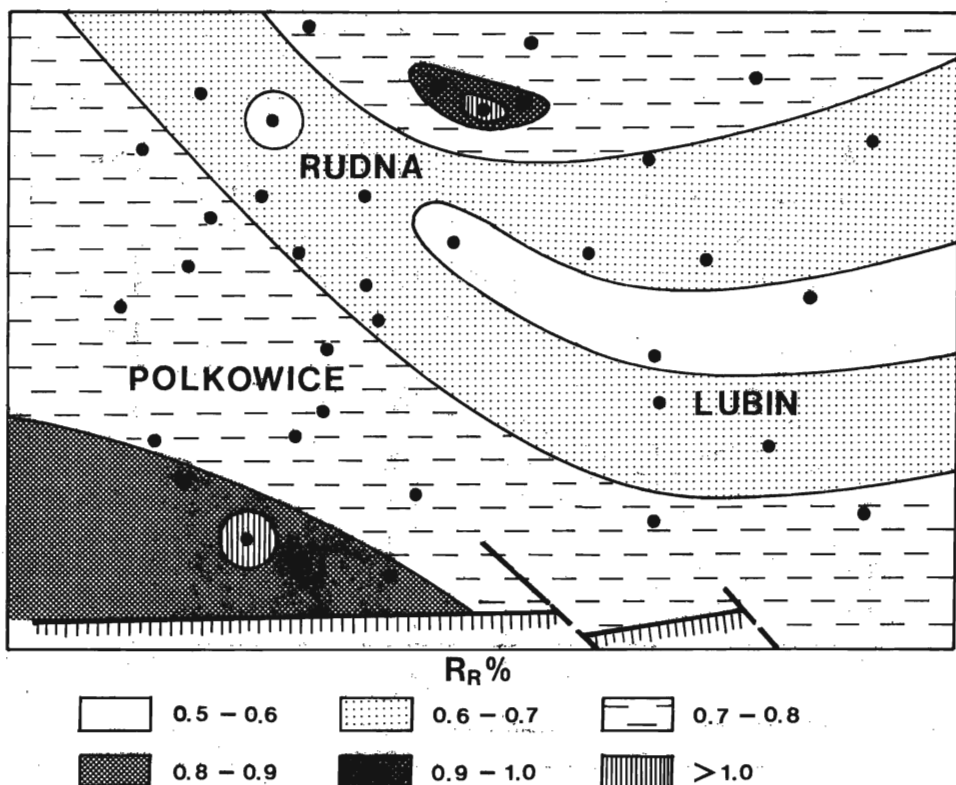


Fig. 10. Map of the vitrinite rank in the area of Lubin, Polkowice and Rudna mines: black dots mark positions of the investigated Kupferschiefer samples

$R_{oil}$ . This suggests that processes of inorganic oxidation of the soluble organic material have also affected (probably not with the same intensity) all available solid vitrinite macerals.

### FLUOROMETRIC ANALYSIS

(written by S. Speczik)

Qualitative spectral fluorescence observations were conducted on polished sections from the entire Kupferschiefer horizon. However, only about 25% of the samples contain liptinite group macerals in enough large quantities. It was already known that some macerals of the vitrinite group exhibit fluorescence, but the investigated vitrinite do not fluoresce.

The most plentiful component of liptinite macerals found is liptodetrinite, which is characteristic of coals that have been deposited under water. Liptodetrinite consists of fragments of degradation residues of spores, cuticles, resinous bodies, nannoplankton or algae. The finely detrital condition of the liptodetrinite prevent quantitative measurements. Other liptinite macerals recognized are alginite with minor sporinite, resinite, and cutinite. Cutinite is more typical of the near-shore facies of the Kupferschiefer (Kupfermergel).

Alginite is usually so compressed that the original cavities appear as a line, a stringer or a diffused band. In some sections, fan-like and hollow-sphere structures typical of alginite were observed. Alginite has a greenish to yellow, yellow-brown fluorescence that contrasts with the dark background of what consists mostly of collinite. It was reported by STACH (1982) that in carbonaceous shales (even of low rank) alginite is often transformed to vitrinite or inertinite. This factor can account for the lower than expected amount of alginite in this type of sediment. Both granular, rounded or flattened tetrahedral structures of miospores were found. A spongy structure may be seen on polished surfaces of some miospores which is attributed to a slight degradation before burial.

All of the investigated liptinite macerals exhibit a greenish, yellow to light orange (sporinite) colors under UV-beam light. This may suggest a low degree of maturity of the organic macerals that correspond to a 0.5 to 0.7 vitrinite random reflectance. The intensity of fluorescence and reflectance are inversely proportional, as the fluorescence decreases with increasing rank of vitrinite.

Quantitative fluorometric measurements were performed on eight polished sections and their corresponding extracts. The new analytical method proposed by HAGEMANN & HOLLERBACH (1981) was employed for the extracts. The shade of color of the extracts change with increasing rank (saturation) from blue to green, yellow, orange to red. A Zeiss-Microscope-Photometer MPM 01K coupled with HBO 100 mercury high pressure lamp as a light source were used. The continuous interference filter (grating-monochromator) with a 5nm interval over the spectral range from 400 to 700nm allowed to measure the intensities of fluorescence for the entire spectrum. The results were recorded by Packard Hewlett computer in the form of spectral distribution curves. The fluorescence spectra were corrected for different spectral responses including the objective, filters, chromatic beam splitter, photomultiplier and all electrical and optical parts that were used. Then

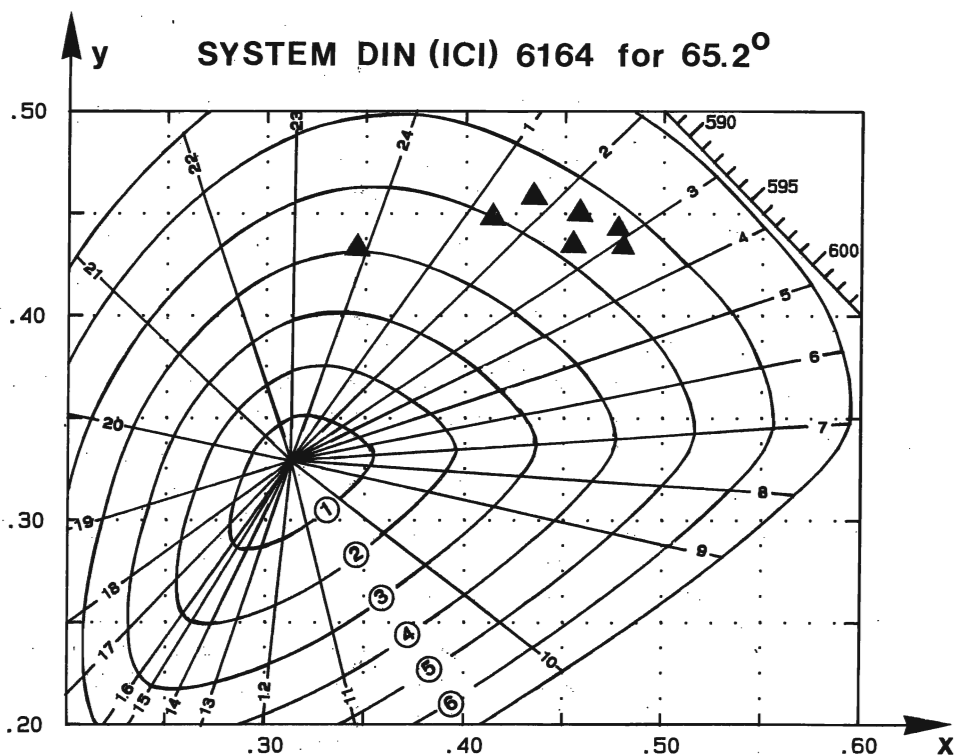


Fig. 11. Results of fluorometric measurements plotted on two-dimensional chromacity diagram (extracts)

the numerical parameters as red/green ratio ( $Q$ ), position of maximum spectrum ( $\lambda$ ), chromacity coefficients, etc. were calculated.

The results of fluorometric analysis confirm the vitrinite investigations. The results of extracts plotted on a two-dimensional chromacity diagram correlate with a measured vitrinite reflectance of 0.6 to 0.8% (Text-fig. 11). A good coherence exists also between the wave-length (as well as other numerical parameters) and the random reflectance with respect to the results obtained from the polished sections (Text-fig. 12).

The estimated amount of liptinite group macerals correlates with the intensity of oxidation as expressed by the  $Ph/\Sigma MePh$  ratio. Samples with abundant liptinite group macerals are characterized by a low  $Ph/\Sigma MePh$  ratio (between 0.6 to 1.2). The exception to this ratio is revealed by samples that have a very high content of organic carbon ( $C_{org} > 8\%$ ). They can display simultaneously a high  $Ph/\Sigma MePh$  ratio and a high content of liptinite macerals. The latter may be related to the large reducing potential and capacity of the euxinic sediments that are extremely rich in organic carbon.

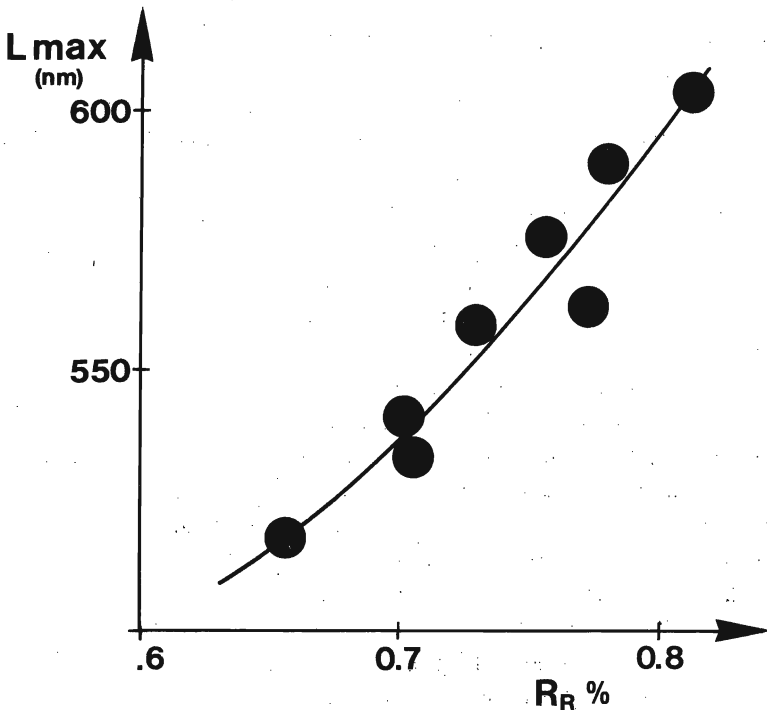


Fig. 12. Correlation between maximum wavelength and vitrinite reflectance (polished sections)

#### DISCUSSION

One of the most important aspects to be evaluated in our discussion is the nature of the oxidation processes affecting the soluble organic material. This effect is manifested by a decrease in the content of saturated hydrocarbons at the expense of heteroaromatic compounds, and partially by removal of organic carbon from the host rocks. The specific composition of this effect departs greatly from the previously known effects (*i. e.* meteoritic weathering, microbial and diagenetic degradation) and suggests the epigenetic oxidation of leachable organic material by oxidized and metal-rich solutions. The Kupferschiefer which is an organic rich sediment ( $\approx 5\%$  organic carbon) provides sufficient reducing potential to enable redox reactions, to take place when contacted by oxygenated metal bearing brines.

Symptoms of oxidation processes were also observed on solid organic material. Oxidation rims are generally thought to be products of heat during oxidation (ALPERN & MAUME 1969). However, the formation of oxidation rims depends not only on the temperature but also on the availability of oxygen (GOODARZI 1986). Chemically, vitrinite is composed of a variety of humins which consist of an aromatic nucleus sur-

rounded by peripheral aliphatic groups. They are hydrocarbons of microbial origin, chemically bonded (*i. e.* esters) to humic substances as well as lipid or bituminous material assimilated within vitrinite during diagenesis (chemisorbtion). With increasing rank the peripheral groups ( $\text{OH}^-$ ,  $\text{COOH}^-$ ,  $\text{CH}_3^-$ ) are lost and the aromatic nuclei become larger. At the same time the hydrogen and oxygen content decreases.

It is believed that the observed oxidation indices on organic particles can be linked to two different processes. The first process is weathering and natural oxidation of allochthonous or redeposited vitrinite. This process was responsible for the formation of the zonal structures and continuous oxidation rims observed for the most part on vitrinite grains from the near-shore environments (Kupfermergel). This oxidation is mostly a surface phenomenon. The second process, characterized by epigenetic oxidation, was caused by oxidized ore-bearing solutions that entered the Kupferschiefer horizon. It appears that oxidation of vitrinite and associated liptinite caused aromatization of aliphatic groups not only on the surface of the vitrinite particles, but affected the entire vitrinite structure. The same tendency of aromatization has already been reported with respect to soluble organic material. It is also known that an increase of aromaticity can result in reflectance increase of coal macerals (GOODARZI 1986). The influence of temperature of oxidized solutions on vitrinite rank as revealed by vitrinite measurements in some locations (*i. e.* paleohighs, major tectonic zones) can not be neglected,

In southwestern Poland the most intense oxidized sediments were found at the base of the Kupferschiefer horizon in contact with the underlying Rote Fäule facies. The increasing alteration of the bitumen towards the Rote Fäule facies suggests that the alteration was caused by ascending solutions (brines). As a result, alkanes which are molecules of high reducing potential are the first to be removed from the bitumen. The results confirm the findings of RENTZSCH (1974) who showed that the H/C ratio in the Kupferschiefer increases with increasing distance from the Rote Fäule facies.

The oxidation effects are not detectable in areas of low, syndiagenetic (mostly pyritic) mineralization in the Kupferschiefer horizon. In the Richelsdorf/Spessart-Rhön area the contribution of organic material oxidation to base metal precipitation is not manifested by organic geochemical analysis (PÜTTMANN, MARZ & SPECZIK 1987b). The high content of hopanes, steranes and diasterenes (compounds which are very sensitive to strong oxidation) in the bitumen of the Lower Rhine Basin indicate an absence of strong oxidizing conditions. This is consistent with the fact that the Rotliegendes sediment, as a potential source of oxidizing solutions, is absent in the Lower Rhine Basin.



The content of vanadium, nickel and chromium does not correlate with secondary oxidation parameters *i. e.*  $Ph/\Sigma MePh$  ratio and MPI-1 index. These metals are credibly of syngenetic origin, as suggested by WEDEPOHL (1964). The content of zinc, cobalt, copper and lead correlates well with the  $Ph/\Sigma MePh$  ratio (MERZ 1986). For this reason it is believed that base metal enrichment in the Kupferschiefer horizon of southwestern Poland occurred after early diagenesis of the sediment. When the  $Ph/\Sigma MePh$  ratio reaches about 1 economic concentrations of these metals are present, more intense oxidation of soluble organic material resulting in  $Ph/\Sigma MePh$  ratio greater than 3 correlates well with low base metal contents. This can be explained as resulting in acidification of the Kupferschiefer horizon. The solubility of metals increases with growing pH, and metals are transported to areas of lower oxidation (EUGSTER 1985).

In conclusion, we believe that oxidized and metal-bearing solutions (brines) governed the enrichment of Kupferschiefer sediments. The movement of solutions is related to major tectonic structures associated

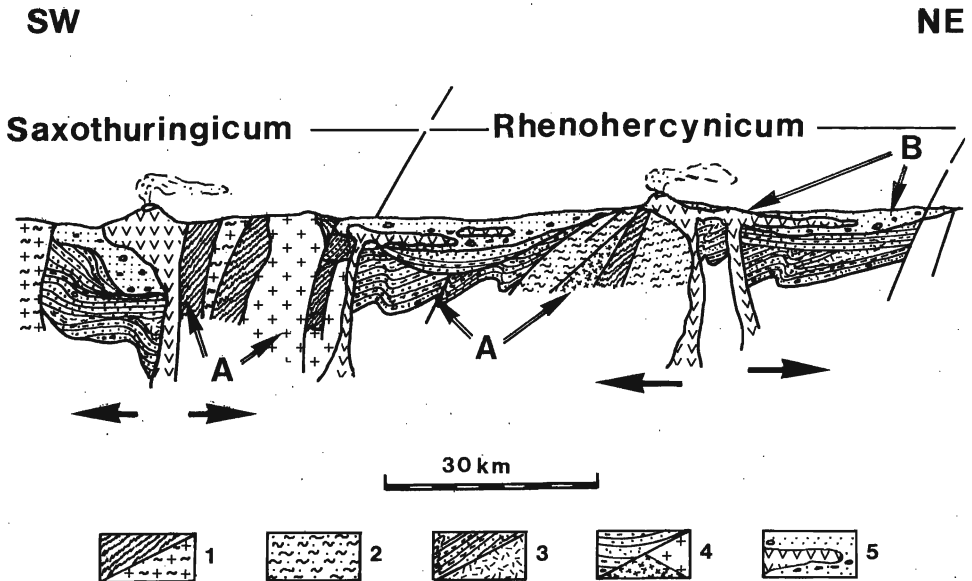


Fig. 13. Metallogeny and geologic development of the Fore-Sudetic Region in the Late Autunian

1 — Precambrian granitoids and metamorphic rocks, 2 — older Paleozoic epimetamorphic rocks, 3 — Lower Carboniferous flysch and basic extrusives, 4 — Upper Carboniferous molasse and intermediate to acid intrusives and extrusives, 5 — Lower Permian red bed sediments and volcanics

A — rocks of the first metal source: basic, intermediate and acid intrusives and extrusives, sedimentary and metamorphic rocks of different age from Precambrian to Carboniferous: B — rocks of the second metal source: Rotliegendes sediments and volcanics

with rift zones (Text-fig. 13). Two processes were responsible for a gradual base metal preconcentration in late Variscan time resulting in composite character of the observed mineralization (SPECZIK & *al.* 1986). Intraformational processes stimulated by a high paleogeothermal field of the Variscan externide belt evolved highly saline brines enriched in metals (the source suggested first). The brines were intermittently injected into and mixed with subsurface water of the Rotliegendes intramontane troughs (second source). Brines of regionally varying composition are believed to give rise to base metal occurrences of differing mineralogical composition and tenor in Central Europe.

Low-temperature, oxidizing ore-bearing solutions ascended through the epigenetic Rote Fäule zone, but were limited to these areas where hydraulic communication between subsurface waters and the Kupferschiefer bed existed. These areas are correlated with major tectonic zones and the Variscan paleohighs located along the border between the Saxothuringian and the Rhenohercynian zones of the Variscan externides. The Kupferschiefer horizon, acting as a geochemical hydrogen barrier was the site of redox-type reactions between ( $S^{-2}$ ,  $HS^{-}$ ) produced by microbial activity, hydrocarbons and base metals. Processes of reduction resulted in base metal precipitation while oxidation processes were occurring in hydrocarbon. Because of differences in the content and composition of the organic material as well as the composition of the oxidizing fluids elaborated, the reactions give rise to difference in the certain occurrences.

Metal leached from the Rotliegendes formation at the time of Kupferschiefer sedimentation resulted in a background syngenetic metal content throughout the basin. More metal was introduced during the Kupferschiefer diagenesis when low temperature brines ascended through the Rotliegendes. These two processes seem to be of major importance for ore-grade occurrences in southwestern Poland, but they are of lesser significance in the in Richelsdorf/Spessart-Rhön areas what is reflected by their low tenor. The mineralization in those areas is mostly influenced by a higher rank of maturation of the Kupferschiefer bed.

#### CONCLUDING REMARKS

Organic geochemical studies of soluble organic material as well as vitrinite and liptinite investigations have appeared to be a useful tool in studying the extent of maturation (oxidation) of organic material in the Kupferschiefer sediments. A positive correlation exist between the content and composition of organic material and processes of mineralization. Hence, these investigations provide a new insight into the pro-

blem of the origin of base metal mineralizations associated with organic-rich shales.

The organic material of the Kupferschiefer horizon in certain locations (i. e. border of Saxothuringian and Rhenohercynian zones in southwestern Poland) reveals inorganic oxidation effect. The spatial distribution of this effect and its position to the epigenetic Roté Fäule zone suggests an epigenetic base metal enrichment by ascending oxidizing solutions. These processes were facilitated by elevated heat flow related to the Variscan plate motion. The intensity of secondary oxidation of leachable organic material correlates well with the content of base metals in the Kupferschiefer horizon. The latter observation and a new distinguished oxidation parameter ( $Ph/\Sigma MePh$  ratio) could be used as a new tool in mineral exploration.

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**GENEZA MINERALIZACJI ŁUPKA MIEDZIONOŚNEGO  
W ŚWIETLE BADAŃ ORGANO-GEOCHEMICZNYCH I ANALIZY  
MACERAŁÓW WĘGLA**

(Streszczenie)

W rejonach intensywnej mineralizacji łupka miedzionośnego w obrębie formacji cechsztyńskiej Europy Środkowej rozpoznany został efekt epigenetycznego utleniania ekstrahowalnej substancji organicznej. Specyficzna kompozycja tego efektu wyróżnia go (patrz fig. 1—2) od wcześniej znanych ze środowiska geologicznego reakcji utleniania substancji organicznej (wietrzenia, bakteryjnej lub diagenetycznej degradacji). Zawartość metali ciężkich oraz intensywność oksydacji mierzona stosunkiem zawartości fenantrenu do sumy metylfenantrenów wzrasta w kierunku epigenetycznej facji Rote Fäule (patrz fig. 3—4). W obszarach zasadniczo niezmineralizowanych lub o słabej mineralizacji syndiagenetycznej efekt utleniania jest niedostrzegalny (patrz fig. 5).

Podobny efekt utleniania stałej substancji organicznej stwierdzony został badaniami wityrynytu i liptynytu (patrz fig. 6—9 oraz 11—12). Badania te, niezależnie od badań organo-geochemicznych, potwierdziły zasadniczo niski stopień dojrzałości rozpatrywanej substancji organicznej. Rozpoznano słabe anomalie gradientu termicznego w obrębie horyzontu łupka miedzionośnego. Anomalie te, zlokalizowane w pobliżu waryscyjskich paleowzniesień oraz głębokich rozłamów tektonicznych, korelują się przestrzennie z obszarami występowania mineralizacji typu złożowego (patrz fig. 10).

Wysunięto przypuszczenie, iż ascensyjne, utlenicze i zmineralizowane roztwory odpowiedzialne są za epigenetyczne wzbogacenie łupka miedzionośnego w obszarach odpowiadających głównym strefom tektonicznym (ryftowym). Łupek miedzionośny spełniał rolę geochemicznego ekranu zasobnego w  $HS^-$ , zaś ekran ten był miejscem reakcji red-ox, w wyniku których metale ciężkie ulegały redukcji (pre-cypitacji), a węglowodory utlenianiu (patrz fig. 13).