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Kupferschiefer mineralization in the light of organic geochemistry and coal petrology studies*

The paper provides evidence for the contribution of organic matter and its secondary oxidation to the mechanism of metal precipitation in the Permian Kupferschiefer formation of southwestern Poland. Both solid (kerogen) and soluble organic material reveal symptoms of epigenetic oxidation in certain areas of the Kupferschiefer formation that display ore-grade mineralization (Lubin – Sieroszowice and Konrad deposits). The specific composition of oxidation effects differs greatly from previously known oxidation effects of organic material. Thus, it is suggested, that oxidized metal-bearing solutions came into contact with hydrogen-rich Kupferschiefer in areas related to major tectonic zones and Variscan palaeohighs. The Kupferschiefer, acting as a geochemical trap for metal, was a site of redox-type reactions. The reduction processes resulted in base metal precipitation while oxidation affected the hydrocarbons. The Rote Fäule zones served as conduits for mostly ascending solutions. The horizontal distribution pattern of the oxidation marking compounds in the Kupferschiefer formation implies that the oxidation of organic material, and therefore mineralization, most likely occurred during late diagenesis or even early catagenesis.

INTRODUCTION

The debate about the origin of the strata bound deposits associated with black shales e.g. Kupferschiefer of Central Europe has continued for more than 50 years. Although these deposits show many similarites, individual authors principally emphasize other aspects of their origin based on their own experience gained mostly from ore-grade areas of Kupferschiefer formation. The author believe that the emplacement and formation of these deposits were governed by one major process with minor variations depending upon geological, geochemical, and other related parameters. To find new data that can support this idea an effort has been made to compare the Kupferschiefer in the areas that are recognized as of ore-grade mineralization with those where mineralization is absent by means of various aspects of their petrographical, mineralogical, and geochemical composition, geological setting etc.

Some parameters, mostly structural, that controlled the mineralization are already known e.g. the preferential location of ore-grade occurrences on the border of Rhenohercynian and Saxothuringian belts, their correlation to the shore-line (in some locations), to the Rote Fäule facies, and above all to the position of Zechstein sea palaeohighs (J. Rentzsch, 1974; S. Speczik *et al.*, 1986; D. J. Voughan *et al.*, 1989). However, not much is known about the mineralogical and geochemical differences between the Kupferschiefer of ore-grade and barren areas. The mentioned comparative studies revealed that Kupferschiefer shales (marls) of the barren and mineralized areas are with some polarietis and exceptions generally the same. The most important differences are the occurrence of base metal mineralization and the rank and composition of organic matter.

The role of organic matter in black shale typ ore mineralization has been discussed in more than a hundred papers (e.g. J. D. Saxby, 1976; T. H. Giordano, 1985; H. P. Eugster, 1985). Various primary and secondary mechanisms that involved the contribution of organic matter in metal accumulation and precipitation have been suggested. Also the problem of organic matter in the Kupferschiefer and correlation of S^{2-} to metal content have gained the attention of many scientists (e.g. C. Harańczyk, 1972; J. Rentzsch, 1974).

The Kupferschiefer of Central Europe has an average organic carbon content of 5%. In investigated samples it varies from 0.5 to 14%, average from 1.5 to 8%. The amount of soluble organic material (bituminen) in the examined samples varies from 60 to 6400 ppm. The most plentiful component of organic macerals in both ore-grade and barren Kupferschiefer rocks is variably bituminous and in places oxidized vitrinite. Liptinite (alginite) dominantes in places that have a high soluble organic material content, while in near-shore environments allochthonous inertinate prevails over the vitrinite and liptinite. Because of the kerogen composition, coal petrology investigations by optical means and simultaneous vitrinite reflectance determinations, supported by a limited number of quantitative fluorometric measurements, were the most common methods used in this study.

Organic geochemical studies were primarily conducted to assess the calculated vitrinite rank using compounds termed chemical fossils or geolipids (B. M. Didyk *et al.*, 1978) and to indicate palaeoenvironmental conditions during sedimentation. Their second aim was to determine detailed chemical characteristic of soluble organic material in ore-grade and barren areas of the Kupferschiefer. The later investigations yielded very interesting results, important for genetic discussion. The samples used in this investigation come either from cores, mine profiles or surface exposures situated in the North-Sudetic Syncline and Fore-Sudetic Monocline (southwestern Poland). A detailed analytical procedure for organic geochemical studies is described by W. Püttmann *et al.* (1987), while the coal petrology methods employed are presented by S. Speczik and W. Püttmann (1987).

COAL PETROLOGY STUDIES

Kerogen in the Kupferschiefer horizon forms a complicated and dense network composed of horizontal plus minor vertical stringers, as well as thin layers and pseudoveinlets composed mostly of bituminite (Pl. I, Fig. 1) with minor virtinite (collinite) and liptinite. Structurless collinite contains minor tellinite cells filled with collinite and liptinite group macerals. Kerogen of more distant facies (Kupferschiefer shale), in contrast with its near-shore equivalent (Kupfermergel), is variously impregnated and cemented with liptinite macerals, and at some places even contains strongly fluorescing liquid expulsions. The texture, form and petrographic character of kerogen suggests that it was mostly derived from algae-type material, with bitumen trapped in ultra-fine pores of vitrinite.

Vitrinite and liptinite group macerals which are associated with Kupferschiefer containing ore-grade mineralization (Pl. I, Fig. 2) reveal patchy textures, rims and smear films along grain edges having differences in refractive index and colour. These textures are thought to result from a secondary oxidation that took place after vitrinitization. Reflectograms for this type of vitrinite have an irregular or even bimodal distribution pattern reflecting its variable degree of oxidation. Vitrinites which are associated with barren facies of the Kupferschiefer prinicipally display reflectograms with regular distribution patterns. The vitrinite random reflectances in the greater part of the investigated area are generally low, at some places even lower than expected. There is also a general correlation between the depth of sample collection and vitrinite reflectance, except for samples that reveal pronounced symptoms of oxidation of organic material or have an extremely high hydrogen content (S. Speczik, W. Püttmann, 1987). It is probable that the hydrogen enrichment in kerogen of the Rudna – Sieroszowice area, characterized by its strongly anoxic milieu, caused lower vitrinite reflectance.

The location of the ore-grade occurrences in the Kupferschiefer horizon correlates well with low-rank vitrinite anomalies that are encountered in the geothermal field of the Kupferschiefer formation. In the southern part of the Fore-Sudetic Monocline these anomalies also relate to high rank anomalies earlier recognized in the Carboniferous basement (S. Speczik *et al.*, 1986), and locally to the position of the shore-line and the Zechstein sea palaeohighs (Fig. 1).

It is generally thought that the degree of coalification (vitrinite rank) depends mainly on the maximum temperature and to a minor degree on the "effective" heating time (M. Teichmüller, 1987). No important role is attached to such factors as pH, Eh, pore fluid composition and partial pressure of water. Chemically, the rank of vitrinite is related to the degree of aromatization of the humic complexes of coal (F. Goodarzi, 1986). The results of this investigation suggest that the temperature and also chemical influence of the process of epigenetic oxidation of vitrinite elevate its rank . It is envisaged that humic substances and lipoid or bituminous material assimilated within vitrinite during chemisorption were subject to oxidation catalyzed by a high base metal content in pore water. With low degree of oxidation the aliphatic peripheral groups were lost only on the surface of vitrinite particles, while intensive oxidation affected the entire kerogen structure composed of vitrinite and liptinite.

The influence of elevated temperature and tectonic stress in some locations (palaeohighs, major shear zones) may be also important. In the tectonically crumpled pitchy shales of the Rudna and Polkowice mines the optical character of vitrinite is changed to a bi-axial positive geometry. Elevated heat conductivity, and therefore a higher geothermal gradient in the strongly disturbed Odra and Dolsk deep fracture zones finds its manifestation on the Kupferschiefer vitrinite rank map of southwestern Poland (S. Speczik, W. Püttmann, 1987). The importance of coalification studies for tectonic and palaeogeothermal studies have already been stressed by many authors (e.g. R. M. Bustin, 1986; M. Teichmüller, 1987). The time factor can be neglected as it was found that in liquid dominated (hydrothermal)

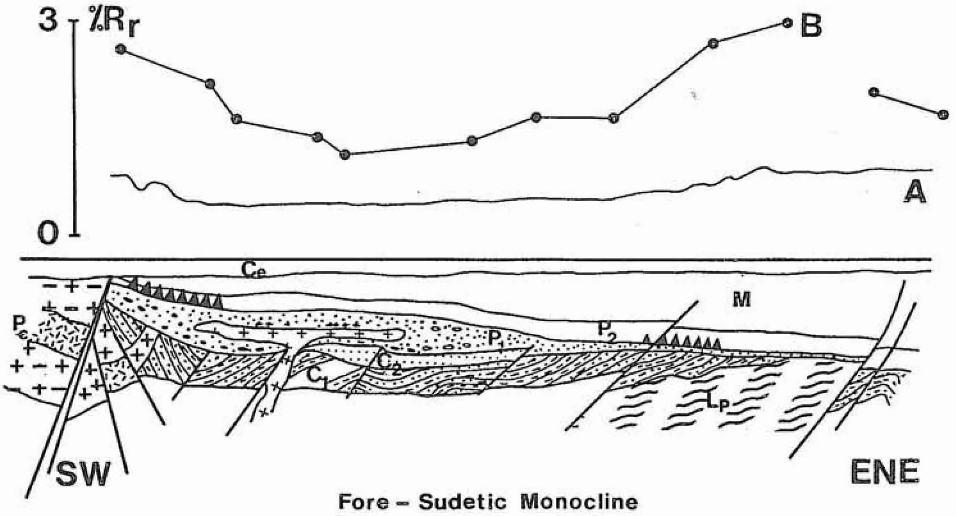

Fig. 1. Geologic cross-section trough the southern part of Fore-Sudetic Monocline

A — vitrinite rank of Kupferschiefer formation; B — vitrinite rank of the Carboniferous basement; P_{ϵ} — Precambrian, L_p — Lower Palaeozoic, C_1, C_2 — Lower and Upper Carboniferous, P_1, P_2 — Lower and Upper Zechstein, M — Mesozoic, C_e — Cenozoic; black triangles marking position of ore-grade occurrences

Geologiczny przekrój przez południową część monokliny przedsudeckiej

A — rank witrinitu z poziomu łupku miedzionośnego; B — rank witrinitu podłoża karbońskiego; P_{ϵ} — prekambr, L_p — dolny paleozoik, C_1, C_2 — dolny i górny karbon, P_1, P_2 — dolny i górny cechsztyn, M — mezozoik, C_e — kenozoik; czarne trójkąty pokazują lokalizację mineralizacji złożowej

systems a duration of 10 000 years is sufficient for the stabilization of organic matter (C. E. Barker, 1983).

The liptinite macerals have greenish, yellow and sporadically light orange (sporinite) colours under UV-excited luminescence (Pl. II; Figs. 1, 2). This may suggest a low degree of maturity of liptinite macerals which corresponds to vitrinite random reflectance ranging from 0.5 to 0.7%. There is also a good correlation between fluorometric parameters (i.e. red/green ratio — *Q*, wavelength, position of maximum spectrum), and vitrinite random reflectance (S. Speczik, W. Püttmann, 1987). Moreover, the maximum intensity of the fluorescence spectra is shifted to shorter wavelengths in samples approaching the Rote Fäule zone, which causes the increase of fluorescence intensities in the same direction (W. Püttmann *et al.*, 1987). The green shift of fluorescence maxima is recognized as an oxidation parameter.

ORGANIC GEOCHEMICAL STUDIES

Detailed results of organic geochemical studies were presented by S. Speczik, W. Püttmann (1987). Thus, in this paper only maturity parameters and the correlation between coal petrology and organic geochemical studies will be emphasized.

Soluble organic compounds that associate with oxidized solid organic matter reveal even more pronounced symptoms of oxidation. Saturated hydrocarbons and alkyled aromatic compounds are significantly depleted in comparison to non-altered shale samples of a similar maturation. Instead, unsubstituted di- and tricyclic aromatic hydrocarbons are the dominant components of the extractable bitumen. Additionally, polycyclic aromatic hydrocarbons (PAH) associated with polycyclic aromatic sulphur hydrocarbons (PASH) are common in some samples. The latter are considered to have originated from the underlying basement and were carried up to the Kupferschiefer horizon in post-depositional time (W. Püttmann, W. Göbel, 1990). The specific chemical composition of oxidation effect of soluble organic material differs greatly from previously known oxidation effects (in geological environments) and confirms the presumption that the observed changes in microscopic properties of vitrinite and liptinite macerals may be related to inorganic oxidation processes. Organic geochemical parameters (in ore-grade regions) that could be related to vitrinite random reflectance (i.e. pristane/phytane, hopane/moretane ratios, CPI-index) contribute no information about the maturity of organic matter because of the influence of the oxidation processes. The samples that reveal distinct differences in aromatic composition have similar pristane/phytane ratios. This suggests that these chemofossils were affected equally by secondary oxidation during later stages of diagenesis. In some less oxidized samples moretanes can be recognized. The C_{30}moretane/C_{30}hopane ratio of 0.35 to 0.45 point to a low degree of maturation of organic material.

It was found that the ratio of phenanthrenes to sum of metylphenanthrenes (Ph/ΣMePh) provides a measure for the intensity of alteration. Unoxidized or slightly oxidized samples (Ph/ΣMePh = 0.6–1.2) have a mean reflectance of whole reflectogram (R_w) which is generally low, within the range 0.5 to 0.8% R_{oil}. Oxidized samples (Ph/ΣMePh = 1.5–3.0) are characterized by mean reflectance (R_w) from 1.0 to 1.4% R_{oil}. Pronounced oxidation of soluble organic material is manifested by an accompanying increase of R_w up to 1.6% R_{oil}. The corresponding random vitrinite reflectance R_r only slightly increases (Fig. 2).

The intensity of oxidation effects increases towards the oxidized epigenetic Rote Fäule facies, whereas the base metal content decreases in the same direction. In the Kupferschiefer horizontal section the content of the oxidation indicating-compounds increases from the top to the bottom. The most oxidized horizon is at the base of the Kupferschiefer, which may suggest an ascending movement of oxidized solutions. The composition and distribution pattern of oxidized compounds in the lower part of the Kupferschiefer, relative to its upper part suggest that oxidation of the Kupferschiefer most likely occurred during late diagenesis and early catagenesis. Similar observations supporting the post-diagenetic origin of ore-grade mineralization come from recent stable isotope studies (A. Bechtel, W. Püttmann, 1992; A. Bechtel, S. Hoernes, 1993).

Oxidation effects were not detected in regions of the Kupferschiefer without ore-grade mineralization. The composition of soluble organic material in samples of these regions is typical of a common diagenetic evolution. The pristane/phytane and moretane ratios here allow us to confirm the earlier measured vitrinite reflectance values (S. Speczik, W. Püttmann, 1987).

GENETIC MODEL

Opinions may vary as to which parameters are more meaningful in discussion on the origin of base metal deposits associated with the black shales. It is suggested that the four most important parameters are: the source of metal, the mode of metal transport, the mechanism of metal emplacement and precipitation, and the time of deposition.

The source of metal — our results generally confirm a two — or multi-source, composite character of the metal provenance suggested by S. Speczik *et al.* (1986), H. Kucha (1986), and D. J. Voughan *et al.* (1989). These concepts best explain the differences in composition and the tenor of mineralization in particular deposits/locations. It is envisaged that the first source is connected with the evolution of the Rotliegendes sediments and brines as well as with the deposition of the Kupferschiefer shales/marls on top of the red-bed section. It resulted partly in the syngenetic, background (mostly pyritic) mineralization observed elsewhere in the Kupferschiefer formation of Central Europe. The second source with abrupt variations in the composition and tenor is related to intraformational processes in the intimately associated basement that evolved oxidized, saline and metal rich-brines. This source was not uniform and the Kupferschiefer horizon was fed by brines of different composition from regionally separated sources. The divergent plate movement during the post-Variscan and related elevated heat flow promoted processes of metal mobilization (S. Speczik, 1993).

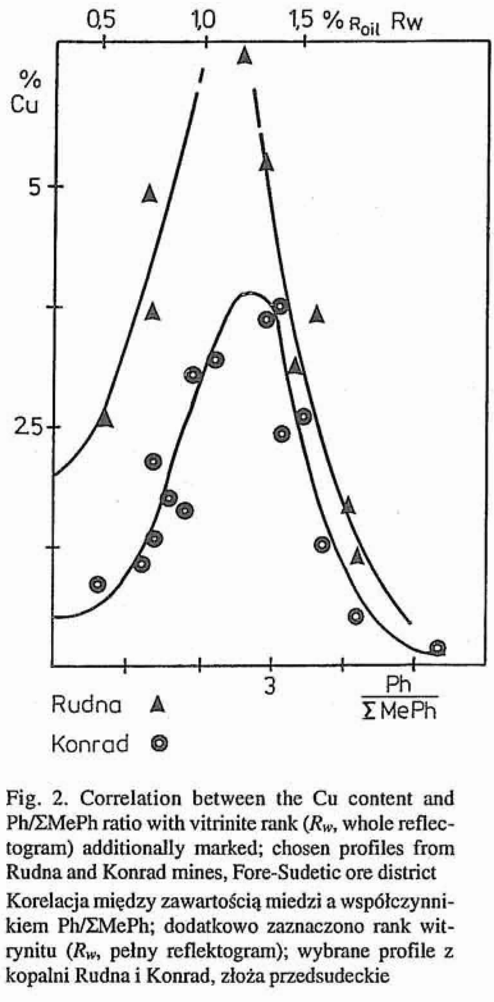

Fig. 2. Correlation between the Cu content and Ph/ΣMePh ratio with vitrinite rank (R_w, whole reflectogram) additionally marked; chosen profiles from Rudna and Konrad mines, Fore-Sudetic ore district

Korelacja między zawartością miedzi a współczynnikiem Ph/ΣMePh; dodatkowo zaznaczono rank witrynitu (R_w, pełny reflektogram); wybrane profile z kopalni Rudna i Konrad, złoża przedsudeckie

The mode of transport — both the results of the fluorometric and organic geochemical studies suggest an ascending character of oxidized solutions (the source suggested second). The solutions ascended through the epigenetic Rote Fäule zones in the areas where palaeohydrological regime allowed the hydraulic communication between the subsurface water and the Kupferschiefer. It is believed that oxidized solutions had an increased base metal content. The redistribution of syndiagenetic mineralization with subsequent relocation and reconcentration (on a large scale) by oxidized solutions seems to be highly improbable, as background and ore-grade mineralizations have principally different element composition. It is possible that epigenetic solutions had an appreciable content of bitumens which may have acted as important complexing agent.

The mechanism of metal precipitation — an oxidation effect of solid and soluble organic matter, and its general correlation with base metal distribution confirm the concept of the Kupferschiefer acting as a geochemical hydrogen-sulphide barrier for ascending solutions. The hydrogen-rich Kupferschiefer probably had enough reducing equivalents to be a site of redox-type reactions between (S^{2-}, HS^{-})(of biogenic origin) hydrocarbons and oxygen rich metal solutions. The processes of reduction governed metal emplacement while oxidation changed the composition and state of organic matter. The validity of this concept has been recently challenged by W. Püttmann *et al.* (1990) who suggested that thermocatalitic production of sulphide sulphur may have played an important role in areas of ore-grade mineralization. Despite this, in the later concept the organic matter remains important as a reducing agent and proton donor.

The time of mineralization — the first source contributed metals during sedimentation and early diagenesis of the Kupferschiefer formation. The second source, responsible for ore-grade mineralization, was active after kerogen reached a certain maturity stage during its diagenetic evolution.

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REFERENCES

BARKER C. E. (1983) — Influence of time on metamorphism of sedimentary organic matter in liquid-dominanted geothermal systems, western North America. Geology, **11**, p. 384–388.

BECHTEL A., PÜTTMANN W. (1992) — Combined isotopic biomarker investigations of temperature- and facies- dependent variations in the Kupferschiefer of the Lower Rhine Basin. Chem. Geol., **102**, p. 23–40.

BECHTEL A., HOERNES S. (1993) — Stable isotopic variations of clay minerals: A key to the understanding of Kupferschiefer-type mineralization, Germany. Geochim. Cosmochim. Acta, **57**, p. 1799–1816.

BUSTIN R. M. (1986) — Organic maturity of Late Cretaceous and Tertiary measures, Canadian Arctic Archipelago. Int. J. Coal Geology, **6**, p. 71–106.

DIDYK B. M., SIMONEIT B. R., BRASSEL S. C., ELINGTON G. (1978) — Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature, no. 272, p. 216–222.

EUGSTER H. P. (1985) — Oil shales, evaporites and ore deposits. Geochim. Cosmochim. Acta, **49**, p. 619–635.

GIORDANO T. H. (1985) — A preliminary evaluation of organic ligands and metal-organic complexing in Mississippi Valley-type ore solutions. Econ. Geol., **80**, p. 96–106.

GOODARZI F. (1986) — Optical properties of oxidized resinite. Fuel, no. 66, p. 260–265.

HARAŃCZYK C. (1972) — Ore mineralization of the Lower Zechstein euxinic sediments in the Fore-Sudetic Monocline (in Polish with English summary). Arch. Miner., **30**, p. 13–173, no. 1–2.

KUCHA H. (1986) — Two brine model of the genesis of strata-bound Zechstein deposits (Kupferschiefer type), Poland. Miner. Deposita, **21**, p. 70–80.

PÜTTMANN W., GÖBEL W. (1990) — The Permian Kupferschiefer of southwestern Poland: a geochemical trap for migrating, metal-bearing solutions. Appl. Geochem., **5**, p. 227—235.

PÜTTMANN W., HAGEMANN H. W., MERZ C., SPECZIK S. (1987) — Influence of organic material on mineralization processes in the Permian Kupferschiefer formation, Poland. Org. Geochem., **13**, p. 357–363, no. 1–3.

PÜTTMANN W., HEPPENHEMER H., DIEDEL R. (1990) — Accumulation of copper in the Permian Kupferschiefer: A result of post-depositional redox reactions. Org. Geochem., **16**, p. 1145–1156, no. 5–6.

RENTZSCH J. (1974) — The Kupferschiefer in comparison with the deposits of the Zambian Copperbelt. Cent. Soc. Geol. Belg., p. 395–413.

SAXBY J. D. (1976) — The significance of organic matter in ore genesis. In: Handbook of strata-bound and stratiform ore (ed. K. H. Wolf), p. 11–133. Elsevier, Amsterdam.

SPECZIK S. (1993) — The origin of Kupferschiefer mineralization in the Variscan Fold Belt of southwestern Poland. In: Rhenohercynian and Subvariscan Fold Belts (ed. R. A. Gayer, O. Greling, K. Vogiel), p. 369–383. Vieweg, Wiesbaden.

SPECZIK S., PÜTTMANN W. (1987) — Origin of Kupferschiefer mineralization as suggested by coal petrology and organic geochemical studies. Acta Geol. Pol., **37**, p. 167–187, no. 3–4.

SPECZIK S., SKOWRONEK C., FRIEDRICH G., DIEDEL R., SCHUMACHER C., SCHMIDT F. -P. (1986) — The environment of generation of some base metal Zechstein occurrences in Central Europe. Acta Geol. Pol., **36**, p. 1–35, no. 1–3.

TEICHMÜLLER M. (1987) — Recent advances in coalification studies and their application to geology. In: Coal and coal-bearing strata: recent advances (ed. A. C. Scott). Geol. Soc. Spec. Publ., **32**, p. 127–169.

VAUGHAN D. J., SWEENEY A., FRIEDRICH G., DIEDEL R., HARAŃCZYK C. (1989) — The Kupferschiefer: An overview with an apprisal of different types of mineralization. Econ. Geol., **84**, p. 1003–1027.

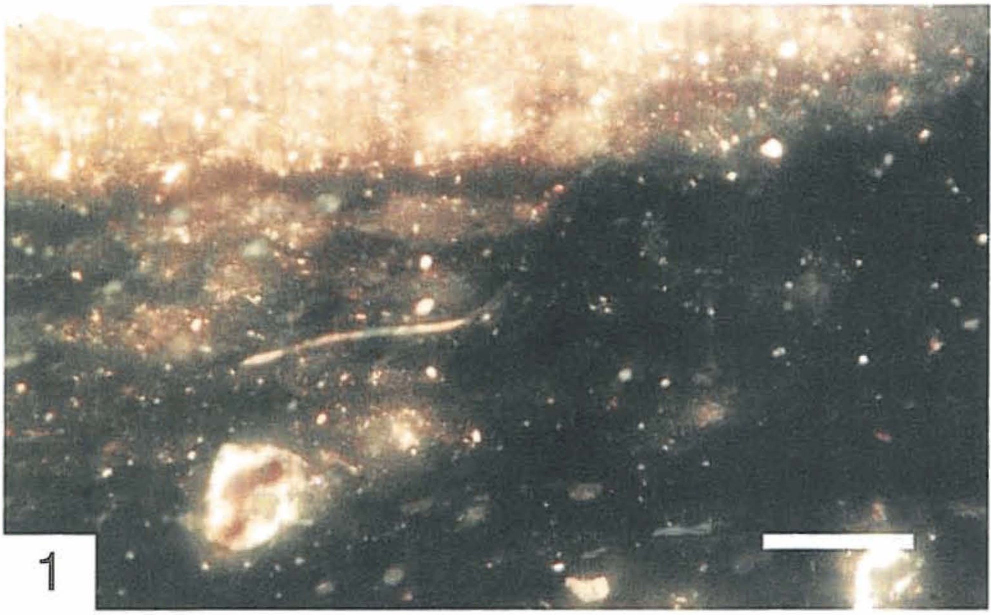
Stanisław SPECZIK

GENEZA ŁUPKÓW MIEDZIONOŚNYCH W ŚWIETLE BADAŃ ORGANO-GEOCHEMICZNYCH I PETROLOGII WĘGLA

Streszczenie

Przedstawiono dowody na udział w procesie precypitacji metali ciężkich materii organicznej, zawartej w łupku miedzionośnym. Zarówno stała materia organiczna (kerogen), jak i rozpuszczalna (bitumen) noszą symptomy epigenetycznej oksydacji w strefach mineralizacji złożowej (fig. 1 i 2; tabl. I i II). W strefach płonnych efektów tej oksydacji nie rozpoznano. Specyficzna kompozycja związków organicznych wskazujących na epigenetyczne utlenienie różni się od wcześniej znanych efektów oksydacji, takich jak biodegradacja, utlenienie meteoryczne czy też wymywanie wodne (*water washing effect*).

Powyższe obserwacje sugerują, że zoksydowane i zmineralizowane roztwory znalazły się w kontakcie z zasobnym w wodór horyzontem łupku miedzionośnego w rejonach bliskich kontaktowi między strefą saksońsko-turyngską i reńsko-hercyńską, w szczególności w pobliżu waryscyjskich paleowzniesień. Łupek miedzionośny spełniał tu rolę geochemicznej pułapki dla migrujących fluidów i był miejscem reakcji typu redox. Proces redukcji zaowocował precypitacją metali ciężkich, podczas gdy oksydacja dotyczyła materii organicznej w skale. Dystrybucja horyzontalna związków składających się na efekt oksydacji w łupku miedzionośnym sugeruje wznoszący charakter fluidów. Analiza składu rozpuszczonych bituminów wskazuje nadto, że oksydacja, a co za tym idzie mineralizacja typu złożowego, zdarzyły się już po osiągnięciu przez materię organiczną pewnego poziomu dojrzałości, odpowiadającego późnej diagenezie. Mamy tu zatem do czynienia z endogenicznym, postdiagenetycznym typem mineralizacji.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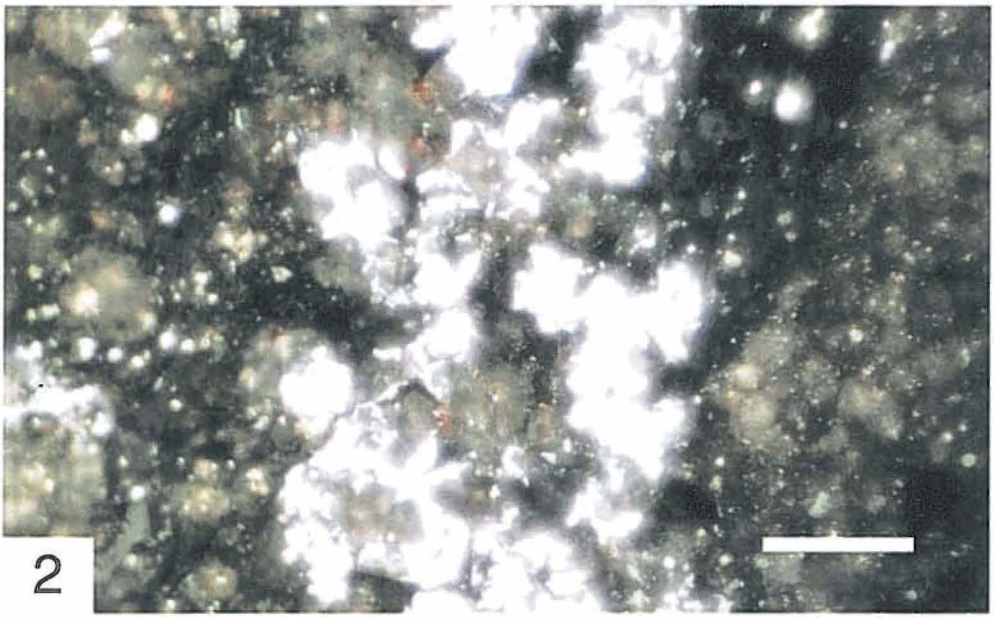
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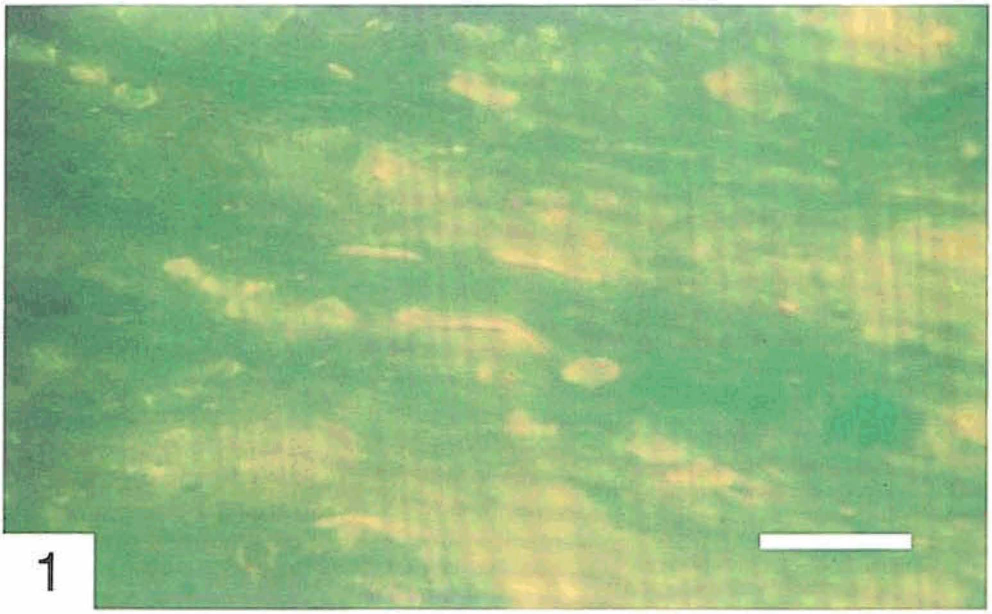
Stanisław SPECZIK — Kupferschiefer mineralization in the light of organic geochemistry and coal petrology studies

PLATE I

Fig. 1. Bituminite in border dolomite, Polkowice mine. Depth 466.0 m. Reflected light. Scale bar 1 mm
Bituminit z dolomitu granicznego, kopalnia Polkowice. Głębokość 466,0 m. Światło odbite. Skala 1 mm

Fig. 2. Vitrinite-liptinite network, associated with ore-grade mineralization, Polkowice mine. Depth 466.2 m. Reflected light. Scale bar 1 mm
Siateczka witrynitowo-liptynitowa w zmineralizowanym łupku, kopalnia Polkowice. Głębokość 466,2 m. Światło odbite. Skala 1 mm



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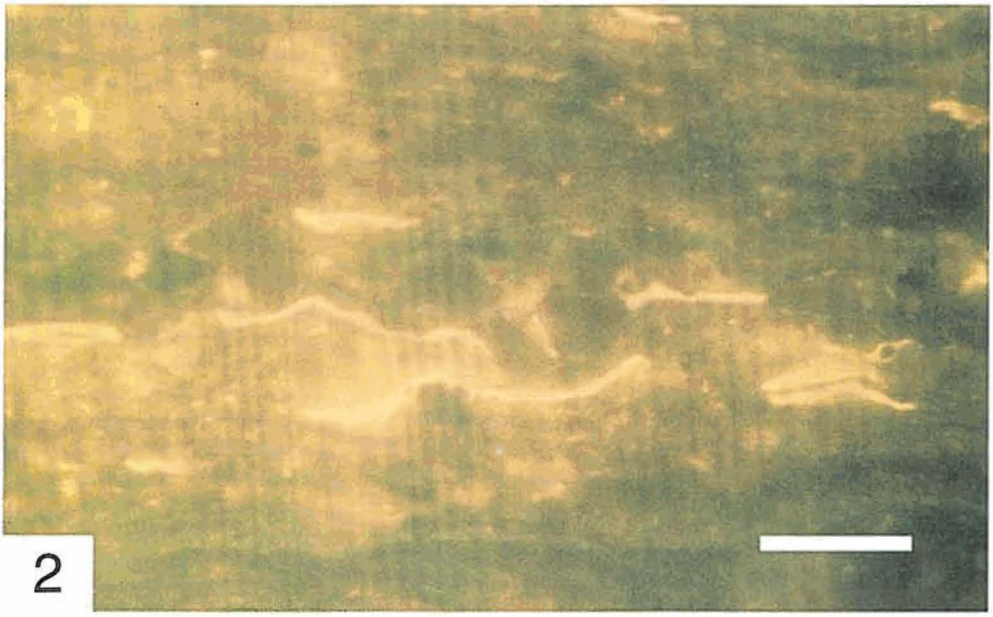

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PLATE II

Fig. 1. Weekly fluorescing, greenish liptynite of Lubin mine. UV-beam light. Depth 616.0 m. Scale bar 10 μm
Słabo fluoryzujący, zielonawy liptynit z kopalni Lubin. Ultrafiolet. Głębokość 616,0 m. Skala 10 μm
Fig. 2. Strongly fluorescing, yellow liptynite of Rudna mine. UV-beam light. Depth 950.0 m. Scale bar 10 μm
Mocno fluoryzujący, żółty liptynit z kopalni Rudna. Ultrafiolet. Głębokość 950,0 m. Skala 10 μm