

THE ORIGIN OF ORGANIC MATTER IN LOWER SILESIAN COPPER-BEARING SHALES

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A b s t r a c t: Stratified Lower Silesian copper deposits, similar to other deposits of this type, are enriched in organic matter. Microscope analyses of this substance occurring in the examined lithofacies of copper-bearing shales indicate that this organic material consists predominantly of structureless organic debris. Recognizable organic debris (vascular bundle, wood remains and palynomorphs) occur in subordinate amounts. The estimation of chemical nature of the quantitatively dominant but microscopically unidentifiable organic matter at the molecular level, was carried out using gas capillary chromatographic analysis of the pyrolysis products of kerogen Py(610°C)-GC. Kerogen occurring in the copper-bearing shales consists of aliphatic macromolecules (n-alkanes and n-alk-1-enes were identified among the pyrolysis products). Thus composition is characteristic for biopolymers which are highly resistant to (bio)chemical degradation occurring in algae (algaenan) and protective envelopes of higher plants (suberan and cutan). However, since no such tissues were encountered microscopically, organic matter must be derived from marine algae.

The presence of thiophene structural units in kerogen indicates anaerobic (H₂S) conditions in the sedimentous environment. When compared with other types of organic material, the structureless organic matter is enriched in metal sulphides. The sulphides are directly bound to structureless organic matter and occur as framboids. Organic matter is enveloping the sulphide concentrations. This indicates the important role of this organic matter in framboid formation by the isolation of precipitated iron sulphide phases from sedimentation environment and protection of these sulphides from replacement by copper sulphides due to action of Cu-bearing solutions.

Key words: copper-bearing shales, kerogen, Py-GC, highly aliphatic biopolymer, algaenan, framboids.

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INTRODUCTION

The present studies deal with the organic matter occurring in the Zechstein copper-bearing shales (Kupferschiefer) from the Lower Silesian copper deposits, SW Poland. This German term "Kupferschiefer" implies very thin, stratified sulphide-bearing series, occurring between Rotliegendes continental

facies (Lower Permian) and transgressive, usually carbonate Zechstein sediments (Upper Permian). A detailed description of this geological setting is presented e.g. by Oszczepalski (1986).

Geochemical studies of organic matter from the Sudetic Monocline were carried out by Sawłowicz (1991) who also reviewed earlier publications on this subject. On the other hand, Püttmann *et al.* (1990) have examined mainly extractable organic matter (EOM) from the North Sudetic Syncline. Both authors are emphasizing secondary alterations, first of all oxidation, of organic matter and its potential reducing role in the origin of the deposit. However, these investigations did not lead to the definitive determination of biological precursors of this organic matter, the origin of which is generally considered to be sapropelic (Harańczyk, 1986).

The aim of this study was to identify organic remains from the copper-bearing shales and to determine the relationship between the occurrence of individual macerals (organic matter types) and the presence of sulphides entrapped within organic matter. To solve these issue, two weight fractions of organic matter, separated in heavy liquid, were subjected to microscope examination in transmittant light and the morphology of individual grains was studied using scanning microscopy (SEM).

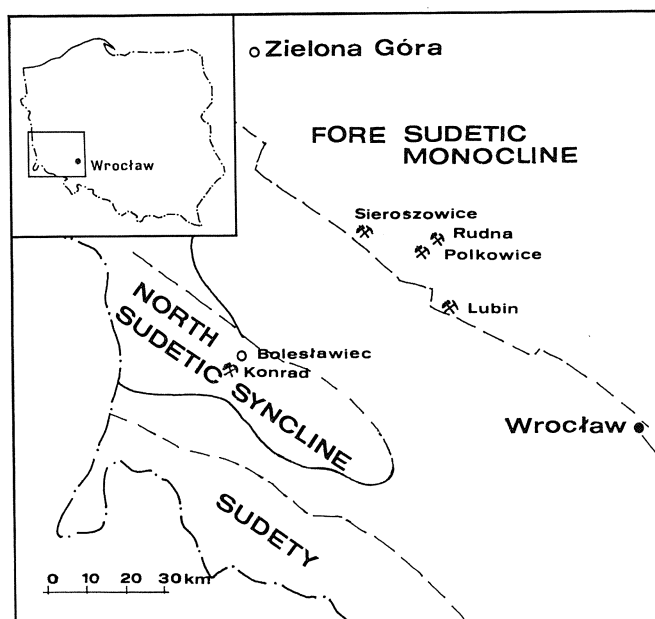
Since complete identification of organic remains was impossible using only the microscopic method, seven representative samples were selected for more detailed investigation of kerogen type at the molecular level. A new analytical technique, for this material, was applied – namely Curie point pyrolysis gas chromatography Py(610°C)-GC (Nip, 1987). The identification of the pyrolysis products was carried out by means of mass spectrometry Py(610°C)-GC-MS. The identification of chemical structure at molecular level allowed to define biological precursors of organic matter occurring in copper-bearing shales.

MATERIALS

The materials studied were collected from the Lower Silesian copper-bearing beds within the Fore Sudetic Monocline (Fig. 1). The samples comes from accessible mining fields of the Rudna North (galleries N-4, N-6 and W-249) and Lubin Główny. Their detailed position in the geological cross-section is presented when discussing lithological characteristics of sediments. Basing the choice on lithological characteristics, ten samples were selected for laboratory examinations, whereby the symbols of those seven subjected to geochemical study are underlined.

The geological setting of the area in question is described in detail e.g. by Niśkiewicz (1980) and Oszczepalski (1986). According to Oszczepalski (1986), white sandstone (Bs1) and the overlying copper-bearing shales (T1) initiate the Zechstein sedimentary sequence in this area. Further upwards,

Fig. 1 Location of the area investigated on a sketch map of Poland (the left hand corner) and the geological map of the Lower Silesia Mining District indicating the location of the mines



copper-bearing shales pass gradually into the Zechstein limestone (Ca1). Locally, boundary limestone (Ca1p) appears between the sandstones (Bs1) and copper-bearing shales (T1).

The following lithological units can be distinguished within the sampled profiles (Fig. 2):

I – boundary dolomite (locally lacking) – usually gray, coarse-grained, being a facial variety of boundary limestone (Ca1p), 0 - 20 cm thick, represented by sample RPN-Dol.

II – "dirtying" shale, black, structureless or, scarcely, fine-laminated, containing the highest amounts of organic carbon. It is from several to 50 cm thick and represented by samples RPN-1 (N-6), RPN-9 (N-6), RPN-1 (W-249), RPN-4 (W-249).

III – laminated marly shale, black or dark gray, 20 - 50 cm thick, represented by samples RPN-3 (N-4), L-15.

IV – carbonates (a facial variety of the Zechstein limestone (Ca1)), gray partly marly, laminated in the bottom part, represented by samples RPN-4 (N-4), RPN-9 (W-249). They grade into massive varieties, represented by sample RPN-5 (N-4), taken only in this part which belongs to the ore-bearing series.

All the above mentioned units are, in general, mineralized. Mineralization occurs locally in the top part of Rotliegendes which, in this case, is often white in colour. The dominant ore minerals are iron and copper sulphides (pyrite, chalcopyrite, bornite, digenite, chalcocite, covellite) (Mayer and Pies-trzyński, 1985).

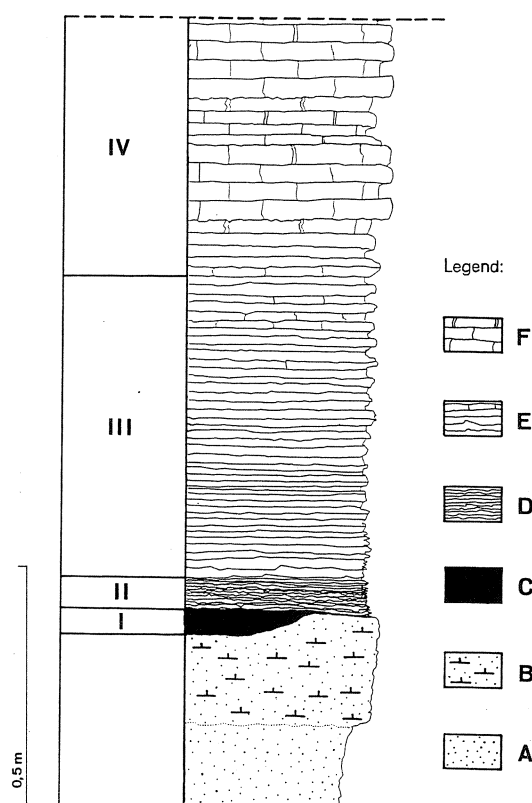


Fig. 2 The lithologic column of the ore-bearing series. *A* – sandstone (Bs1), *B* – sandstone cemented with anhydrite (Bs1), *C* – boundary dolomite (Calp), *D* – organic-rich shale, Kupferschiefer (T1), *E* – marly shale, Kupferschiefer (T1), *F* – carbonates (Cal)

METHODS

Methods of organic matter maceration

The crushed samples (about 10 g) were twice acid treated (HCl followed by HF). Then, the organic matter from the residue was obtained by washing, sieving (25 μm) and heavy liquid (ZnCl_2 solution) separation. The heavy liquid drifting fraction was collected separately from that being in suspension in order to select the heavier organic fraction with entrapped sulphides from the sulphide-lean (lighter). They were referred to as heavy and light fractions, respectively. The obtained residues were applied on cover slips (22 x 22 mm) and mounted in Depex. In each slide all recognizable palynomorphs were considered as 100%. Moreover, the ratio of palynomorphs to amorphous material was estimated.

Organic geochemical analysis

The kerogen for pyrolysis was obtained from the organic matter unseparated from the mineral matrix by Soxhlet's extraction with the toluene/methanol (1:3, v/v) for 48h.

Pyrolysis-gas chromatography Py(610°C)-GC. It was carried out using Varian 3700 gas chromatograph equipped with a Curie point pyrolysis device and a fused silica capillary column CP Sil-CB (25m x 0.32mm, film thickness 0.42 μ m). The 610°C Curie point ferromagnetic wires were used. Heating time was 10 s. Hydrogen was applied as carrier gas. The programmed oven heating ratio was the following: an isothermal period of 5 min at 0°C, then 3°C/min from 0°C - 320 °C and a final isothermal period of 10 min at 320°C. Pyrolysis products of kerogen were examined by a FID detection system.

Gas chromatography - mass spectroscopy Py(610°C)-GC-MS. It was carried out using a Hewlett-Packard 5840 gas chromatograph combined with a VG-70S mass spectrometer which operated with electron energy at 70 eV and the mass range $m/z = 50 - 800$ was scanned every 1.8 sec. The gas chromatograph was equipped with the same columns as described above. Helium was used as carrier gas. The oven heating ratio was programmed as for the Py-GC unit.

RESULTS

Palynology and organic petrography

Palynofacies were characterized using the terminology proposed by Van Bergen *et al.* (1990). Organic material examined is completely dominated by orange and brown organic debris, the content of which ranges from 85.00 to 99.5 %. The remaining part is represented by palynomorphs. Their content increases when going upwards along the profile. The type of organic matter is uniform in all the investigated samples.

Palynology. In the samples examined distinct dominance of miospores (97.7%) over acrytarchs (2.3 %) is observed. The most abundant genus is *Lueckisporites vrikkieae* Potonie et Klass (1954) (Pl. I: 1). Less frequent are taxons of the genera: *Jugasporites* (Pl. I: 3), *Klausipollenites* (Pl. I: 4), *Triadispora*, *Limitisporites* (Pl. I: 5), *Cordaitina* (Pl. I: 7), *Hamiapollenites*, *Lunatisporites* (Pl. I: 7), *Veryhachium* (Pl. I: 8) and *Leiospheridia*. Acrytarchs are represented by three genera: *Baltisphaeridium* (Pl. I: 7), *Veryhachium* (Pl. I: 8) *Leiospheridia*. Taking into account the applied method of separation (sieves 25 μ m), it may be supposed that acrytarchs real content is higher.

Organic petrography. Organic debris occurring in these rocks can be subdivided into two groups:

- i. Structureless organic debris (exinite-type) (Pl. I: 9) which in several samples practically represents the whole organic material. Two varieties of this debris were found to occur. The first is characterized by distinctly shaped margins and occurs in the form of transparent orange flakes (Pl. II: 1). The second is distinctly porous, spongy and its colour changes from orange to dark brown (Pl. III: 1).

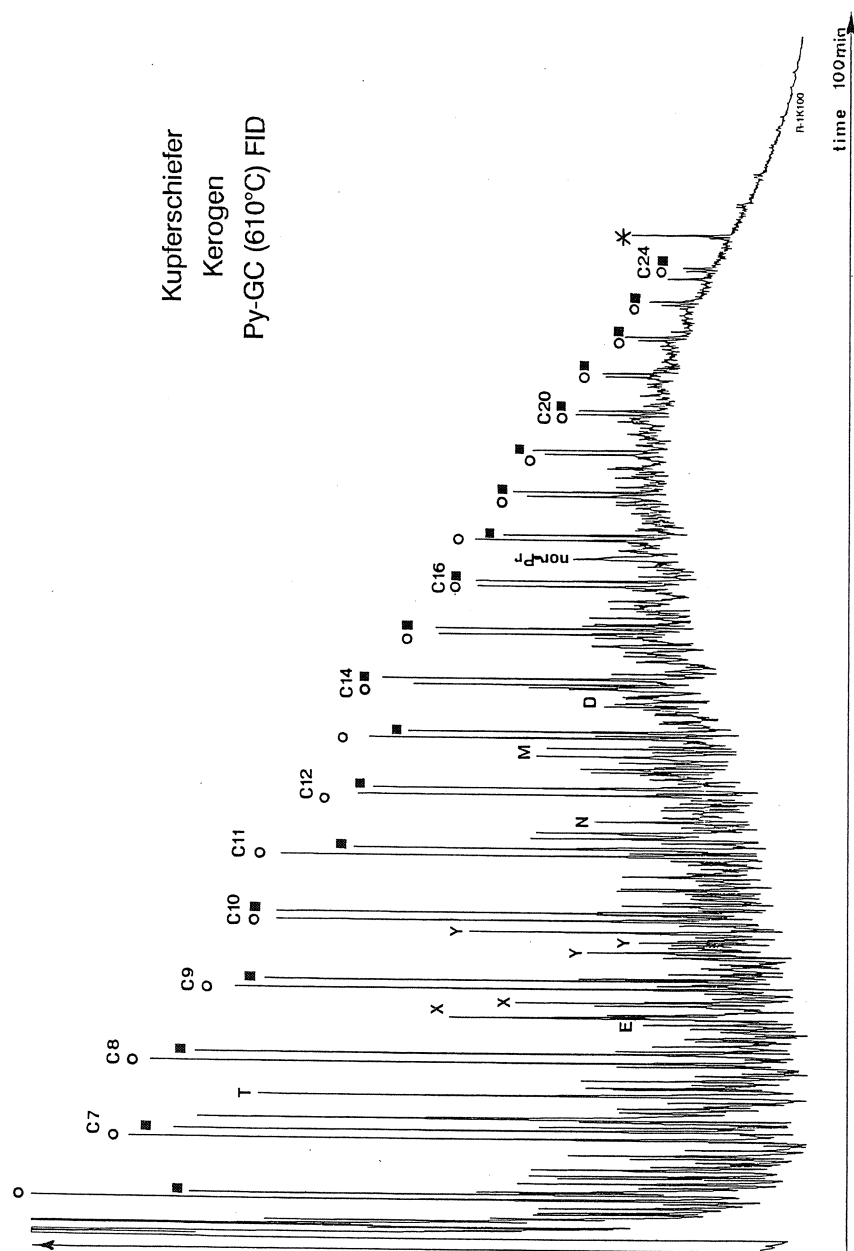


Fig. 3 Gas chromatogram of the kerogen pyrolysis products. o – n-alk-1-enes, ■ – n-alk-1-anes, C7 – the numbers refer to the number of carbon atoms of n-alk-1-enes and n-alkanes, T – toluene, E – ethylbenzenes, X – xylene (dimethylbenzenes), N – naphthalene, M – methyl-naphthalenes, D – dimethylnaphthalenes, nor-Pr – nor-pristane, * – impurities

ii. Structural organic debris. This type of organic matter is represented by fragments of land plants (most often vitrinite) such as: elongated pieces of wood (Pl. I: 10; Pl. II: 2), vascular veins or sieving plates.

The whole organic material is poorly preserved. It contains numerous pores and depressions, often filled with opaque rounded sulphide aggregates. The sulphides are often entrapped within organic grains (Pl. I: 3; Pl. III: 2). In the pollen grains sulphides are mainly concentrated within their central bodies. On the other hand, sulphides abound in structureless organic debris. Consequently, just this type of organic matter has been enriched with heavier fraction when applying this separation method.

Scanning microscope images reveal the inner arrangement of grains of metal sulphides, not removed during demineralization in acids. They are represented only by framboids of various types. One of these framboids, consisting of larger grains (as nuclei) and surrounded by smaller ones grouped in outer (partly destroyed layer) is presented in Pl. III: 2. Moreover, organic envelopes, embedding individual framboid grains are visible in the picture.

Pyrolysis gas chromatographic analysis Py(610°C)-GC

The products of pyrolysis were identified, if necessary, by means of mass spectroscopy Py(610°C)-GC-MS and the obtained spectra interpreted by comparing them with the data presented in McLafferty and Streufer's (1989) catalogue.

A high content of organic carbon (TOC) in the material analyzed (on the average 6% TOC) allowed to use for pyrolysis, kerogen which was not separated from the mineral matrix. Since all the obtained gas chromatograms are similar, only one of them as representative (sample RPn-9 (W-249)) is presented in Fig. 3.

The pyrolysis products of all the samples examined are dominated by a homologue series of n-alkanes and n-alk-1-enes, whereby the most intense peaks are due to hydrocarbons characterized by the length of chains from C₆ to C₁₁ (Fig. 3). Among isoprenoids, the peak corresponding to nor-pristane is observed. Only toluene is as common as aliphatic compounds, being even the dominant organic component eg. in samples RPn-9 (W-249) and L-15. Other alkyl derivatives of benzene are represented by xylene (C₂-alkylbenzenes) and C₃-alkylbenzene. Bicyclic aromatic hydrocarbons are represented by the naphthalene homologue series. The most intense peaks are due to methylnaphthalene isomers. The 1-methylnaphthalene peak is twice as intense as that of 2-methylnaphthalene. Polycyclic aromatic hydrocarbons are not detectable. Sulphur organic compounds are represented by thiophene and benzothiophene derivatives.

CONCLUSIONS

Kerogen, defined as organic matter insoluble in generally applied organic solvents (Durand, 1980), was until recently considered as a product of random condensation and polymerization reactions of relatively small molecules formed in sediments as the result of degradation of biomass. Thus formed protokerogen is, subsequently, in the course reactions, transformed into insoluble, non-hydrolyzable macromolecular polymer – kerogen (Brooks, 1981; Tissot and Welte, 1984).

Actually, however, it was found that the origin of kerogen is due to selective preservation in sedimentary environment of “biomacromolecules” – some primary macromolecules (Tegelaar *et al.*, 1989). Consequently, kerogen is no longer treated only as the result of the accidental processes modified by purely geological factors. Therefore, it is often possible to relate its chemical structure to that of its biological precursors.

In the case of amorphous (structureless) organic matter from the copper-bearing shales, gas capillary chromatographic analysis of its kerogen pyrolysis products has shown that this organic matter consists almost exclusively of aliphatic structural units. In nature, insoluble, non-hydrolysable, macromolecular highly aliphatic resistant to (bio)chemical degradation biopolymers form protective envelopes of higher plants (cutan* and suberan*) as well as cell walls of same algae species (algaenan*) (Nip, 1987; Tegelaar *et al.*, 1989; Goth *et al.*, 1988). The obtained chromatograms are as those of kerogen of the documented algal origin due to preserved morphology which were encountered in Messel Oil Shale (Goth *et al.*, 1988). They are also similar to Py-GC chromatograms of cutin separated from the bituminous coal (Nip, 1987).

Till now, only hypotheses concerning the origin of organic matter in the Lower Silesia copper-bearing shales have been presented. Phytoplankton, algae and bacteria were proposed as its source material (fide Sawłowicz, 1991). The results of the present studies allow us to exclude the participation of some organism groups in formation of the kerogen as well as to concentrate further research on algae and higher plants. Because of small amounts of spores and pollens encountered (from 0.5 to 15%) and subordinate content of higher plants remains in the analyzed palynofacies, it is concluded that the kerogen in question is not composed of cutan and suberan only. It should be emphasized that in both these types of organic matter primary morphology is usually preserved that is not observed in organic matter of the copper-bearing shales. After elimination of higher plants as the source of organic matter, only algaenan has highly aliphatic nature and therefore, can be considered as the source substance for kerogen. Apart from geochemical data, algal origin of

* - the terms refer to the chemical compounds of which the maceral is built off, eg. alginite is built of algaenan (Tegelaar *et al.*, 1989)

this matter is suggested also by sediment structures of the copper-bearing shales, similar to those reported for sediments of the documented algal origin (Goth *et al.*, 1988).

Beside of that, thiophene structures were found in kerogen of the copper-bearing shale. These types of structural units document indirectly the presence of anaerobic, sulphate reducing bacteria by recording the products of their metabolism (Sinninghe Damste & de Leeuw, 1992). Thiophene derivatives are the reaction products of hydrogen sulphide, mainly produced by bacteria, with labile organic compounds (op. cit., 1992). Consequently, since the labile organic compounds occur in relatively fresh sediments, the organic sulphur compounds are the indicators of H₂S-oversaturated oxygen-lean environment existing during the sedimentation.

It is worth emphasizing the observed phenomenon of incorporation of metal sulphides into the organic matter. Microscope observations have shown that even multiple treatment with acids does not lead to complete removal of sulphides from organic matter. Some part of sulphides, displaying only framboidal morphology (Pl. III: 2) is strongly bound to structureless organic debris what was confirmed by enrichment of heavy fraction in this group of minerals. Pyrite is dominant in this group as insoluble in acids applied in the maceration process.

In a sediment, the preservation of framboids is possible in the case of rapid isolation of newly formed sulphide phases from the solvent. The role of this isolating phase can be played by organic matter (Ferrand, 1970), which is preserved in the form of organic envelopes around framboids in the case of copper-bearing shales in question (Pl. III: 2). Moreover, iron sulphides had to survive the process of replacement of iron by copper ions due to difference in electrochemical properties of these chemical elements. The coexistence of pyrite and copper sulphides in the closest vicinity implies selectivity of this process to some grains. This selectivity is explained by the lower speed of the replacement reaction for pyrite than for iron monosulphides (Sawłowicz, 1992).

However, the occurrence of organic envelopes sealing iron sulphide grains (Pl. III: 2) suggests that they caused the persistence of iron sulfides, no matter what the affinity of iron sulphide phases for the copper replacement and how abundant the copper ions in the later stage of mineralization process.

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REFERENCES

- van Bergen, P. F., Janssen, N. M. M., Alfrink, M. & Kerp, J. H. F., 1990. Recognition of organic matter types in standard palynological slides. In: Fermont, W. J. J. & Weegink, J. W. (Eds.), *Proc. of Inter. Symp. on Organic Petrology, Zeist, The Netherlands, 1990*, 45: 9 – 22.
- Brooks, J., 1981. Organic maturation of sedimentary organic matter and petroleum exploration, A Review. In: Brooks, J. (Ed.), *Organic Maturation Studies and Fossil Fuel Exploration*, Academic Press, London, N. York, Toronto, Sydney, San Francisco, 1 – 37.
- Durand, B., 1980. Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen. In: Durand, B., (Ed.), *Kerogen*. Technip, Paris, 13 – 14.
- Farrand, M., 1970. Framboidal Sulphides Precipitated Synthetically. *Mineral. Deposita*, 5: 237 – 247.
- Goth, K., de Leeuw, J. W., Püttmann, W. & Tegelaar, E. W., 1988. Origin of Messel Oil Shale kerogen. *Nature*, 336: 759 – 761.
- Harańczyk, Cz., 1986. Zechstein copper-bearing shales in Poland. Lagoonal environments and sapropel model of genesis. In: Friedrich, G. et al. (Ed.), *Geology and metallogeny of copper deposits*, Springer-Verlag, Berlin, 461 – 476.
- Mayer, W. & Piestrzyński, A., 1985. Ore Minerals from Lower Zechstein Sediments at the Rudna Mine, Fore-Sudetic Monocline, SW Poland. *Prace Mineralogiczne*, WG Warszawa, 75: 1 – 72.
- McLafferty, F. W. & Strauffer, D. B., 1989. *The Wiley/NBS Registry of Mass Spectral Data*. N. York, Chichester, Brisbane, Toronto, Singapore, vol. 1-6.
- Nip, M., 1987. *Chemical characterization of coals, coal macerals and their precursors, A study by analytical pyrolysis*. Ph. D. Thesis, Technische Universiteit Delft, Drukkerij Giethoorn Meppel, Holland, 205 pp.
- Niśkiewicz, J., 1980. Zjawiska metasomatozy w cechsztyńskich złożach miedzi (Metasomatic phenomena in the Zechstein copper ore deposits of Lower Silesia). *Geol. Sudetica*, 15: 7 – 75.
- Oszczepalski, S., 1986. On the Zechstein copper shale lithofacies and paleoenvironments in SW Poland. The English Zechstein and Related Topics. In: Harnwood, G. M. & Smith, D. B. (Eds.), *Geol. Soc. Spec. Publ.*, 22.
- Püttmann, W. & Goßel, W., 1990. The Permian Kupferschiefer of southwest Poland: a geochemical trap for migrating, metal-bearing solutions. *Appl. Geochem.*, 5: 227 – 235.
- Sawłowicz, Z., 1991. Organic matter in the Zechstein Kupferschiefer from the Fore-Sudetic Monocline (Poland), II. Kerogen. *Min. Pol.*, 22: 49 – 68.
- Sawłowicz, Z., 1992. Primary sulphide mineralization in Cu-Fe-S zones of Kupferschiefer, Fore-Sudetic monocline, Poland. *Trans. Instn Min. Metall. (sec. B: Appl. Earth Sci.)*, 101: B1-B8.
- Sinninghe Damste, J. S. & de Leeuw, J. W., 1992. Organically-bound sulphur in coal: a molecular approach. *Fuel Proc. Tech.*, 30: 109 – 178.
- Tegelaar, E. W., de Leeuw, L. W., Derenne, S. & Largeau, C., 1989. A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta*, 53: 3103 – 3106.
- Tissot, B. P. & Welte, D. H., 1984. *Petroleum Formation and Occurrence*. 2nd edn., Springer-Verlag, Berlin, Heidelberg, N. York, Tokyo.

Streszczenie

**POCHODZENIE SUBSTANCJI ORGANICZNEJ W ŁUPKACH
MIEDZIONOŚNYCH DOLNEGO ŚLĄSKA****M. J. Rospondek, A. Fijałkowska & A. Lewandowska**

Stratyfikowane złoża miedzi, do których należą złoża dolnośląskie, są często wzbogacone w materię organiczną. Mikroskopowa analiza materii organicznej występującej w przebadanych litofacjach łupka miedzionośnego pokazuje, że materiał ten jest zbudowany głównie z bezstrukturalnych organicznych debris, a rozpoznawalne debris organiczne tj. wiązki przewodzące roślin, fragmenty drewna oraz palinomorfy występują w podrzędnych ilościach. Celem określenia chemicznej natury dominującej ilościowo, mikroskopowo nieidentyfikowalnej materii organicznej na poziomie molekularnym użyto kapilarnej gazowej analizy chromatograficznej produktów pyrolizy kerogenu. Były one identyfikowane na podstawie spektrogramów masowych Py(610°C)-GC-MS. Kerogen występujący w łupku miedzionośnym jest zbudowany z ugrupowań alifatycznych (stwierdzono n-alkany i n-alk-1-eny). Tak zbudowane są odporne na degradację biopolimery wysepujące w glonach (algaenan) i epidermalnych błonach roślin wyższych (suberan i cutan). Ponieważ nie stwierdzono mikroskopowo obecności epidermalnych błon roślin, eliminuje to rośliny wyższe i wskazuje to na glonowe źródło materii organicznej. Obecność strukturalnych jednostek tiofenu w kerogenie jest wskaźnikiem anaerobowych warunków w środowisku sedymentacyjnym. Bezstrukturalna materia organiczna wzbogacona jest w siarczki w porównaniu z innymi typami materiału organicznego. Siarczki metali są bezpośrednio związane z amorficznym materiałem organicznym i występują wyłącznie jako framboidy. Materia organiczna tworzy otoczki wokół ziarn siarczków, które dokumentują rolę jaką odegrała ona w procesie złożowym: a) umożliwiła powstanie framboidów przez odizolowanie wydzielonych faz siarczkowych od środowiska sedymentacyjnego, b) odcięła uformowane framboidy do miedzionośnych roztworów mineralizujących umożliwiając zachowanie się siarczków żelaza.

EXPLANATION OF PLATES

Plate I

All magnifications are about x1000 (if not stated otherwise).

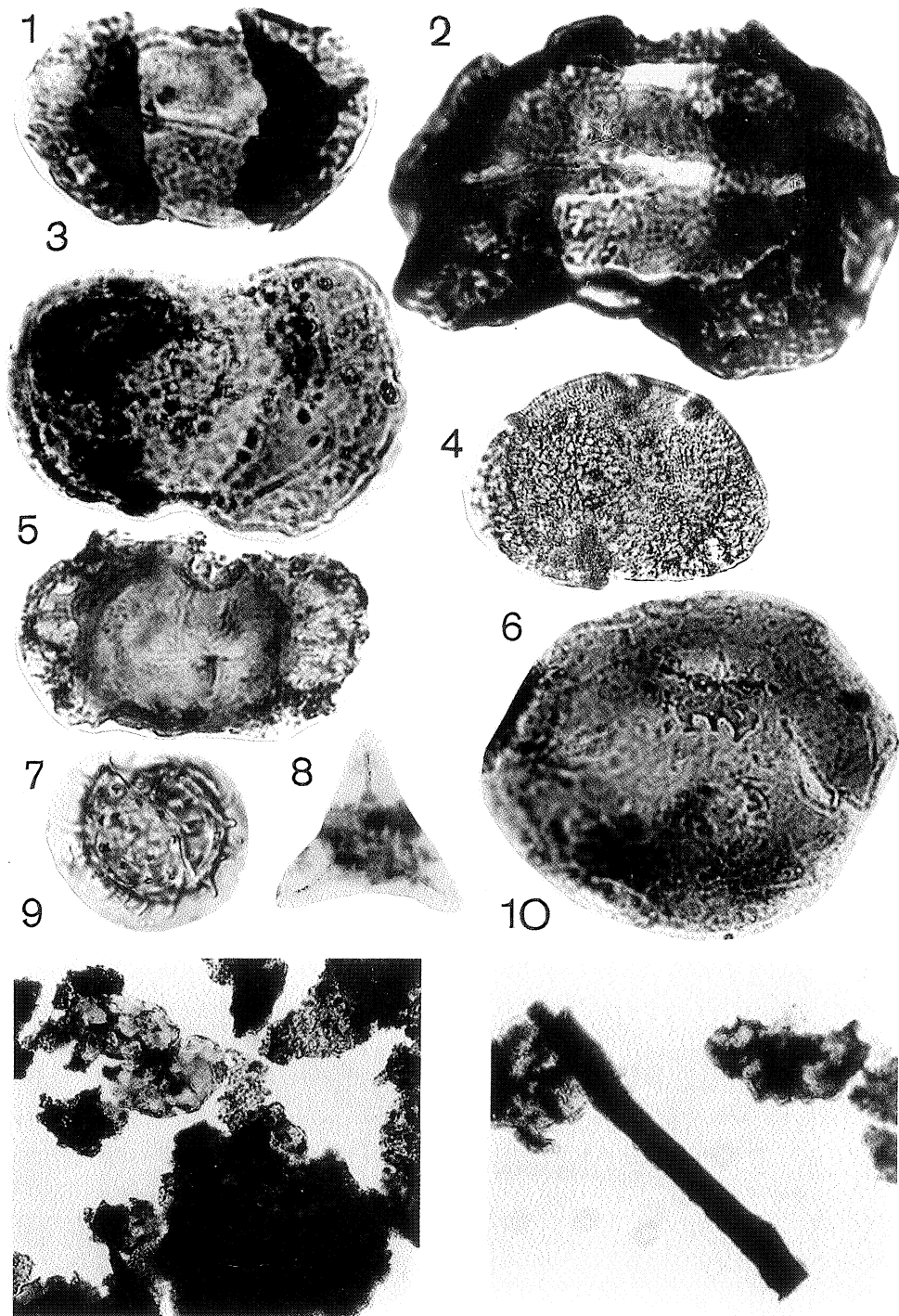
- 1 — *Lueckisporites virkkiae* Potonié et Klaus, 1954 Norm Aa. Unit II, sample RPn-1 (N-6), light fraction
- 2 — *Lunatisporites noviaulensis* (Leschik) Scheuring, 1970. Unit IV, sample RPn-5 (N-4), heavy fraction
- 3 — *Jugasporites paradelasaucei* Klaus, 1963. Unit II, sample RPn-1 (N-6), light fraction
- 4 — *Klausipollenites schaubergeri* (Potonié et Klaus) Jansonius, 1962. Unit II, sample RPn-1 (N-6), light fraction
- 5 — *Limitisporites moersensis* (Grebe) Klaus, 1963. Unit II, sample RPn-1 (N-6), light fraction
- 6 — *Cordaitina donetziana* Inosova, 1976. Unit IV, sample RPn-5 (N-4), heavy fraction
- 7 — *Baltisphaeridium* sp. Unit II, sample RPn - 9 (N-6), light fraction
- 8 — *Verhachium reductum* var. *trispinoides* Jekhowsky, 1961. Unit III, sample RPn-1 (N-4), light fraction
- 9 — Concentration of palynomorphs within structureless organic debris, x200. Unit II, sample RPn-1 (W-249), light fraction
- 10 — Structural organic debris - wood remains (vitrinite). Unit III, sample L-15, light fraction

Plate II

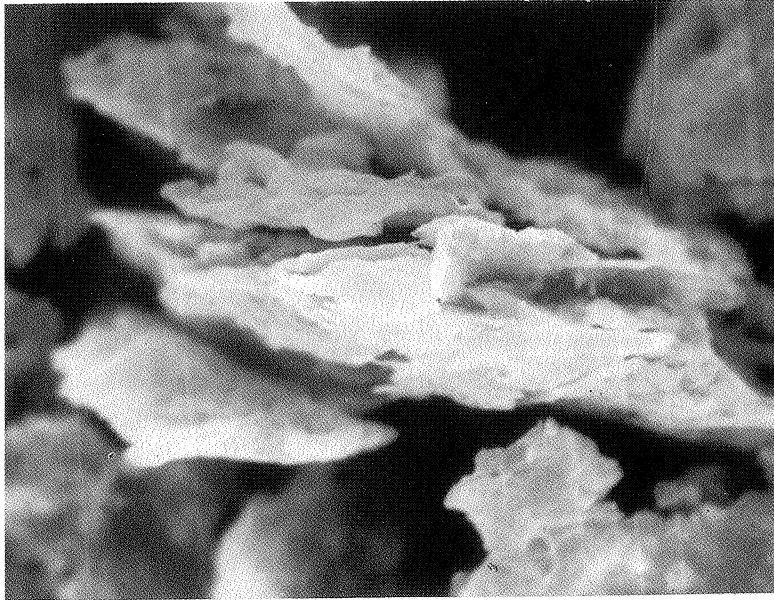
- 1 — Structureless organic debris (exinite - type), SEM x600. Unit II, sample RPn - 9 (N-6), light fraction
- 2 — Structural organic debris – wood remains (vitrinite), SEM x600. Unit II, sample RPn-1 (W-249), light fraction

Plate III

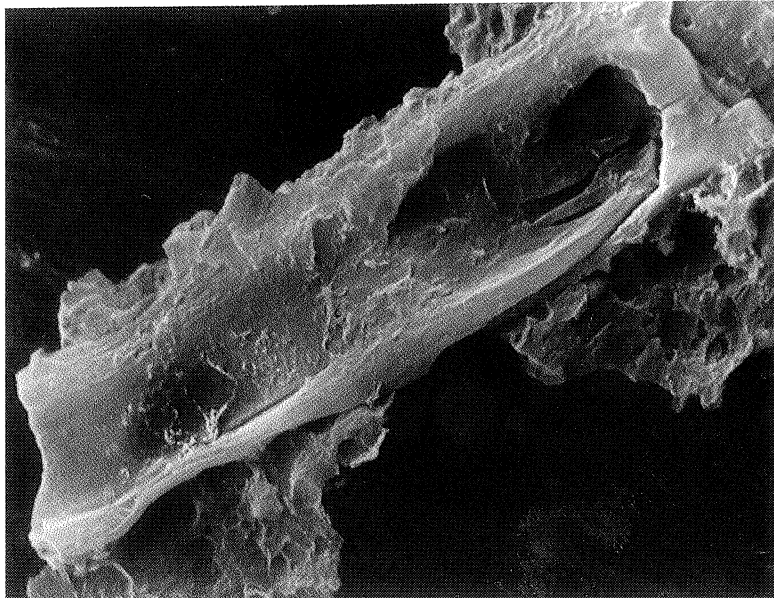
- 1 — Structureless organic debris (exinite - type), SEM x2000. Unit II, sample RPn - 9 (N-6)
- 2 — Framboid within structureless organic matter forming an organic envelope (partly destroyed) with distinct organic rims around individual grains (in the right side), SEM x 7200. Unit II, sample RPn - 9 (N-6)



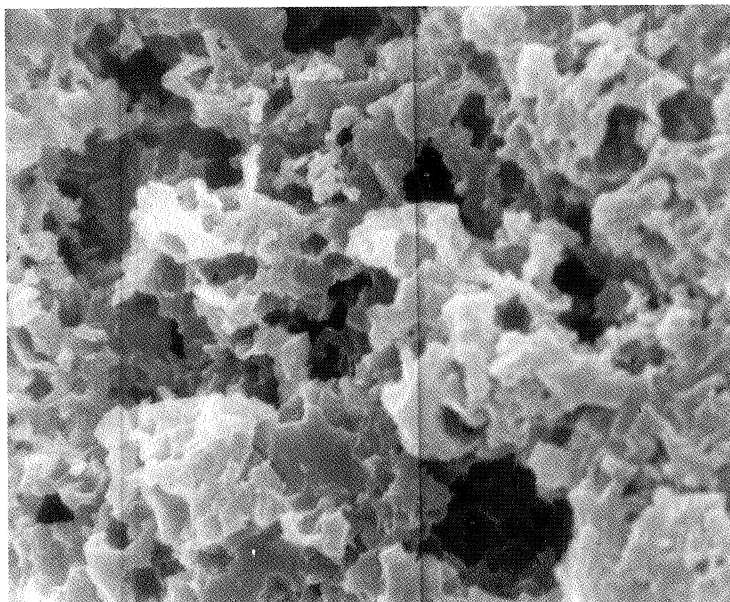
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2

