GEOCHEMICAL INTERPRETATION AND COMPARISON OF BIOMARKER COMPOSITION OF BITUMENS OBTAINED FROM COALS AND SURR OUNDING ROCKS

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A b s t r a c t . The bitumens obtained as the extraction products from a series of coals and surrounding rocks samples were fractionated onto aliphatic, aromatic and polar fractions. Aliphatic and aromatic fractions were then submitted to analysis using modern gas chromatography — mass spectrometry method. The distribution of n-alkanes was compared and parameters values characterising conditions of sedimentation and type of primary organic matter were calculated. In aliphatic fractions, a series of biomarkers was also identified as steranes, diasteranes, tricyclic diterpanes, hopanes and moretanes. The relatively high content of diasteranes was observed in the bitumens from shales bordering on coals. It confirms the literature data indicating possibility of catalytic influence of claystones on arrangement of steranes to diasteranes. The values of parameters calculated from the data characterising distribution of hopanes have indicated a possibility of generation of oils by some of analysed coals: flame as well as orthocoking coals.

The aromatic compounds were also identified, mainly phenanthrenes being an important stage of aromatisation process of fossil organic matter.

The comparison of characteristics of bitumens obtained from coals and surrounding rocks suggests a possibility of migration of various groups of organic compounds from coal layers to rocks bordering on them. The migration of organic mobile matter seems to be as well a result of a great difference of concentration between coal and surrounding rocks layers as of action of circulating waters or hydrothermal solutions. The temperature gradient and local intrusive bodies are of great significance for processes of oil migration. The examinations and conclusions presented in this work should be, however, taken as the introductory ones and have to be confirmed by analysis of a greater number of samples of various geological characteristics.

K e y w o r d s : coal, coal shales, bitumens, biomarkers, gc–ms, thermal maturity.

INTRODUCTION

The problem of coexistence of organic and inorganic matter in natural conditions is interesting for various reasons, applied as well as cognitive ones. The possibilities were examined of the utilisation of rocks surrounding coal bed among others because of a charge of environment by their storage on the waste dumps. The knowledge of composition and properties of rocks surrounding coal bed is also of importance for mining, among others in consideration of necessity of prevision of changes in roof and floor during exploitation. It is also important an estimation of elution trends or designation of erosion area and so on.

The coal layers and surrounding rocks are interrelated by spatial and genetic dependencies. Their common feature is a mutual influence of components and structures in vicinity of their contact. The influence of coals on their roof and floor rocks was observed . Near to the contact with coal, a thin transitional zone can exist containing alternately lamines of coal and shale (coal-shale, shale-coal).

Other economic aspect of investigations of interaction of organic and inorganic matter in sediment, it is a possibility of utilisation of trace elements present in fossil fuel beds. Migration of trace elements as well as their retention in coals is controlled to a considerable degree by formation of organo-mineral complexes of various nature (Lewińska-Preis, Matuszewska, 2000).

The interactions between organic and inorganic matters in sediment seem to be especially important cognitive problem. From the point of view of these interactions in natural condi-

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tions, the problem of genesis, transformations and properties of clay minerals is especially interesting. They can act as acceptors and donors of electrons. Their catalytic action is known in many reactions, including polymerisation. They may also protect organic molecules against weathering and biological factors. Clay minerals may stimulate growth of micro-organisms considering adsorption of alimentary substance and toxic excretions (Van der Marel, Beutelspracher, 1976). The considerable possibilities of interactions enable control of a reciprocal dependence of organic and clay matter as early as at first stages of sedimentation. In process of transformation of clay minerals, the substances responsible for mineral destruction contain the most probably organic acids able to influence the silicate minerals. The process of precipitation of kaolinite from solutions rich in organic matter during decarboxylation process is also well known, characterising one of the stages of transformation of sedimentary organic substance (Curtis, 1987). Moreover, the clay minerals are considered to be the potential markers for estimation of depth and temperature of various hydrothermal phenomena. Chlorite is considered e.g. as a kind of geothermometer (Chamley, 1989).

The examinations of relation between degree of coalification of fossil organic matter and mineral facies have shown that the higher is carbon content in organic compounds, the higher is degradation of clay complexes. The simple clay minerals subjected to degradation in succession are ordered in a series: palygorskite, smectite, chlorite, illite, kaolinite (Sigl *et al.*, 1978). The main stage of ordered series smectite-illite during diagenesis of clays comes frequently shortly before the oil generation and migration.

It was also stated that parameters of crystalline state of illite are paralell with changes of reflectance of vitrinites, what can help in estimation of degree of thermal maturation and hydrocarbon generation. The presence of a high quantity of smectite in sunk sedimentary rocks seems to favour the generation and migration of hydrocarbons. The interlayer spaces of smectite can receive a great amount of organic products, which constitute potential precursors for hydrocarbons. Smectites act also as an important reservoir of water. During diagenesis this water may be a carrier necessary for migration of hydrocarbons. Moreover, smectite is probably a catalyser of decarboxylation process (Chamley, 1989). It was also stated that clay minerals

can have catalytic influence on the aromatization process of steranes, rearrangement of steranes to diasteranes (Jovančićević *et al.*, 1992). Clay minerals can catalyse also the isomerisation reactions (Mackenzie *et al.*, 1982).

The dynamics of interactions between organic and inorganic sedimentary matter depends in a high degree on the migration of mineral and organic matter in the rocks. This phenomenon is controlled by type of rocks, their sorptivity, porosity and heat conductivity. It is well known that the heat carried enables a transformation of organic matter and also generation and offtake of gases and bitumens from source rocks.

The problem of organic substance transport in inorganic rocks seems to be recognised to the lower degree than migration of inorganic substance. It may be a result of a considerable variety in composition of fossil organic matter and its instability. This last mentioned feature is especially marked in strongly oxidative environments, in zones of high activity of micro-organisms, and in relation to catalytic action of a series minerals on transformation processes (Jones, 1984).

The theoretical expectations and experimental data concerning migration of various types of fossil organic matter give a general migration model after which the macromolecular, especially polar polyfunctional compounds are the most immobile. The contents of this type compounds in coal bitumens were considerably higher than in extracts of sandstones and claystones from direct contact with coal layer (Bzowska *et al.*, 2000).

With circulating waters, the monomolecular polar compounds can migrate from natural sources or being also products of oxidation. These compounds may be detained in strongly adsorbing environments. Among migrating polar compounds transported by hydrothermal solutions, the organic acids form a considerable part as well as other carbonyl groups containing compounds (Fabiańska *et al.*, 1999).

The complexity of organic substance migration problem in rocks causes necessity of investigation by stages and this work has a partial, preliminary character.

The goal of this work was a comparison of composition of chosen groups of components isolated from extracts obtained from coals and surrounding rocks. The possibility of migration of organic matter from coals to surrounding rocks was also submitted into discussion.

EXPERIMENTAL

The objects of analysis were orthocoking coals and rocks surrounding coal layer (roof and floor-shales) from Borynia, Moszczenica and Jastrzębie mines (Rybnik Coal District). For comparison, a vitrain and two coal-shales were examined from direct and indirect neighbourhood of flame coal layer from Siersza mine (Upper Vistula Coal District) as well as a sample of montmorillonite from Milowice coal mine. The shales examined were of various shade of greyness and of solid construction without visible coal interlayers.

The samples were powdered and submitted into extraction using Soxhlet apparatus and methylene chloride: methanol

mixture (97:3 v/v) as a solvent. The extracts (bitumens) were then fractionated onto aliphatic, aromatic and polar groups of compounds with the use of thin layer chromatography method. The Merck`s silicagel precoated plates and n-hexane as a mobile phase were used for this purpose.

Gas-chromatography–mass spectrometry combined method (gc–ms) was used for identification of particular compounds of obtained aliphatic and aromatic fractions. The analyses were made using a gc–ms apparatus of Hewlett-Packard firm (5971 series). The capillary column of HP5 type (length: 25 m, internal diameter: 0.2 mm) was used, covered by methylsilicone (95%)

and phenylsilicone (5%) phase with thickness of 0.33 μm. The temperature program was: 50–290°C with the rate of growth: 3°C/min. The carrier gas used was helium with the rate of flow: 1 cm³/min.

RESULTS AND DISCUSSION

In Table 1 the extraction yields are presented estimated for analysed coals and surrounding rocks. These yields were about two to about twenty times lower for surrounding coal shales than for respective coal samples.

Table 1

Estimation of extraction yield

Mine	Sample type	Extraction yield [%]
Borynia	coal	0.59
	floor-shale	0.41
	roof-shale	0,15
Jastrzębie	coal	0.19
	floor-shale	0.09
	roof-shale	0.05
Moszczenica	coal	0.38
	floor-shale	0.02
	roof-shale	0.06
Siersza	vitrain	1.41
	floor-shale in direct contact with coal layer	0.07
	floor-shale	0.05
Milowice	montmorillonite	0.02

Some of the data estimated for analysed samples can suggest that a migration process was possible from coal layers to surrounding rocks. Among examined samples of orthocoking coals, the greatest bitumen yield (0.59%) was stated for the coal from Borynia mine. Simultaneously, there is also a high bitumen yield estimated for samples representing surrounding rocks (0.41 and 0.15%). These data could indicate a possibility of migration process in this case. The smallest bitumen yield among investigated coals was estimated for sample from Jastrzębie mine. Among examined coal-shales, the lowest bitumen yield was stated for floor-shale from Moszczenica mine: 0.02%. The same value was shown for analysed montmorillonite sample. In the case of vitrain from the flame coal from Siersza mine, the highest yield of bitumen (1.41%) was estimated with simultaneous low bitumen yield from surrounding rocks. In this case (in relation to analysed orthocoking coals), some factors extorting the migration process could be considerably weaker: e.g. lower gradient of temperature and pressure responsible also for difference in degree of coalification between flame and orthocoking coals. There could also be other type of sedimentary organic matter (samples were taken from various coal basins: Upper Vistula and Rybnik Coal Districts).

Another factor could cause a relatively more intensive natural "distillation" process in the case of coals from Rybnik Coal District: a phenomenon of an additional flows of heat caused by magmatic intrusions (Probierz, 1989) and/or natural process of burning of coal layers (Lipiarski, 2001), suspected in this region.

Figure 1 presents a triangular diagram where weight percentage is marked of aliphatic, aromatic and polar fractions isolated from analysed bitumens. Among these three groups of compounds, all samples show a maximal contents of polar compounds (60–90%). Most of the examined shales (roof as well as floor-shales) show maximal contents of polar compounds (80–90%). Among polar compounds eluted from coal--shales containing clay minerals, there is a characteristic (stated using infrared absorption spectroscopy and tlc chromatography) presence of compounds (as e.g. alcohols, phenols, aldehydes, ketones and organic acids) capable to form organo-mineral complexes with these minerals.

The lowest weight percentages of polar compounds were estimated for bitumens from floor-shales from Borynia and Moszczenica mines. Simultaneously, the aromatic compounds are in these cases of higher amounts than for bitumens from respective coals, and the highest among all the analysed bitumens. The decrease of polar structures and increase of aromatic
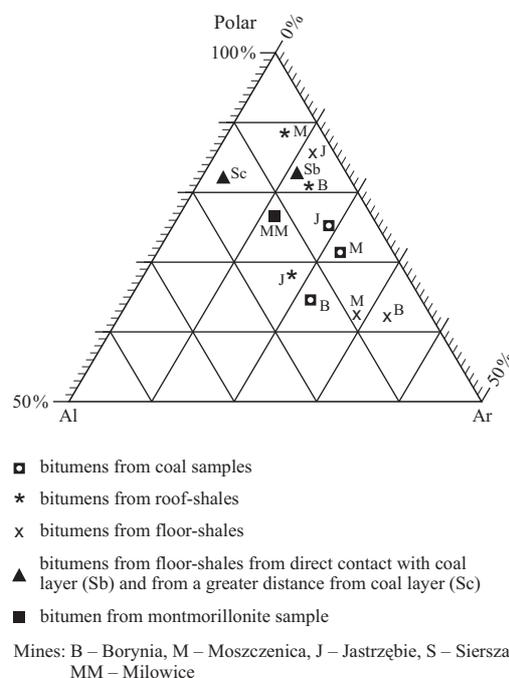

bitumens from coal samples

＊ bitumens from roof-shales

× bitumens from floor-shales

▲ bitumens from floor-shales from direct contact with coal layer (Sb) and from a greater distance from coal layer (Sc)

■ bitumen from montmorillonite sample

Mines: B – Borynia, M – Moszczenica, J – Jastrzębie, S – Siersza, MM – Milowice

Fig. 1. Diagram of distribution of fractions (aliphatic Al, aromatic Ar and polar one) in the bitumens obtained from analysed coal and coal shales

compounds are indicators of advanced process of thermal maturation of fossil organic matter.

The results obtained could also suggest, however, the migration direction of particular groups of compounds from coal layer into surrounding rocks.

The weight percentage of aliphatic compound fractions for majority of examined bitumens does not exceed 10%. The percentage of aliphatics is higher than 10% only for bitumens from: floor-shale from indirect contact with coal layer of Siersza mine, montmorillonite from Milowice mine, roof-shale from Jastrzębie mine, and coal sample from Borynia mine (Fig. 1). It should be mentioned that the content of aliphatic compounds is considerably higher in bitumen from floor-shale from indirect contact in relation to this from direct contact from Siersza mine (the inverse relation was observed for contents of aromatic compounds). There is also interesting similarity in amounts of aliphatics in first of the last mentioned samples and in bitumen from analysed montmorillonite.

The weight percentage of aromatic compounds is the lowest for bitumen from floor-shale from indirect contact with flame coal (Siersza mine) and is the highest for bitumens from floor-shales bording on orthocoking coals (Moszczenica and Borynia mines). It is worth to notice that for bitumen from roof-shale from Jastrzębie mine the high content is simultaneously observed of aliphatic and aromatic compounds. The aromatic group of compounds is here in the same proportion as for bitumen from respective coal.

It seems also worth to underlined that for analysed bitumens from orthocoking coals and some shales, a content of aromatic hydrocarbons is about twice higher (about 20%) than content of aliphatic ones (about 10%) (Fig. 1).

The results presented above indicate that some differences in concentration of particular groups of organic matter may suggest a possibility of migration according to "geochromatographic" phenomenon (Peters, Moldowan, 1993).

As it was stated earlier, the polar compounds predominate, especially for roof-shale bitumens. The migration process of polar compounds is very probable taking into account a possibility of their good solubility in circulating waters. In the case of examined coal-shales from Siersza mine a high, similar concentration of polar compounds in respective bitumens (Fig. 1) may be a result of migration of polar compounds from the neighbouring flame coal layer.

A high contents of oxygen and, therefore, of polar compounds is very characteristic for coals of low coalification degree, like coals predominating in Siersza mine.

Content of aliphatic groups of compounds shows relatively low differentiation between analysed samples what can suggest a generally considerable migration potential of aliphatic compounds from coal to surrounding rocks (in a process of equalisation of concentration).

Among analysed samples, the highest contents of aromatic compounds were noted for bitumens obtained from orthocoking coals but also from the two respective neighbouring floor-shales (Fig. 1). The high content of aromatic compounds in the last case may be a result of migration process but also of catalytic influence of clay minerals in shales on aromatisation processes. There is also possible an action of additional heat flows derived from intrusions or coal burning phenomena suspected in region of coal sampling.

Alkanes

Distribution of n-alkanes in bitumen samples was characterised on the basis of the recorded mass chromatograms, a software using, at the value of m/z 71 characteristic for n-alkanes.

The exemplary mass chromatograms of this type are presented for chosen samples on Figures 2–5. On Figure 2 the distributions of n-alkanes in aliphatic fractions isolated from bitumens are shown: from a coal from Borynia mine and from a roof-shale bordrering on the coal layer. The symbols C_n were used for description of n-alkanes, where "n" is a number of carbon (C) atoms in the chain. The symbols Pr and Ph have been used for description of acyclic isoprenoids: pristane and phytane neighbouring on the analysed mass chromatograms with n-alkanes: C_{17} and C_{18}, respectively. The broad range of intensive peaks of n-alkanes C_{16}–C_{26} shown on Figure 2a indicates a high thermal maturity of organic matter of analysed coal sample and/or a great variety of sources of this matter. In a case of bitumen from roof of this coal layer, the lower contribution was observed of n-alkanes with longer chain.
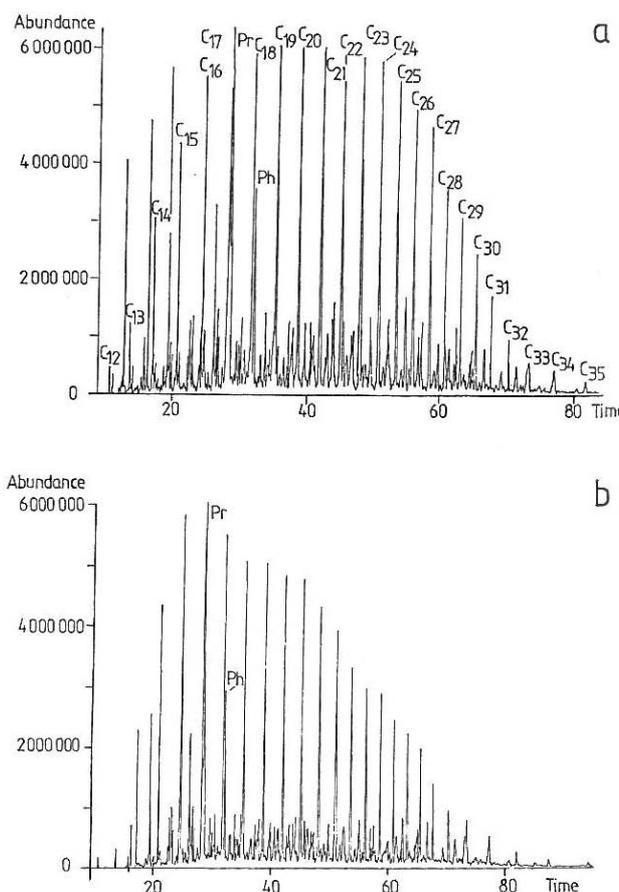

Fig. 2. Distribution of n-alkanes (m/z 71) in the bitumens from orthocoking coal (a) and roof-shale (b) from Borynia mine
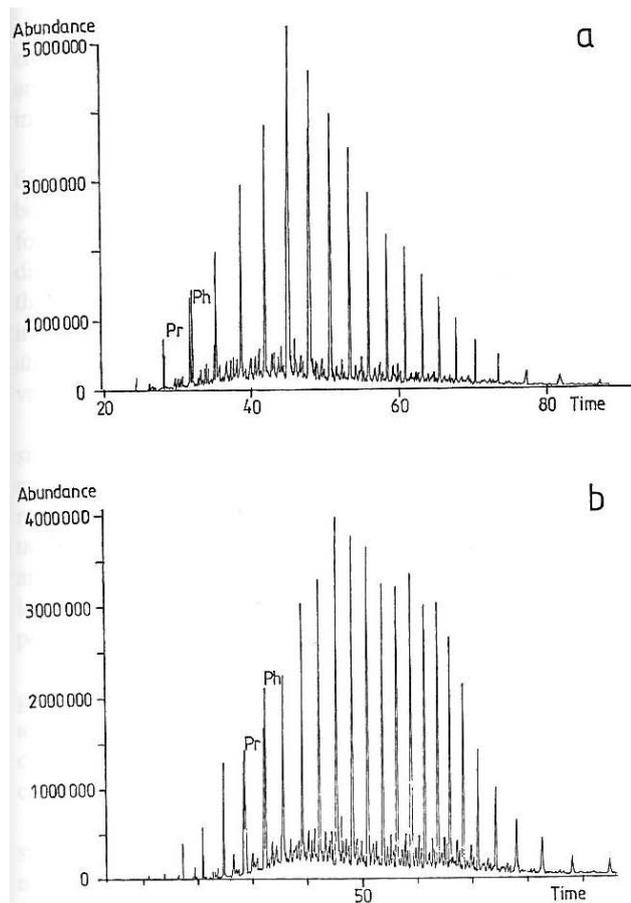
Fig. 3. Distribution of n-alkanes (m/z 71) in the bitumens from floor-shale [Sc] (a) and floor-shale from direct contact with flame coal layer [Sb] (b) from Siersza mine

Fig. 4. Distribution of n-alkanes (m/z 71) in the bitumen from montmorillonite sample from Milowice mine

Figures 3a and b show a distribution of n-alkanes in bitumens obtained from floor-shale from indirect (a) and direct (b) contact with coal layer from Siersza mine. At generally similar shape of this distribution and maximum at C_{22} peaks, the bitumen from the shale from direct contact with coal is characterised by relatively higher intensity of peaks derived from n-alkanes of longer chains. For bitumen from flame coal vitrain from Siersza mine, a generally similar shape of n-alkane distribution was observed as for bitumen from floor-shale from direct contact with respective coal layer. The sample from vitrain was differring, however, by higher amounts of pristane in relation to phytane.

Figure 4 presents a distribution of n-alkanes in aliphatic fraction of bitumen obtained for comparison from montmorillonite from Milowice coal mine. This distribution resembles another one observed for bitumen from a floor-shale from indirect contact with coal layer from Siersza mine (Fig. 3a). In this case, however, three peaks predominate: C_{22}–C_{24}.

Figures 5a and b present a distribution of n-alkanes in the case of bitumens from coal from Jastrzębie mine (a) and from surrounding roof-shale (b). The predomination of shorter n-alkane chains for bitumen from coal (Fig. 5a) might be a result of a great input of marine or lacustrine algae source of organic matter (Hunt, 1995). In this case of a coal sample from the
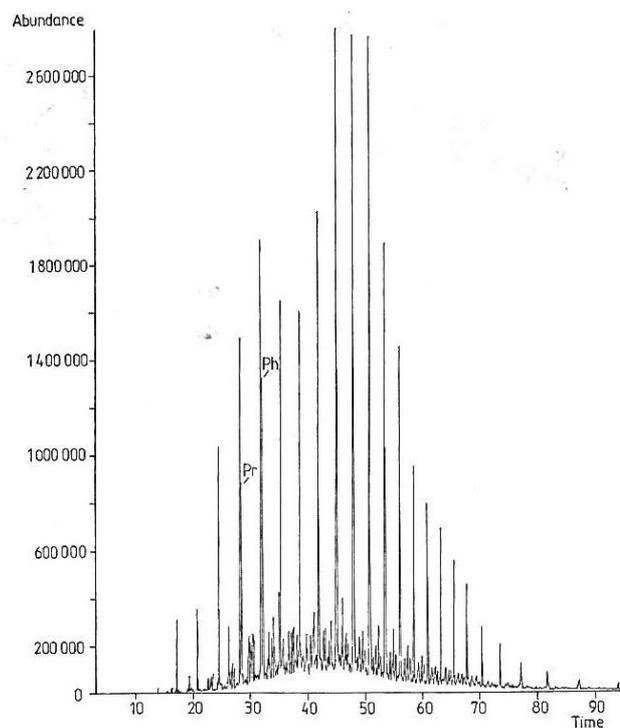
part of Rybnik Coal District, where thermal action of intrusions was stated, there should be also taken into account a possibility of thermal destruction of longer chains of n-alkanes into the shorter ones. It should be mentioned that n-alkane distribution shape for respective floor-shale bitumen is here similar to this one for coal bitumen. The distribution of n-alkanes in bitumen from roof-shale (Fig. 5b) shows a relatively higher amounts of chains with a greater number of carbon atoms. In this case a secondary input is probable of terrestrial organic matter; C_{28}–C_{32} n-alkanes may originate from terrestrial plant wax (*op. cit.*).

The distribution of n-alkanes in bitumens of samples derived from Moszczenica mine was not presented on figures but this distribution resembles generally this one characterising samples derived from Jastrzębie mine.

The values of parameters presented in Table 2 were calculated on the basis of mass chromatograms of m/z 71. These parameters are usually used for description of oils and organic matter dispersed in rocks e.g. for characterisation of deposition conditions (oxic, suboxic, anoxic) or of source of fossil organic matter (e.g. marine, lacustrine, terrestrial). The pristane (Pr) and phytane (Ph) contribution is here a very important indicator. These isoprenoids are formed during diagenesis probably from phytol side chain of chlorophyll *a*. Pristane may be formed in a process of oxidation and decarboxylation. Phytane can be formed e.g. in a process of hydrogenation and reduction (Peters, Moldowan, 1993). The Pr/Ph ratio estimated as a quotient of intensities of peaks attributed to Pr and Ph may be,
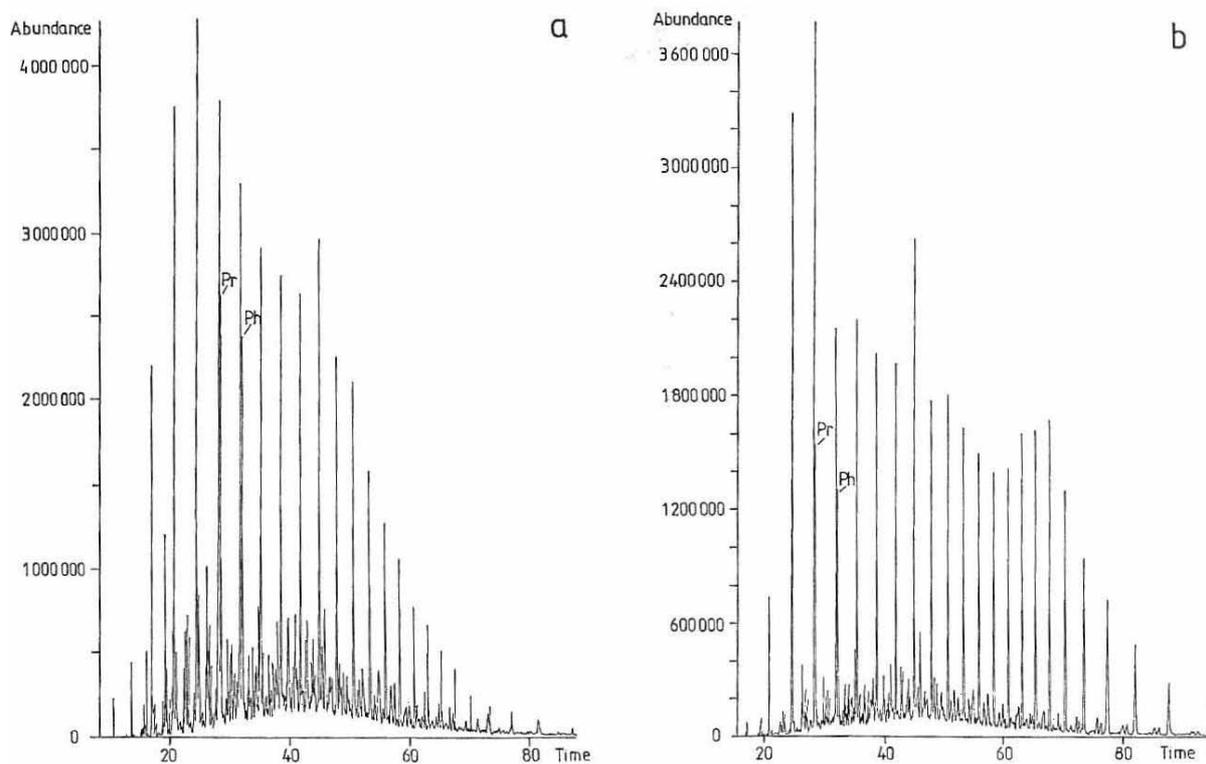
Fig. 5. Distribution of n-alkanes (m/z 71) in the bitumens from orthocoking coal (a) and the roof-shale (b) from Jastrzębie mine

<div style="text-align:right">

Table 2

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The values of parameters estimated from mass chromatograms (m/z71) for bitumens

Parent samples of analysed bitumens	Pr/Ph	Pr/C_{17}	Ph/C_{18}	$\dfrac{Pr + Ph}{C_{17} + C_{18}}$	CPI
Borynia mine:					
coal	1.9	1.2	0.6	0.9	1.0
roof-shale	2.1	1.1	0.5	0.8	1.0
floor-shale	3.1	1.2	0.4	0.8	1.0
Jastrzębie mine:					
coal	1.1	0.7	0.7	0.7	1.0
roof-shale	1.2	0.4	0.6	0.5	1.0
floor-shale	1.1	0.5	0.7	0.3	1.1
Moszczenica mine:					
coal	1.8	0.3	0.2	0.3	1.0
roof-shale	1.3	0.5	0.5	0.5	1.1
floor-shale	0.8	0.1	0.6	0.2	1.0
Siersza mine:					
vitrain	1.8	1.8	0.7	1.1	1.2
floor-shale in direct contact with coal layer	0.7	1.1	1.3	1.0	1.0
floor-shale	0.4	0.7	1.0	0.9	1.0
Milowice mine:					
montmorillonite	0.7	0.6	0.7	0.7	1.0

Pr/Ph — pristane to phytane ratio, Pr/C_{17} — pristane to n-alkane C_{17} ratio, Ph/C_{18} — phytane to n-alkane C_{18} ratio, CPI — index ratio of n-alkanes containing odd (C_{25}–C_{31}) and even (C_{24}–C_{32}) carbon atom numbers

therefore, an indicator of deposition conditions. The ratio Pr/Ph >1 may suggest the oxidative conditions of deposition, and very low values of this parameter (<0.6) can indicate organic matter deposed in anoxic, usually hypersalinar conditions. Moreover, for oils the values of Pr/Ph ≥3 ratio were attributed to terrestrial organic matter. The values of Pr/Ph ≤2 indicate marine derivation of organic matter and values of Pr/Ph of about 1–3 may testify to its lacustrine (algal) provenance. The Pr/C_{17} ratio is also an indicator of environment of deposition. The values of Pr/C_{17} >0.6 and Pr/C_{17} <0.5 can indicate terrestrial or marine environment, respectively (*op. cit.*).

It should be here mentioned, however, that the values of parameters under discussion are dependent on coalification degree. With thermal maturation of organic matter, values of parameter Pr/Ph increase (Alexander *et al.*, 1981) and values of Pr/C_{17} and Ph/C_{18} decrease (due to the increasing prevalence of the n-paraffins), and in the case of hard coals their utilisation is limited.

Both last mentioned ratios increase furthermore with biodegradation due to the loss of the n-paraffins (Hunt, 1995). It is because for analysed samples the parameters based on aliphatic compounds will be used mainly for general comparisons of values calculated for bitumens from coals and surrounding rocks.

The values were also estimated here for parameter $(Pr + Ph)/(C_{17} + C_{18})$, submitted to lower degree to influence of coalification process. Cooper (1990) has indicated that high contents of pristane and phytane in relation to n-alkanes C_{17} and C_{18} ($[(Pr + Ph)/(C_{17} + C_{18})] > 1$) suggested that organisms

influencing a sedimentary organic matter were derived from environment not distant from sedimentation place. Among analysed samples this situation could take place approximately in the case of samples from Siersza mine.

Carbon Preference Index (CPI) has been defined as a relative contribution of n-alkanes with odd and even number of carbon atoms in a range of C_{23}–C_{31}. This parameter was utilised for characteristics of sources and thermal maturity of oils and dispersed organic matter (Bray, Evans, 1961). The values of this parameter of about 1.0, obtained for all analysed samples, indicate a thermal maturity of organic matter of examined coals and surrounding rocks. A weak differentiation of the obtained values causes uselessness of this parameter for any comparisons.

Generally, the data presented in Table 2 show that the most similar characteristics of bitumens from coal and surrounding rocks can be observed first of all for samples from Jastrzębie mine but also for samples from Borynia mine. The similar values of particular parameters obtained for bitumens from coals and neighbouring rocks may suggest the migration process leading to equalisation of content of respective group of compounds between coal layer and surrounding rocks.

One should, however, suppose that a part of organic matter, genetically similar, could exist in coal and shale layers as early as from the first stages of sedimentation. This organic matter could be submitted subsequently to the same trends of chemical transformation.

The values calculated for bitumen from montmorillonite sample (treated here as a comparative sample) (Table 2) are the most similar to these estimated for bitumen from floor-shale from indirect contact with coal layer of Siersza mine.

Steranes

The main diagnostic molecular biomarkers in aliphatic fraction are steranes (m/z 217) and their rearranged analogues (diasteranes). The existence of these compounds was also stated in bitumens analysed here. Figure 6 presents an exemplary distribution of these groups of compounds. The interpretation of peaks presented in the text below was made according to Bendall *et al*. (1991). These authors emphasise that presence of distinctive amounts of diasteranes testify to the deposition environment with high content of clay minerals. Obtained here mass chromatograms m/z 217 of analysed bitumens indicated a considerable contents of diasteranes especially in extracts from coal-shales.

The representative of distribution of steranes: C_{27}, C_{28} and C_{29}-steranes may be used as indicator of deposition conditions. A predomination of C_{29}-steranes over C_{27}-steranes suggests terrestrial source of sedimentary organic matter and the opposite relation can indicate mainly aquatic (marine including) environment (Tissot, Welte, 1978).

For analysed bitumens, the comparison of relative intensities of respective peaks in mass chromatograms m/z 217 has shown the most distinct predomination of C_{29}-steranes in bitumens from samples from Borynia mine. It confirms the highest in this case values of Pr/Ph ratio indicating markedly oxic conditions of sedimentation of terrestrial organic matter.
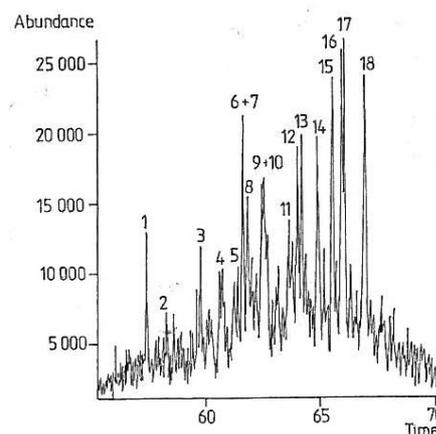

Fig. 6. Distribution of steranes (m/z 217) in the bitumen from the roof-shale from Borynia mine

However, for quantitative comparisons of sterane distribution the following parameter was used: C_{29} [$\alpha20S/(\alpha20S + \alpha20R)$] calculated on the basis of peaks no 15 and no 18 (Fig. 6). The results obtained for analysed samples are presented in Table 3. The data show a considerable difference in dependence on coalification degree between flame and orthocoking coals and surrounding rocks, except for floor-shale sample from Siersza mine. In the last case probable input of organic matter has taken place from other source of higher thermal maturation degree.

Bitumens obtained from coals and respective coal-shales from particular coal mines show similar relative contents of stereoisomers of C_{29}-sterane what can testify to similar but

Table 3

The values of parameter C_{29} ($\alpha\alpha20S/\alpha\alpha20S + \alpha\alpha20R$) estimated for aliphatic fractions of analysed bitumens

Parent sample	Parameter value
Borynia mine:	
coal	0.51
roof-shale	0.50
floor-shale	0.54
Jastrzębie mine:	
coal	0.48
roof-shale	0.41
floor-shale	0.41
Moszczenica mine:	
coal	0.64
roof-shale	0.50
floor-shale	0.63
Siersza mine:	
vitrain	0.10
floor-shale in direct contact with coal layer	0.11
floor-shale	0.47
Milowice mine:	
montmorillonite	0.35

independent genetic source of organic matter or a migration from coals to surrounding rocks.

M/z 217   Steranes and diasteranes

Number of
the band:

| 1	C_{27}	(20S)-13β(H), 17α(H)-diasterane
2	C_{27}	(20R)-13β(H), 17α(H)-diasterane
3	C_{28}	(20S)-13β(H), 17α(H)-diasterane
4	C_{28}	(20R)-13β(H), 17α(H)-diasterane
5	C_{27}	(20S)-5α(H), 14α(H), 17α(H)-cholestane
6	C_{29}	(20S)-13β(H), 17α(H)-diasterane
7	C_{27}	(20R)-5α(H), 14β(H), 17β(H)-cholestane
8	C_{27}	(20S)-5α(H), 14β(H), 17β(H)-cholestane
9	C_{27}	(20R)-5α(H), 14α(H), 17α(H)-cholestane
10	C_{29}	(20R)-13β(H), 17α(H)-diasterane
11	C_{28}	(20S)-5α(H), 14α(H), 17α(H)-24-metylocholestane
12	C_{28}	(20R)-5α(H), 14β(H), 17β(H)-24-metylocholestane
13	C_{28}	(20S)-5α(H), 14β(H), 17β(H)-24-metylocholestane
14	C_{28}	(20R)-5α(H), 14α(H), 17α(H)-24-metylochole-stane
15	C_{29}	(20S)-5α(H), 14α(H), 17α(H)-24-etylocholestane
16	C_{29}	(20R)-5α(H), 14β(H), 17β(H)-24-etylocholestane
17	C_{29}	(20S)-5α(H), 14β(H), 17β(H)-24-etylocholestane
18	C_{29}	(20R)-5α(H), 14α(H), 17α(H)-24-etylocholestane
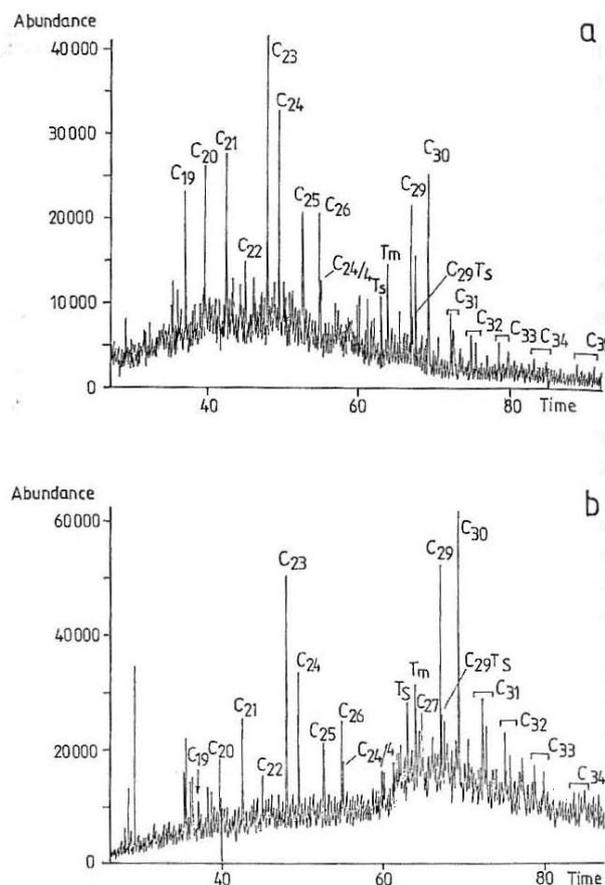
Fig. 7. Distribution of tricyclic diterpanes and hopanes (m/z 191) in bitumens from the coal (a) and roof-shale (b) from Jastrzębie mine

Tricyclic diterpanes and hopanes

Figures 7a and b present an exemplary distribution of tricyclic diterpanes (C_{19}–C_{26}) and hopanes. The existence of tetracyclic terpane $C_{24/4}$ is also marked there. The interpretation is given below of mass chromatogram m/z 191 of groups of hopanes and moretanes, according to (Bendall *et al.*, 1991).

The Tm/Ts ratio can be used also as an indicator of the thermal maturity (Seifert, Moldowan, 1978). With growth of temperature, the content of the compound of lower stability Tm decreases in relation to Ts. For interpretation a following relation was here applied between these two parameters: Ts/(Ts + Tm).

In Table 4 are shown the values of this parameter estimated from mass chromatogram (m/z 191) for a series of analysed samples. The highest values of this parameter were obtained for bitumens from samples from Borynia and Jastrzębie mines and the lowest ones for samples from Siersza mine, according to decrease of coalification degree. Among coal-shale samples, the highest values were estimated for bitumens from roof-shale samples from Borynia and Jastrzębie mines.

The ratio of peaks intensities of diastereoisomers (22S/22[S + R]) of aliphatic hopanoids homologs C_{31} and C_{32} are usually estimated for homohopanes. Among the relatively stables isomers αβ, the ratio of diastereoisomers contents increases with coalification degree of coals (with growth of

thermal maturation degree of organic matter) (Peters, Moldowan, 1993). Seifert and Moldowan (1986) have stated that values of parameter estimated from formula 22S/22[S + R] rise from 0 to about 0.6. Samples showing this ratio in the range 0.50 to 0.54 have barely entered oil generation, while ratios in the range 0.57 to 0.62 indicate that the main phase of oil generation has been reached or surpassed. Some oils exposed to very light thermal stress show 22S/22[S + R] ratios as low as about 0.55. Philp (1982) has described a crude oil from Australia with a 22S/22[S + R] ratio less than 0.50 (using the C_{31} homohopane).

A probable explanation was leaching or "solubilisation" of homohopanes from immature lignites in contact with the reservoir.

Hopanes and moretanes

Ts	C_{27}	18α(H)-22, 29, 30-trisnorneohopane
Tm	C_{27}	17α(H)-22, 29, 30-trisnorhopane
	C_{29}	17α(H), 21β(H)-30-norhopane
	C_{29}	18α(H), 21β(H)-29-norneohopane (C_{29}Ts)
	C_{29}	17β(H), 21α(H)-30-normoretane

C_{30} $17\alpha(H), 21\beta(H)$-hopane

C_{30} $17\beta(H), 21\alpha(H)$-moretane

C_{31} $(22S)$-$17\alpha(H), 21\beta(H)$-homohopane

C_{31} $(22R)$-$17\alpha(H), 21\beta(H)$-homohopane

C_{31} $(22(S+R))$-$17\beta(H), 21\alpha(H)$-homomoretane

C_{32} $(22S)$-$17\alpha(H), 21\beta(H)$-bishomohopane

C_{32} $(22R)$-$17\alpha(H), 21\beta(H)$-bishomohopane

C_{33} $(22S)$-$17\alpha(H), 21\beta(H)$-trishomohopane

C_{33} $(22R)$-$17\alpha(H), 21\beta(H)$-trishomohopane

C_{34} $(22S)$-$17\alpha(H), 21\beta(H)$-tetrakishomohopane

C_{34} $(22R)$-$17\alpha(H), 21\beta(H)$-tetrakishomohopane

C_{35} $(22S)$-$17\alpha(H), 21\beta(H)$-pentakishomohopane

C_{35} $(22R)$-$17\alpha(H), 21\beta(H)$-pentakishomohopane

Table 4

The values of parameters: Ts/(Ts + Tm), C_{31} $\alpha\beta22S$/ C_{31} $\alpha\beta22[S + R]$ and C_{32} $\alpha\beta22S$/C_{32} $\alpha\beta22[S + R]$ estimated for investigated bitumens on the basis of mass chromatograms (m/z191) of hopanes

Parent sample	Ts/(Ts + Tm)	C_{31} (22S/22[S + R])	C_{32} (22S/22[S + R])
Borynia mine:			
coal	0.56	0.56	0.58
roof-shale	0.79	0.58	0.59
floor-shale	0.42	0.58	0.60
Jastrzębie mine:			
coal	0.75	0.58	0.55
roof-shale	0.90	0.57	0.58
floor-shale	0.68	0.39	0.59
Moszczenica mine:			
coal	0.50	0.43	0.47
roof-shale	0.39	0.56	0.56
floor-shale	0.29	0.55	0.52
Siersza mine:			
vitrain	0.16	0.55	0.61
floor-shale in direct contact with coal layer	0.13	0.32	0.38
floor-shale	0.26	0.37	0.46
Milowice mine:			
montmorillonite	0.28	0.45	0.44

The data obtained here for analysed samples (Table 4) indicate therefore (with comparison with literature data) a possibility of generation of oil by orthocoking coals from Borynia and Jastrzębie mines and also by flame coal from Siersza mine (border values of 22S/22[S + R] parameters in the range: 0.55–0.61).

In the case of coal sample from Moszczenica mine, the lower values of parameters under discussion could be a result of mentioned earlier effects of leaching of homohopanes (Philp, 1982). Other parameters as for example phenanthrene indexes presented below indicate, however, a higher degree of thermal maturation of analysed coal from Moszczenica mine in relation to coal samples from Borynia and Jastrzębie mines.

The similarity of these parameters values between bitumines from coals and surrounding rocks, from Borynia and Jastrzębie mines, might additionaly confirm an assumption in these cases of migration possibilities of organic matter from coals to rocks.

Aromatics

For characterisation of coaly organic mater, the especially advantageous parameters are these consisting of estimation of relations between aromatic compounds. The contents of these compounds tend to increase with coalification degree, and it is because they are of a great importance for differentiation of higher stages of thermal maturation.

For aromatic fractions of analysed bitumens, the values of methylphenanthrene index were estimated as follows, after Radke (1988):

$$MPI_3 = \frac{[2 - MP] + [3 - MP]}{[1 - MP] + [9 - MP]}$$

where symbols 2-MP, 3-MP, 1-MP and 9-MP signify respectively: 2-, 3-, 1-, 9-methylsubstituted phenanthrene rings. This index was estimated on the basis of intensity of respective peaks from the mass chromatogram m/z 192 (an example is given for montmorillonite bitumen on Figure 8a). The choice of presented methylphenanthrenes for this formula was justifiable by difference of stability of particular isomers among which isomers 1-MP and 9-MP are of lower stability than isomers 2-MP and 3-MP. It is because the calculated values of MPI_3 parameter should increase with rise of transformation degree of fossil organic matter.

In Table 5 the values of parameter under discussion are presented for analysed samples. Other parameter is there also shown: dimethylphenanthrene index DMPI calculated as a ratio

Table 5

The values of methylphenanthrene index (MPI_3) and dimethylphenanthrene index (DMPI) estimated on the basis of mass chromatograms m/z 192 and m/z 206, respectively, for analysed bitumens

Parent samples	MPI_3	DMPI
Milowice mine:		
montmorillonite	0.9	0.8
Borynia mine:		
ortocoking coal	1.0	1.1
roof-shale	1.0	1.4
floor-shale	1.0	1.3
Jastrzębie mine:		
ortocoking coal	1.3	1.6
roof-shale	not detected	1.4
floor-shale	1.4	1.8
Moszczenica mine:		
ortocoking coal	1.5	1.9
roof-shale	1.4	1.8
floor-shale	1.5	1.6
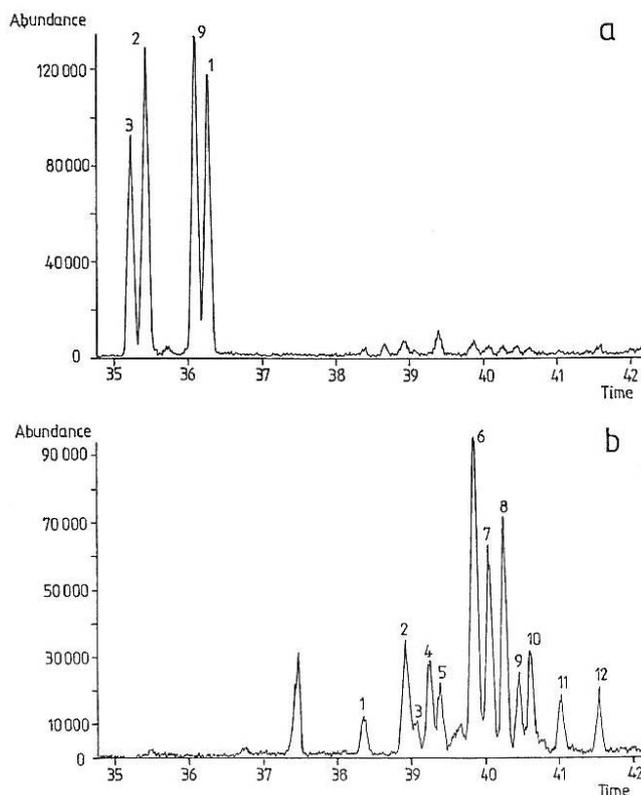
Fig. 8. a: **Distribution of methylphenanthrenes (m/z 192) in bitumen from montmorillonite from Milowice mine**

1 — 1-methylphenanthrene, *2* — 2-methylphenanthrene, *3* — 3-methylphenanthrene, *9* — 9-methylphenanthrene

b: **Distribution of dimethylphenanthrene (m/z 206) in bitumen from montmorillonite from Milowice mine**

1 — 3-ethylphenanthrene, *2* — 9-ethylphenanthrene + 2-ethylphenanthrene, *3* — 1-ethylphenanthrene, *4* — 2, 6-dimethylphenanthrene, *5* — 2, 7-dimethylphenanthrene, *6* — 2, 9- dimethylphenanthrene + 2, 10-dimethylphenanthrene + 3, 10-dimethylphenanthrene + 1, 3-dimethylphenanthrene, *7* — 1, 6-dimethylphenanthrene + 2, 9-dimethylphenanthrene, *8* — 1, 7-dimethylphenanthrene, *9* — 2, 3-dimethylphenanthrene, *10* — 1, 9-dimethylphenanthrene, *11* — 1, 8-dimethylphenanthrene, *12* — 1, 2-dimethylphenanthrene

of intensity of peaks no 8 and 9 derived from 2, 3- and 1, 9- dimethylphenanthrene (Fig. 8b).

The highest values of parameters presented in Table 5 were obtained for bitumens from coal and surrounding rocks from Moszczenica mine. They indicate the highest degree of thermal maturation for these samples. The comparison of the results obtained for particular orthocoking coals and surrounding rocks shows similar characteristics of respective bitumens. It may be a result of migration equalising concentrations and next /or simultaneous process of coalification of organic matter and surrounding rocks, especially when accelerated by action of elevated temperature.

Taking into account a specific structure of orthocoking coals, it seems however, very probable an expulsion process of oil from coal to surrounding rocks.

In a recapitulation it should be mentioned that at first it was considered that humic coals may be only a gas source (Hunt, 1995). It was also stated that only sapropelic boghead and cannel coals can be the oil sources. However, it has appeared that also some humic coals contain appreciable quantities of liptinic material as solid fillings, coatings or invisible impregnations. Many humic coals that appear to be made up primarily of vitrinite and inertinite, under ordinary reflected light show laminations or pockets of fluorescence under reflected blue light. This is characteristic of oil-generating sapropelic organic matter. Such data indicate that some humic

coals and associated coal-shales may contain oil-generating organic matter (*op. cit.*).

In the case of some analysed coals and surrounding rocks, a possibility was stated of organic matter migration from coal layers to surrounding rocks. It was mainly concluded on the ground of the data obtained from calculation of hopanoid distribution parameters (using C_{31} and C_{32} homohopanes) (Table 4). The results obtained from calculations and compared with literature data (Seifert, Moldowan, 1978) suggest that oil prone is the most probable orthocoking coal from Borynia mine but also orthocoking coal from Jastrzębie mine, and it is also possible from the flame coal from Siersza mine. In the last case, however, the relatively low yields of bitumens from surrounding rocks (in relation to the yield for analysed associated coal represented here by vitrain), compared with relative samples from Borynia and Jastrzębie mines have suggested among others the considerable dependence of oil potential on a stage of coalification and thermal gradient.

A hypothesis has been, therefore, made that a stage of orthocoking coal with its specific structure (known as a structure of the "liquid" type) may cause that orthocoking coals can show the oil prone potential. In this coalification stage, the structure of coal macromolecule is already not so cross-linked as in the case of coals of lower coalification degree. In the orthocoking stage of coalification, the thermally destructed peripheric structures give probably an input to coal molecular phase. This input (together with mobile components of liptinite) is probably responsible for formation of bitumens.

It seems, therefore, possible to estimate a probability of organic matter migration in the short distance between coal and surrounding rocks by comparison of extraction yields, group composition of bitumens (taking, however, into consideration a process of geochromatography), and distribution of chosen individual biomarkers. It should be confirmed, however, by comparison of analysis results of greater number of samples of various genesis and characteristics.

CONCLUSIONS

In this work the results were submitted to discussion concerning the extraction yield, group composition and the data obtained by gc-ms analysis of bitumens isolated from analysed coals and surrounding rocks. It has been stated that some of the analysed coal samples could be oil prone. Using parameters calculated from distribution of chosen homohopanes (C_{31} and C_{32}) and comparing them with literature data, it has been shown that the most probable ability to oil expulsion, among analysed coal samples, were orthocoking coals from Borynia and Jastrzębie.

It enabled to make a hypothesis that in the orthocoking stage of coalification there could be possible the formation of additional amounts of bitumens (besides these from liptinite components) as a result of thermal maturation processes characteristic for this coalification stage. In the case of analysed coals from Rybnik Coal District, this effect of thermal maturation could be enhanced by additional heat flows from regional metamorphism phenomena and/or natural burning processes of coal layers. Other factors (besides temperature gradient and heat of intrusive bodies) responsible for migration of organic matter from coals to surrounding rocks seems to be also a circulating, transporting water (especially in the case of polar compounds), hydrothermal solutions and also probably, to certain degree, a concentration gradient of organic matter between coal layers and surrounding rocks. The investigations and conclusions presented here should be regarded as preliminary ones. It is necessary to investigate yet a greater number of samples of various geological characteristics and to make additional petrological analysis of organic and inorganic rocks as well as a raw of pyrolytic examinations.

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