



## Organic geochemistry of the Grodziec beds (Upper Carboniferous); Upper Silesian Coal Basin, Poland

Grażyna BZOWSKA, Monika FABIĄŃSKA, Aniela MATUSZEWSKA, Maria RACKA and Urszula SKRĘT

Bzowska G., Fabiańska M., Matuszewska A., Racka M. and Skręt U. (2000) — Organic geochemistry of the Grodziec beds (Upper Carboniferous); Upper Silesian Coal Basin, Poland. *Geol. Quart.*, 44 (4): 425–437. Warszawa.

Five lithologically different rock samples from the “Niwka” brickyard exposure, including one coal sample, were geochemically characterised as regards their mineral composition and sedimentary organic matter present in them. Various methods, including: X-ray diffraction, solvent extraction, group separation by preparative thin layer chromatography, infra-red spectroscopy for assessment of the content of different functional groups in total rock extracts and their separated polar compound fractions, and capillary gas chromatography for analysis of aliphatic hydrocarbon fractions. It was found that the “Niwka” brickyard rocks are rich in organic material present as the plant detritus (cane-break) or as compounds adsorbed on clay and carbonaceous minerals. Yields of bitumen extraction, group composition of extracts and content of various functional groups assessed by infra-red spectra seem to be related to mineral composition of the host rocks and type of kerogen present. Higher contents of clay minerals, especially chlorite, enriches both extracts and their polar compound fractions in aliphatic structures while the organic matter of both sandstones analysed contains more condensed aromatic structures and functional oxygen groups. Generally the organic matter of the host rocks was deposited in an oxic environment and belongs to type III kerogen with a dominant terrestrial biogenic source or to type II kerogen of bacterial/terrestrial origin of primary biogenic matter. Its thermal maturity stage can be estimated as end-diagenetic or early catagenetic. The highest maturity is shown by the organic matter in the basal sandstone (the S2 sandstone) and probably is caused by input of older migrating bitumen. Biodegradation of organic matter seems to be influenced by the mineral composition of the host rock, with a high content of clay minerals giving protection.

*Grażyna Bzowska, Monika Fabiańska, Aniela Matuszewska, Maria Racka and Urszula Skręt, Faculty of Earth Sciences, Silesian University, Będzińska 60, PL-42-700 Sosnowiec, Poland (received: April 18, 2000; accepted: May 29, 2000).*

Key words: Upper Silesia, Carboniferous, sedimentary organic matter, bitumen, capillary gas chromatography, infra-red spectrometry, X-ray diffraction, *n*-alkanes, hopanes.

### GEOLOGICAL SETTING

The samples of coal and adjacent strata analysed come from the “Niwka” brickyard (Sosnowiec) where Carboniferous shale and Quaternary clays are exploited. At present, the raw material for bricks production comes only from the basal strata, represented by three distinctive units of Carboniferous deposits. Most of the quarry area is now covered by slipped waste material.

The exposed sedimentary deposits belong to the Upper Namurian A beds (the Grodziec beds). According to the most recent Carboniferous stratigraphy (Bojkowski, 1967; Dembowski, 1972), the Namurian A deposits comprise the marine Kijowiec beds and the Paralic Series with the Pietrkowice, Gruszów, Jakłowice and Poręba beds. In earlier

stratigraphical schemes (Stopa, 1957, 1967), these have been assigned to a “marginal series”. Sediments of this group are formed slightly differently in the western and northeastern parts of the Upper Silesian Coal Basin. In the northeastern region the Malinowice, Sarnów, Florów and Grodziec beds are distinguished. The Grodziec beds start with a thick bed of sandstone, above which the characteristic Barbara marine seam is present (horizon 630). The upper part of these deposits is composed of siltstones and mudstones containing thin intercalations of coal belonging to the 600 group (Ozonkowa, 1979).

In the Sosnowiec area and around “Niwka” the Grodziec beds (now classified as the Poręba beds) are found with a NW–SE strike and an average angle of dip about 15°. Beds of the brickyard are deposited below the 620 bed (Geological documentation 196). Exposed parts of the deposit are represented by three units:

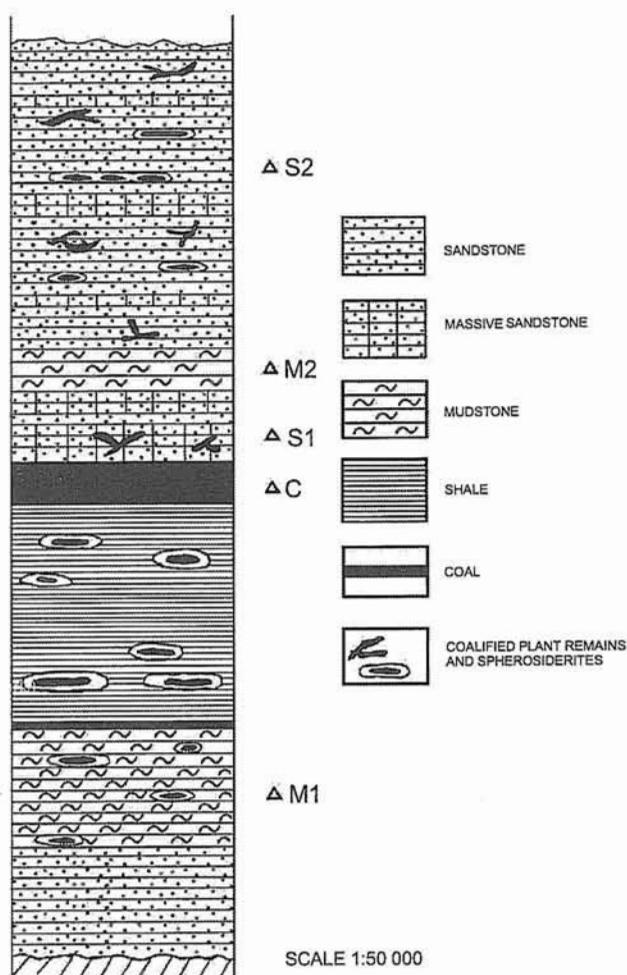
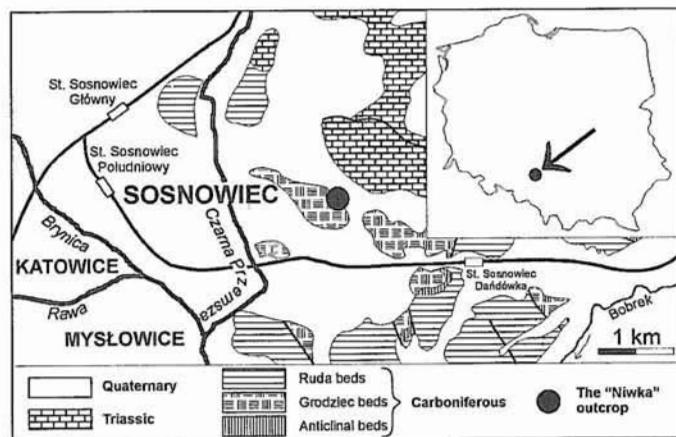


Fig. 1. Location and lithostratigraphic profile of the "Niwka" brickyard exposure

1. Grey silty and sandy mudstones with numerous coalified plants.

2. Variably interbedded light grey sandstones and mudstones and, locally, laminated black siltstones; the sandstone layers contain thin laminae of bright coal.

3. A massive micaceous sandstone.

These deposits often contain nodules of clayey spherosiderite with both sharply bounded and gradational external contacts (Fig. 1).

## AIMS OF WORK

The "Niwka" exposure is of considerable interest. The deposits there belong to the Grodziec beds within the Paralic Series of Upper Carboniferous age, found only in the eastern part of the Upper Silesian Coal Basin, and locally exploited for bituminous coal. The coal is found at depths of tens to a few hundreds of metres but since closure of the mines exploitation of the deeper lying coals has been terminated. As a result, the Grodziec beds are exposed now only in the "Niwka" brickyard exposure. In this part of the basin it is the last exposure of the Carboniferous clay-mudstone-sandstone rocks used in brick production, since all other Carboniferous exposures have been closed and backfilled. Numerous well preserved plant fossils are present at "Niwka" outcrop, especially in the sandstone face. These rocks represent an important part of the regions geological history, which were not characterised geochemically.

We employed chromatographic and spectroscopic analytical methods (Waples and Mahichara, 1991; Peters and Moldowan, 1993). Our research aimed to characterise the geochemistry of the coals of the "Niwka" brickyard together with that of organic matter in the adjacent deposits. The analysis involved solvent extraction, group separation by preparative layer chromatography (PLC) and then capillary gas chromatography/mass spectrometry analysis of aliphatic and aromatic components. Separated polar fractions and total, non-separated extracts of host rocks were analysed by infra-red spectroscopy.

These methods gave information on the type of primary biogenic organic matter, the geochemistry of the depositional environment including the biogeochemical alteration of organic deposits, and an estimation of thermal maturity.

Factors influencing organic composition include the depositional setting and the nature of the co-occurring inorganic phases. The latter can form organic-mineral complexes and act as catalysts or inhibitors of organic geochemical processes (Kowalska *et al.*, 1994). Therefore, organic analysis was preceded by mineralogical characterisation of the host rocks surrounding the coal bed using X-ray diffraction. The relationship of rock composition to the type and amount of extracted organic matter is discussed below.

## EXPERIMENTAL

### SAMPLE DESCRIPTION

Samples of 500–1000 g were taken from the "Niwka" brickyard. Sample properties and lithology are described in Table 1. Samples were dried and manually cleaned from surface contamination. Thin sections were prepared, and analysed using a *Polam R-113* polarising microscope.

Table 1

## Sample properties, lithology, short description and extractability

Sample code	Lithology	Sample description	EOM (% wt:wt)
S2	sandstone	grey sandstone with fragments of coalified appendices and cane break	0.12
M2	mudstone	slightly laminated, grey mudstone layer containing siltstone laminac	0.22
S1	sandstone	poorly laminated, grey, quite hardsandstone with aligned coaly fragments	0.10
C	coal	band of humic bright coal	3.53
M1	mudstone	dark grey mudstone containing laminac of brown siderite	0.43

EOM — extractable organic matter; %, wt:wt — calculated a weight:weight percentage ratio

## X-RAY DIFFRACTION

The mineralogical composition of the rocks was obtained using a *Geigerflex* X-ray diffractometer, *Rigaku-Denki* (Japan), in the following analytical conditions: Co lamp  $\alpha$  with Fe filter, time of limit counting — 3 s, step scanning (ss) — 0.01 or 0.02°. Four rock samples were analysed with the following codes: M1 — from the rock unit (1); S2 and M2 — from the unit (2); and S2 — from the bed (3). Diffractograms were prepared from bulk samples and from separated fractions with a grain diameter of about 1  $\mu$ m; the bulk samples were treated ultrasonically to break down aggregates and for easier separation of the clay fraction.

## INFRA-RED SPECTROSCOPY

The infra-red spectra of coal samples, extracts and eluted polar fractions obtained from the coal and surrounding rocks were obtained using the kalium bromide pellets technique (for solid samples) and the thin film technique (for tar consistency samples). In Table 2 the results of qualitative and semiquantitative analysis are shown. The latter consists of estimation of absorbance values for particular bands and subsequent calculation of normalised values. The normalised value of absorbance is the ratio of the band absorbance to the absorbance of the intense and well shaped band at a wavenumber of 1460  $\text{cm}^{-1}$  (Kett, 1961; Jurkiewicz *et al.*, 1985).

## SEPARATION OF BITUMINOUS FRACTION

The powdered samples were exhaustively solvent extracted in a *Soxhlet* apparatus using a mixture of dichloromethane (DCM) and methanol = 93:7 (volume:volume — v:v) (previously distilled) over 48 hours. Depending on organic matter content, different amounts were treated: 250–300 g for

mudstones and sandstones and 40 g for coal. Table 1 gives the yields of extractable organic matter (EOM) together with results of elemental analysis done by a combustion method.

## GROUP SEPARATION

The host rock extracts were separated by preparative layer chromatography (PLC) into aliphatic, aromatic and polar compound fractions (NSO compounds). Solved samples (50–70 mg in  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 80:20$ ; v:v) were applied as bands onto 20 x 20 cm semi-preparative glass plates pre-coated with silica gel 60 F<sub>254</sub> (Merck); thickness of a sorbent bed = 0.5 mm, previously cleaned by acetone and activated at 105°C (30 min). Plates were developed in a thin layer chromatography tank (TLC) (40 min in saturated vapour conditions) with *n*-hopane used as a developer. The fractions were differentiated by fluorescence of aliphatic (lack of fluorescence) and aromatic bands (blue-violet) in UV light and by comparing with reference compounds (*n*-eicosane, phenanthrene and isoquinoline) developed on the same plate. The received fractions were eluted from silica gel in short glass columns by dichloromethane (aliphatic and aromatic compounds) or by a mixture of  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 80:20$  (v:v) (polar compounds). Figure 2 shows the group composition of samples.

## GAS CHROMATOGRAPHY

The composition of separated aliphatic compounds fractions was analysed by capillary gas chromatography using a *Fisson* gas chromatograph with a Rtx-1 capillary column 25 m long (i.d. = 0.32 mm) coated by a 0.52  $\mu$ m stationary phase in the following conditions: carrier gas — He (*f* — 2.0 ml/min), the temperature program — 100°C (0 min), heating rate to 300°C — 5.5°C/min, final temperature — 310°C (10 min), amount of injected sample — 1.2  $\mu$ l of 0.1  $\mu$ g/ml solution in dichloromethane (DCM), the injector temperature — 315°C,

Table 2

Qualitative interpretation of spectra and normalised values of absorbances of chosen bands from infrared absorption spectra of extracts and eluted polar fractions

Wave-number [cm <sup>-1</sup> ]	Interpretation	Samples									
		extracts					NSO polar fraction (eluted)				
		M1	S1	M2	S2	C	M1	S1	M2	S2	C
3060	v C-H <sub>ar</sub>	0.5	0.8	0.6	0.6	0.6	0.6	0.5	0.7	0.6	0.8
2960	v C-H <sub>al</sub>	2.1	1.6	1.9	1.8	1.6	1.5	1.3	1.4	1.5	1.3
2895	v C-H <sub>al</sub>	1.2	1.1	1.3	1.2	1.0	0.9	0.9	0.9	1.0	1.0
1750	v C=O	0.3	0.3	0.2	0.2	0.2	0.3	0.2	0.3	0.3	0.4
1720	v C=O	0.5	0.6	0.6	0.5	0.4	0.6	0.4	0.6	0.6	0.6
1660	v C=O	0.8	0.6	0.6	1.0	1.0	0.7	0.8	0.7	0.6	0.8
1620	v C=C <sub>ar</sub> v C=O	1.1	0.8	0.9	1.3	1.5	1.0	1.2	1.0	0.9	1.0
1500	v C=C <sub>ar</sub>	0.4	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.7	0.7
1380	δ C-H(CH <sub>3</sub> )	0.7	0.7	0.7	0.7	0.8	0.8	0.9	0.7	0.7	0.9
1270	v C-O	0.6	0.6	0.6	0.5	0.7	0.7	0.7	0.7	0.7	0.8
855	δ C-H <sub>ar</sub>	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2
820	δ C-H <sub>ar</sub>	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2
750	δ C-H <sub>ar</sub>	0.1	0.3	0.3	0.2	0.2	0.2	0.1	0.2	0.3	0.4

v — stretching vibrations; δ — deformation vibration; al, ar — aliphatic and aromatic compounds, respectively; NSO — nitrogen, sulphur and oxygen polar compounds

flame ionisation detector (FID) temperature — 315°C. The gas chromatograph worked together with an IBM computer registering chromatograms using the CHROM-CARD program. Compounds belonging to *n*-alkanes, alkylcyclohexanes, acyclic isoprenoids and hopanes were identified partially by their retention times compared to retention times of standard compounds and partially by comparing chromatograms with data presented in geochemical papers and similar researches done previously by the gas chromatography-mass spectrometry method.

## RESULTS AND DISCUSSION

### GENERAL CHARACTERISTICS OF THE HOST ROCK MINERAL COMPOSITION

The mineral composition of the four rock samples from different lithostratigraphic levels investigated in thin sections and by X-ray diffraction analysis shows variability, both in the crude (non-separated) samples and in their separated fractions of about 1 μm grain size.

Dark grey mudstone (M1) from the second rock unit, with laminae of brown siderite, contains quartz and feldspar grains of fine silt size. The rock is distinctively laminated. Elongated

coaly fragments and tiny mica flakes (muscovite and biotite) are aligned. The mineral composition is similar to the second investigated mudstone of the third unit (M2) with slightly different quantities of particular minerals as confirmed by sample diffractograms (Figs. 3, 4).

The strongest peaks in the diffractogram of the crude sample M1 (non-separated) represent quartz grains the content of which is higher here than in the M2 mudstone. The other mineral constituents, such as: chlorite, plagioclase, siderite, fine-grained muscovite, probably together with biotite, the 2M<sub>1</sub> polytype of illite and kaolinite have been found in amounts of several percentage. The diffractogram base line also indicates the presence of coaly substances, the geochemical analysis of which is described below.

The diffractogram of this mudstone separated fraction (about 1 μm) is characterised by intense reflections of chlorite of clinoclone type, mixed with medium arranged kaolinite. An important component of the rock seems to be the 2M<sub>1</sub> polytype of illite with an admixture of very fine-grained muscovite. Quartz and calcite are also present, together with small quantities of siderite. Coaly organic matter coats pelitic grains of calcite and siderite causing their apparent lightness and presence in the separated 1 μm fraction instead of in the crude sample.

The third rock bed unit is represented by two sandstone sample (S1 and S2) and mudstone (M2). The S1 sandstone is

macroscopically grey, quite hard, with a high content of scattered mica flakes. Its thin section shows silt with irregularly distributed sand grains. This sandstone is poorly laminated, with lamination indicated by elongated coaly fragments. The main components are quartz and less abundant feldspar and mica, represented by muscovite as well as by partially weathered biotite. A large number of lenticular aggregates of fine-grained siderite were found. The groundmass consists of clay minerals identified by X-ray diffraction.

The strongest peaks represent quartz while other mineral constituents, identified as chlorite of clinocllore type with a kaolinite admixture, fine-grained muscovite probably together with biotite, feldspars (albite-oligoclase and probably microcline) and an admixture of siderite, have been found in the range of several percentage. The separated fraction shows mineral reflections attributed to the 1Tc polytype of kaolinite with chlorite, 2M<sub>1</sub> polytype of illite and very small amounts of calcite. Organic matter was also found, decreasing the sharpness of peaks and "dissolving" other mineral phases.

Grey mudstone (M2) of the third unit contains tiny mica flakes and white feldspar grains visible to the naked eye. In thin section it shows slight lamination with aligned mineral grains, especially mica. In some places there are siltstone laminae of various thickness, picked out by mica flakes, of both biotite and muscovite. Mica flakes range, up to 1 mm in diameter. Irregular, lensoid aggregates of very fine-grained siderite were also seen. Quartz and less common feldspar grains are poorly rounded to angular.

The rock groundmass is slightly greenish and its components are difficult to recognise but comprise clay minerals, identified by X-ray diffraction. The diffractogram of the crude sample indicated quartz as the main component, together with chlorite of clinocllore type and 2M<sub>1</sub> polytype of muscovite. Kaolinite and feldspars (acid plagioclase) are present in small quantities. Siderite was found in trace amounts.

The X-ray diffractogram of the 1 µm sample fraction shows the strongest reflections for chlorite of clinocllore type mixed with kaolinite, which form the groundmass of the M2 mudstone. The second important component of the sample is very fine-grained 2M<sub>1</sub> polytype of muscovite, probably mixed with very small amounts of illite. The presence of biotite cannot be confirmed because its reflections largely overlap in with those of muscovite and contents of these mica types are too low compared to the other components to assess them unambiguously.

This sample is characterised by its fine-grain and by the presence of amorphous coaly substances as shown by the raised base line of the diffractograms, and by the oscillation and low distinctness of some reflections.

The last sandstone sample (S2) of this rock unit has light grey laminae with mica flakes and coaly fragments along on bedding planes. Fragments of coalified appendices and cane-break were found on these planes.

In thin section view it shows a variable grain size of angular quartz and feldspar. Some feldspar grains are twinned. There are also flakes of mica: muscovite, biotite and fine-needle

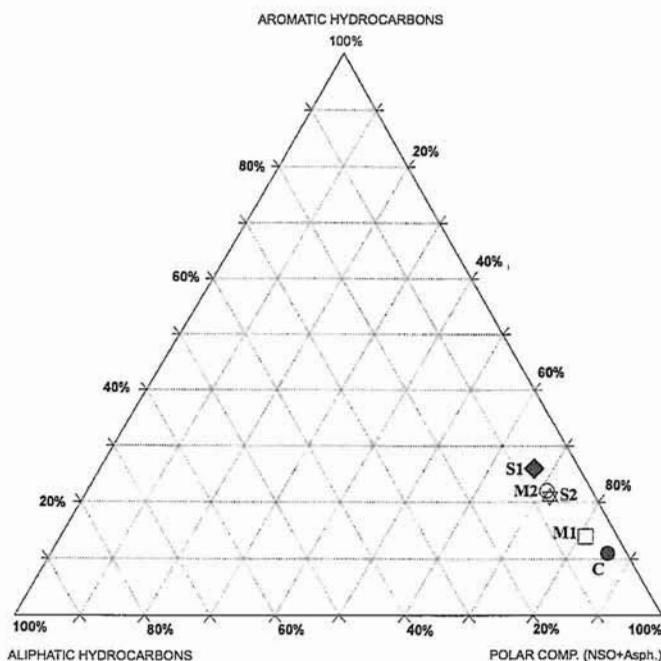


Fig. 2. The group composition of the "Niwka" rock extracts

shaped illite. Biotite flakes have been partly altered to chlorite and a few of them are discoloured, with iron oxyhydroxide rims. Irregular aggregates of very fine-grained siderite and single grains of garnet and zircon were recognised. The rock groundmass is clayey but individual minerals are difficult to identify.

The X-ray diffractogram of the bulk sample is characterised by the highest content of quartz. Other constituents are feldspars (albite-oligoclase) and small amounts of 2M<sub>1</sub> polytype of muscovite and, probably biotite. Low quantities of siderite and ankerite were found. The cement consists of chlorite and kaolinite.

The X-ray diffractogram of the separated fraction (1 µm grain size) has shown that the main cement component is 1Tc polytype of kaolinite with small amounts of calcite and coaly organic matter, as the base line of the diffractogram shows.

#### EXTRACTABILITY AND GROUP COMPOSITION

The yields obtained (Tab. 1) correlate with differences in mineralogical composition. The coal sample (C) with the greatest organic content also shows the highest yield of extract, followed by the mudstone sample, while sample M1 had a higher yield than sample M2. Sample M1 contained the most chlorite, a mineral of high sorptive properties. Coal substance is also associated with calcite and siderite. The lowest yield was in the sandstone samples. The sorptive and catalytic properties of clay minerals (Stoch, 1974; Kowalska *et al.*, 1994) in the rocks adjacent of the coal layer are probably connected with the consider-

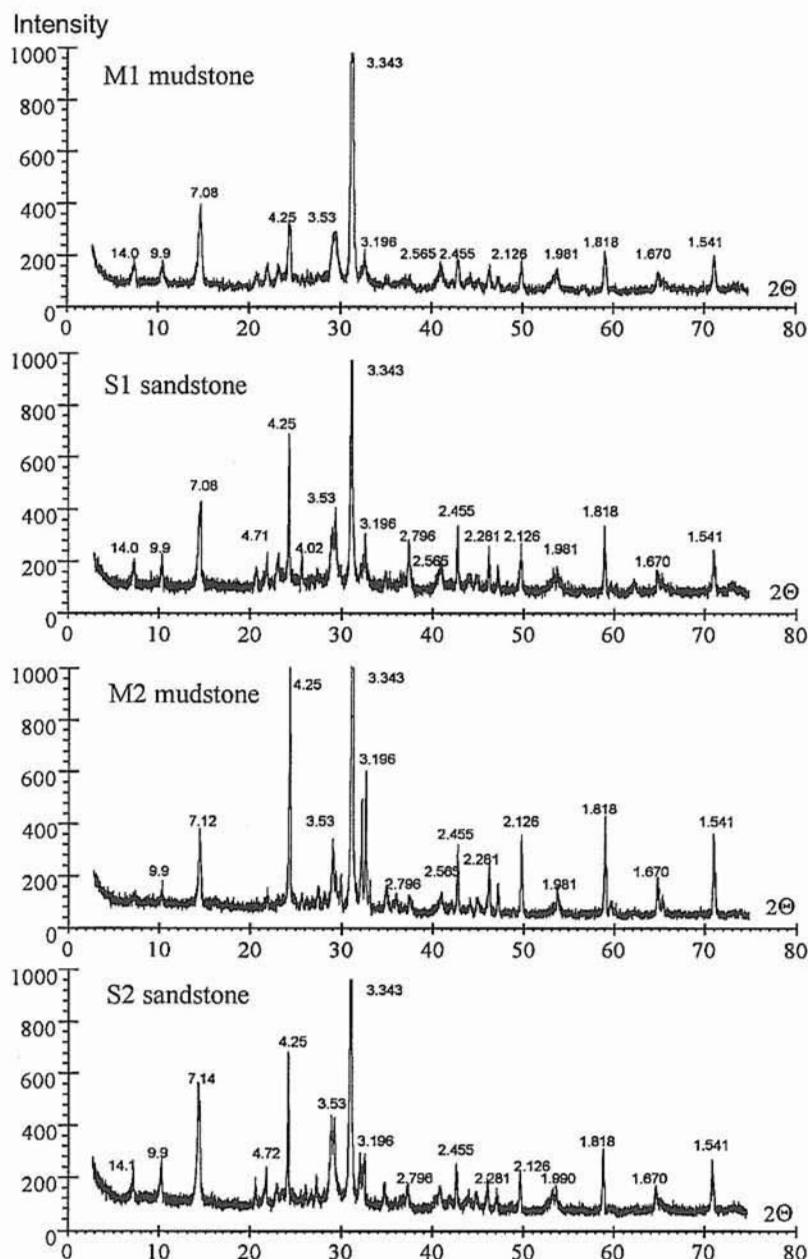


Fig. 3. Diffractograms of natural rock samples from the "Niwka" brickyard

able amount of polar compounds in the extracts obtained. The highest total yield of the polar fraction occurred in the chlorite-rich M1 mudstone sample (Fig. 2), which also showed the lowest yield of non-eluted polar fraction and the greatest yield of eluted polar fraction. This may show that the chemistry of its polar fraction is simple which a relatively low degree of condensation. In the coal sample (C), though, the greatest yields of total polar fraction and non-eluted polar fraction and the lowest yield of eluted polar fraction were obtained. This indicates the condensed and polymolecular character of the organic coal-material.

Generally, the group composition of all extracts is dominated by polar compounds. This is characteristic for terrestrially derived organic matter (i.e. from vascular plants) such as humic coals and type III kerogen and agrees with macroscopic observations (numerous appendices of cane break in both the analysed sandstones and in the layer of humic coal). There is similarity between the group compositions of bituminous extracts of both analysed sandstones (samples S1 and S2) and one of the mudstones (M2) while the group composition of coal bitumen and the extract of mudstone rich in chlorite (M1) were different. Extracts of the first mentioned group were richer in aliphatic compounds (6.6–6.9%) and the lowest aliphatic hy-

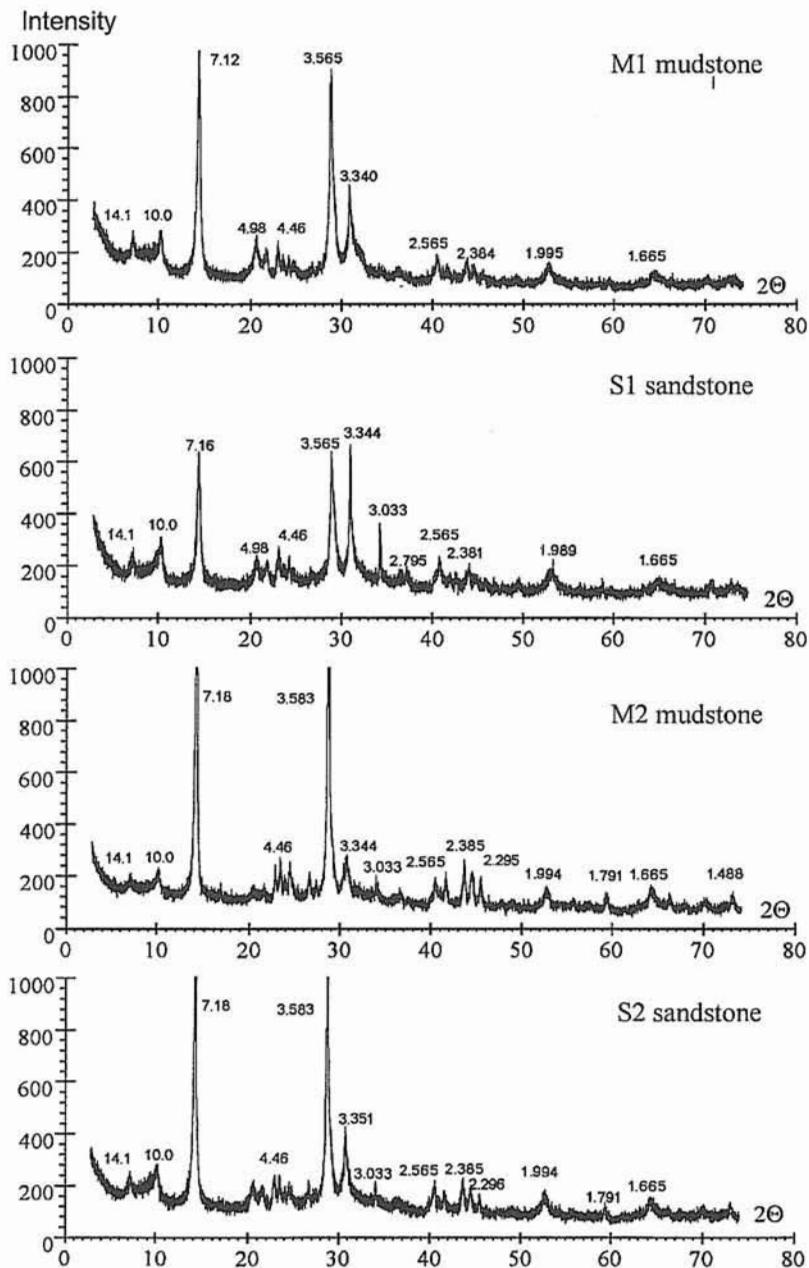


Fig. 4. Diffractograms of separated fractions of the "Niwka" rock samples

drocarbon content has been found in the coal extract (3.5%). The highest concentration of aromatic hydrocarbons was found in the bitumen from sandstone from the base of coal bed and the lowest was in the coal extract.

#### INFRA-RED SPECTROSCOPY RESULTS

The results of infra red analysis are shown in Table 2 and Figure 5a–c. The spectrum of the parent coal shown in Figure 5c indicates a low degree of transformation of coal organic matter as expressed by the magnitude of bands attributed to

aliphatic ( $1460, 2800\text{--}3000\text{ cm}^{-1}$ ), aromatic ( $750\text{--}850\text{ cm}^{-1}$ ) and oxygenic ( $1100\text{--}1300, 1610, 1700\text{ cm}^{-1}$ ) structures.

The IR spectra of extracts and polar fractions are similar in shape (Fig. 5a, b). The most distinctive are bands in attributed to the aliphatic, aromatic and oxygenic groups, respectively at:  $1380, 1460, 2800\text{--}3000\text{ cm}^{-1}$ ;  $700\text{--}900, 1500\text{--}1600, 3060\text{ cm}^{-1}$ ;  $1000\text{--}1300, 1600\text{--}1800\text{ cm}^{-1}$ . Comparison of normalised absorbance values indicates a generally higher contribution of oxygenic structures of the C=O and C–O type in the eluted polar fractions than in the total extracts (Tab. 2). However, the aliphatic structure contribution is lower in the separated polar

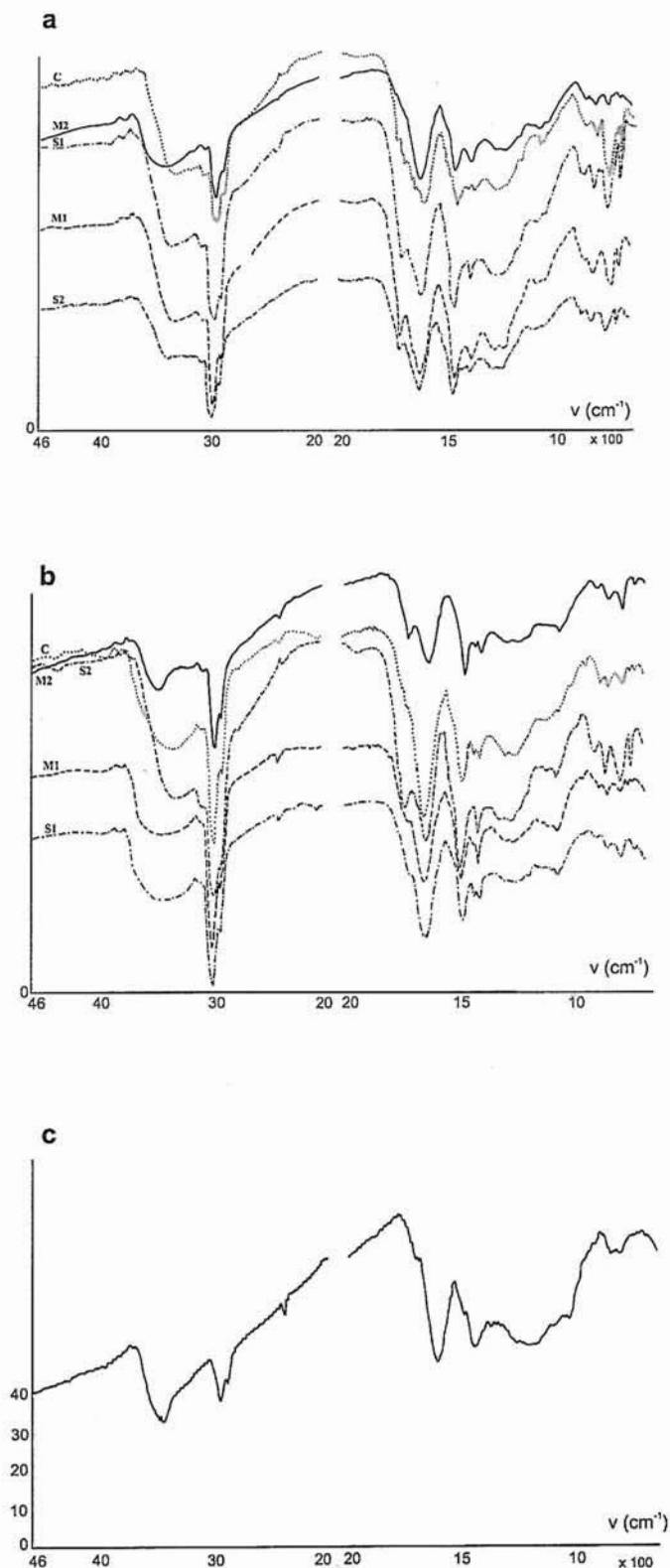


Fig. 5. IR spectra of the chosen samples: a — the rock extracts, b — NSO fractions of polar compounds separated from the rock extracts, c — coal

fractions than in the extracts ( $2800\text{--}3000\text{ cm}^{-1}$ ), mainly due to elimination of aliphatic compounds from the extracts by TLC

separation. Methyl group bands ( $1380\text{ cm}^{-1}$ ) are an exception, suggesting that polar compounds have high degree of alkyl substitution, among them methyl groups. A range of spectra correspond with aromatic polar groups included in aromatic rings (see relative intensity of bands at:  $700\text{--}900$ ,  $1500\text{ cm}^{-1}$ ).

The coal extract composition, with its higher content of aromatic structures ( $1500$ ,  $1620\text{ cm}^{-1}$ ) and lower contribution of aliphatic groups ( $2800\text{--}3000\text{ cm}^{-1}$ ), except methyl groups ( $1380\text{ cm}^{-1}$ ), differs notably from that of the rock extracts. There is also a lower contribution of the oxygen group  $\text{C}=\text{O}$  ( $1600\text{--}1800\text{ cm}^{-1}$ ) here. While the rock extracts are richer in such polar structures as aliphatic carboxylic acids ( $1750\text{ cm}^{-1}$ ) and aromatic or unsaturated carboxylic acids ( $1720\text{ cm}^{-1}$ ), the coal extract shows that high amounts of quinone  $\text{C}=\text{O}$  groups are present as well as  $\text{C}-\text{O}$  groups ( $1100\text{--}1300\text{ cm}^{-1}$ ), probably forming parts of heterocyclic structures.

A comparison of absorbance normalised values (Tab. 2) estimated from IR spectra of the sandstone (S1 and S2) and mudstone (M1 and M2) extracts shows a slightly higher contribution of aliphatic structures ( $2960\text{ cm}^{-1}$ ) and some oxygen groups ( $1270\text{ cm}^{-1}$ ) in mudstones. A comparison of normalised values of absorbance of extracts from the sandstones in the roof (S2) and in the floor (S1) of the coal layer shows that the first extract is characterised by higher amounts of polar structures ( $\text{C}=\text{O}$  quinone type groups at  $1660\text{ cm}^{-1}$ ) and lower quantities of carbonyl groups  $\text{C}=\text{O}$  ( $1720$ ,  $1750\text{ cm}^{-1}$ ) and  $\text{C}-\text{O}$  groups ( $1270\text{ cm}^{-1}$ ). This extract contains also aliphatic ( $2800\text{--}3000\text{ cm}^{-1}$ ) and aromatic structures ( $1620\text{ cm}^{-1}$ ) with a high degree of substitution (the weak bands originating from  $\text{C}-\text{H}$  bonds in aromatic structures:  $700\text{--}900$ ,  $3060\text{ cm}^{-1}$ ). Among polar fractions the coal polar fraction (C) differs from the other by its higher normalised values of absorbance of oxygen group bands at:  $1270$ ,  $1660$ ,  $1720$ ,  $1750\text{ cm}^{-1}$ . Moreover, a higher content of aliphatic structures ( $2960\text{ cm}^{-1}$ ) can be seen here, when compared with the other polar fractions. The S1 sandstone polar fraction shows much higher quantities of aromatic  $\text{C}-\text{H}$  bonds ( $600\text{--}900\text{ cm}^{-1}$ ) and higher levels of aliphatic structures ( $2800\text{--}3000\text{ cm}^{-1}$ ) compared with that of the S2 sandstone. Among oxygen groups there are lower contents of  $\text{C}-\text{O}$  bonds ( $1270\text{ cm}^{-1}$ ) and higher of  $\text{C}=\text{O}$  ( $1720$ ,  $1750\text{ cm}^{-1}$ ). The eluted polar fractions from mudstone extracts show higher contents of aliphatic structures ( $2800\text{--}3000\text{ cm}^{-1}$ ) in the M1 mudstone than in the M2 one. Slightly lower contents of aromatic  $\text{C}=\text{C}$  ( $1620\text{ cm}^{-1}$ ) and  $\text{C}-\text{H}$  ( $750$ ,  $3060\text{ cm}^{-1}$ ) bonds in the polar fraction from the first of these seems to be related to the low aromatic fraction yield from the extract of this rock.

#### GAS CHROMATOGRAPHY RESULTS AND THEIR DISCUSSION

Environment of deposition, and levels of biodegradation and thermal maturity of organic matter were assessed by gas chromatography of aliphatic fractions using commonly applied biomarker parameters. Their calculated values are shown in the Table 3. All analysed fractions contain aliphatic hydrocarbons belonging to the following groups: *n*-alkanes dominating in concentrations, alkylcyclohexanes and methylalkylcyclohexanes, acyclic and cyclic isoprenoids among them pristane, phytane and farnesane, diterpanes being indicators of terrestrial matter input (Alexander *et al.*, 1986; Noble *et al.*, 1986), and, in

Table 3

## Biomarker ratios based upon gas chromatographic analysis of aliphatic fractions

Biomarker ratio	Sample				
	M1	S1	M2	S2	C
Pr/Ph	2.49	3.42	2.50	1.89	2.05
Pr/ <i>n</i> -C <sub>17</sub>	1.72	2.10	1.71	1.92	2.92
Ph/ <i>n</i> -C <sub>18</sub>	0.61	0.52	0.59	0.77	1.11
Σ1/Σ2	0.91	0.53	0.79	0.69	0.36
CPI	1.44	1.17	1.39	1.22	1.11
C <sub>31</sub> αβS/(S+R)	0.28	0.28	0.38	0.49	0.31

Pr/Ph — pristane/phytane, used as an indicator of depositional environment oxicity; Σ1/Σ2 — ratio of concentrations of short-chain *n*-alkanes (*n*-C<sub>14</sub>–*n*-C<sub>22</sub>) to long-chain *n*-alkanes (*n*-C<sub>23</sub>–*n*-C<sub>37</sub>) indicating input of microbial and vascular plants in source kerogen; CPI — carbon preference index formula: 
$$\text{CPI} = 1/2 \left( \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}} + \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34}} \right)$$
 carbon preference index decreases to 1.0 with increasing thermal maturity; C<sub>31</sub>αβS/(S+R) — 17α(H), 21β(H)-29-homohopane 22S/[17α(H), 21β(H)-29-homohopane 22S + 17α(H), 21β(H)-29-homohopane 22R]; ratio value increases with thermal maturity from 0 to about 0.6 due to generation of geodiastercometr 22S from biologically formed 22R

much lower concentrations, pentacyclic triterpanes (hopanes) in the range C<sub>29</sub>–C<sub>32</sub>, compounds testifying to bacterial influence (Ourisson *et al.*, 1979). The examples of GC chromatograms are presented in Figure 6.

## ENVIRONMENT OF DEPOSITION AND SOURCES OF ORGANIC MATTER

Analysis of GC chromatograms indicated that, in all aliphatic compound fractions, *n*-alkanes with from 15 to 33 carbon atoms dominated. In three samples (bitumen from the S1 sandstone, coal and M2 mudstone) a bimodal distribution was found with maximal concentrations *n*-C<sub>16</sub>–*n*-C<sub>17</sub> *n*-alkanes (range associated with plankton-derived organic material in kerogen) and *n*-C<sub>27</sub>–*n*-C<sub>29</sub> (range associated with higher vascular plants). This type of *n*-alkane distribution is characteristic for the bituminous fraction of humic coals and type III kerogen with a dominant terrestrial organic matter input. In both mudstones organic matter shows a dominance of short-chain *n*-alkanes as indicated by the Σ1/Σ2 ratio in Table 3. In the case of both sandstones and coal extracts the values of Σ1/Σ2 ratio are much lower.

Broad clusters of *n*-alkanes in the range *n*-C<sub>19</sub>–*n*-C<sub>27</sub> with almost equal concentrations dominate in the aliphatic hydrocarbon distribution of the second mudstone (M1) and sandstone (S2) extracts. This type of distribution is similar to those found in bitumens derived from type II kerogens coming from planktonic/bacterial or bacterial/terrestrial biogenic matter. The last one is more probable as a source of the hydrocarbons ana-

lysed. It has been found in Permian Gondwana coals (Disnar and Harouna, 1994).

In all samples, regardless of lithology and mineral composition, some higher vascular plant input was found as shown by the presence of an unidentified peak of diterpane derived from precursors present mainly in gymnosperm resins. Another indication of terrestrial matter input is the predominance of odd over even carbon number *n*-alkanes, characteristic for hydrocarbons derived from cuticular waxes.

The pristane/phytane ratio is a commonly applied geochemical parameter used for assessment of depositional environment oxicity. It is based upon the amount of available oxygen and reaction type of phytol defunctionalisation (Didyk *et al.*, 1978). Generally, in oxic conditions, the dominant product of defunctionalisation is pristane while in anoxic conditions it is phytane. Though this relationship may not be so simple (ten Haven *et al.*, 1985), with other than phytol source of these two compounds, this parameter is widely applied and seems to work well if the organic matter analysed is sufficiently mature.

The highest Pr/Ph ratio (3.40) is shown by one of the sandstones (S1) (Tab. 3) indicating an oxic depositional environment and the lowest is of the S2 sandstone. Both mudstones are characterised by similar Pr/Ph, Pr/*n*-C<sub>17</sub> and Pr/*n*-C<sub>18</sub> ratios, indicating similar environmental conditions.

The biodegradation of the organic matter was assessed by the rise of the GC chromatograms base line caused by the presence of a "hump" of URC (unresolved compounds) (Conan, 1984; Palmer, 1993). The ratio of the highest base line rise to the height of the highest *n*-alkane peak was applied. It shows

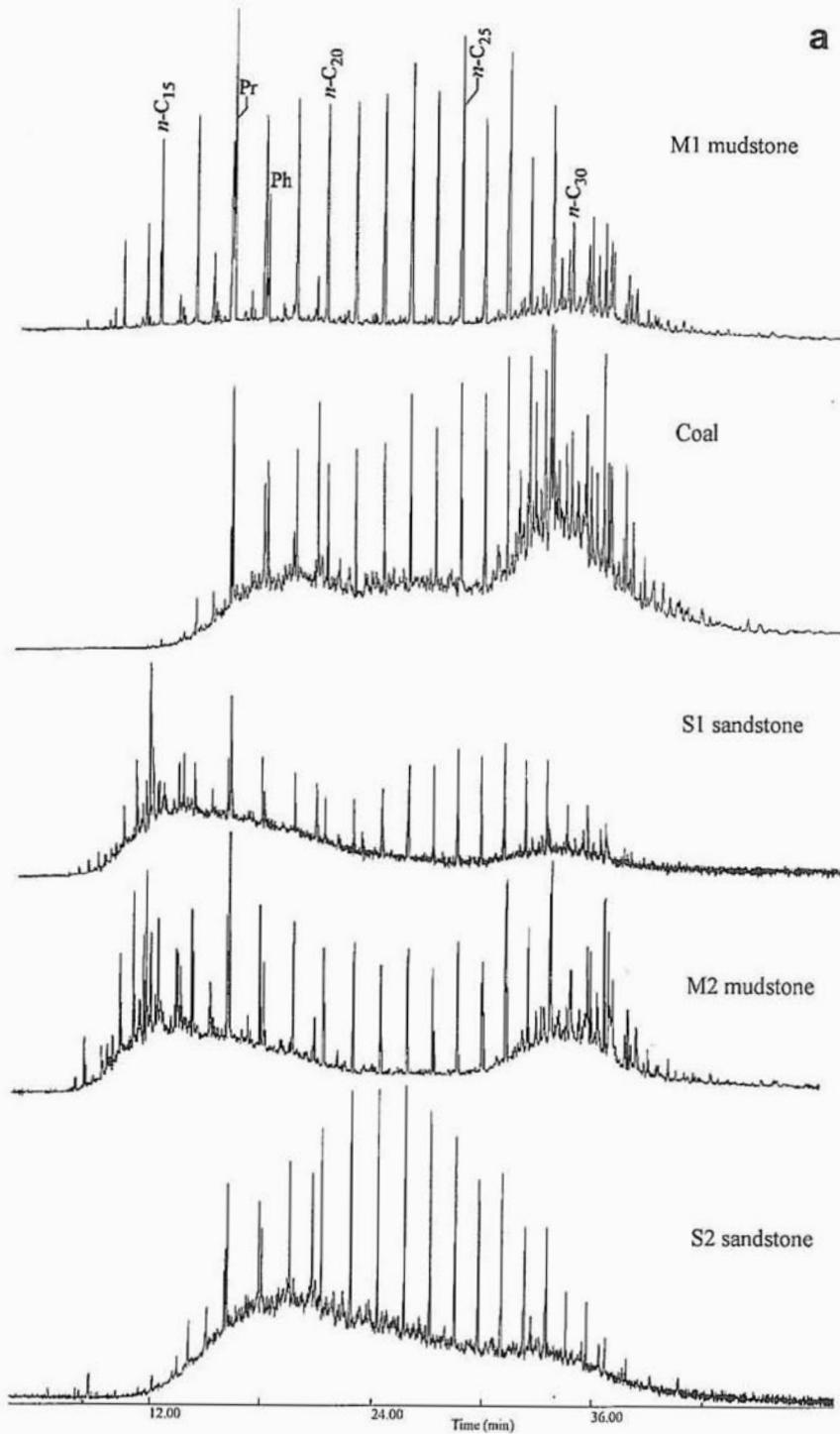
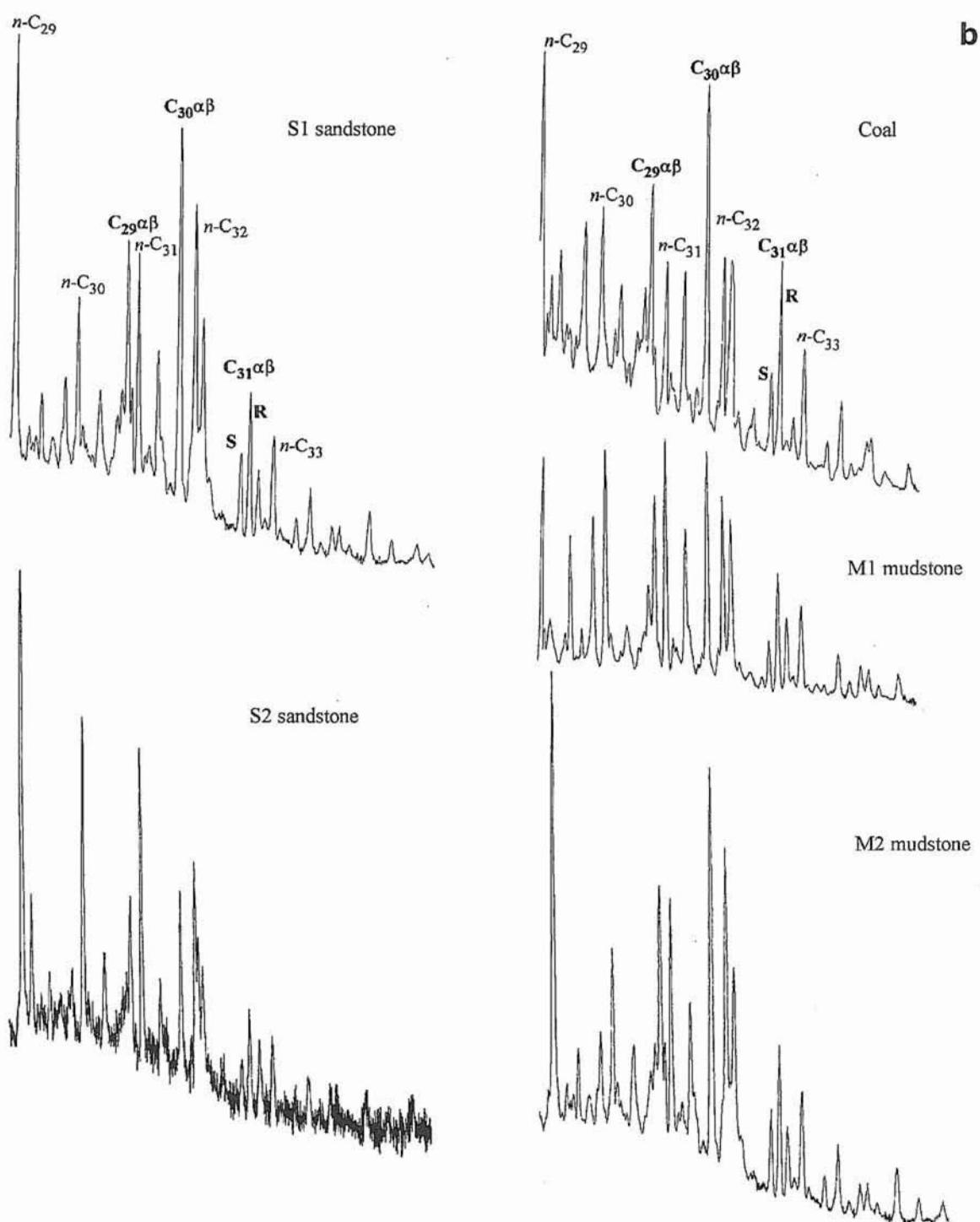


Fig. 6. GC chromatograms of aliphatic  
a — total GC chromatograms of aliphatic fractions,

that the organic matter of all samples has been strongly biodegraded, except for the extract of one of the mudstones (M1), which may be related to the protective influence of chlorite. Among other samples, relatively low biodegradation was shown by the coal aliphatic fraction and high biodegradation by the S1 sandstone.

#### THERMAL MATURITY OF ORGANIC MATTER

The maturity stage of the organic matter was assessed by the commonly observed predominance of odd over even carbon atom number in *n*-alkane distribution decreasing with increasing coalification (Bray and Evans, 1961). Mathematically



fractions of chosen samples

**b** — distribution of hopanes (partial GC chromatograms)

this relationship is expressed as the carbon preference index (CPI). It was found that analysed organic matter maturity reaches the end — diagenetic or very early catagenetic stage (beginning of oil window, compared to  $R_o$  values of about 0.5–0.6) (CPI in the range 1.1–1.5). This assessment agrees

with previous research concerning organic matter maturity in this region (Belka, 1993).

Both sandstone samples (S1 and S2) show much lower values of this parameter than the other samples despite the close sampling in the quarry. This difference could be caused by a low input of terrestrial organic matter in these sandstones or its

changes caused by water currents removing part of cuticular waxes, the main source of these *n*-alkanes, and or enrichment in bacterial matter. In case of the S2 sandstone the input of older bitumen (oil migrating throughout pores of the rock) is also possible, especially when *n*-alkane distribution indicates a dominance of bacterially derived hydrocarbons and the analysed sandstone contains numerous appendices of cane-break. The C<sub>31</sub> hopane diastereomers ratio (explained below), relatively higher in this sample than in the others, supports this supposition. Also the low Pr/Ph ratio, indicating terrestrial organic matter deposited in oxic environment, and higher Σ1/Σ2 ratio, seems to confirm the additional input of older bitumen. This sample was also water washed which caused partial removal of short-chain *n*-alkanes.

The high concentration of hopanes (pentacyclic triterpanes) in the analysed aliphatic fractions makes it possible to assess maturity by biomarker ratios based upon these compounds (Rullkotter and Marzi, 1988; Peters and Moldowan, 1993). The ratio of 17α(H), 21β(H)-29-homohopane 22S (abbreviated as C<sub>31</sub>αβ22S hopane) to the sum of 17α(H), 21β(H)-29-homohopane 22S and 17α(H), 21β(H)-29-homohopane 22R (C<sub>31</sub>αβ22R hopane) was applied (Tab. 3). The ratio values tend to increase with increasing thermal maturity to a value about 0.60 due to increasing concentrations of geochemically formed C<sub>31</sub>αβ22S hopane.

The M1 mudstone, S1 sandstone and coal samples show almost similar hopane diastereomer ratios (0.28–0.30) indicating that maturity of their organic matter did not reach the end of diagenesis being at the intermediate thermal evolution stage. The M2 mudstone and especially the S2 sandstone show much higher ratios (0.39 and 0.49 respectively), in the case of the sandstone (S2) probably caused by an input of older, migrating bitumen. This problem requires more detailed analysis by gas chromatography-mass spectrometry, a topic of continuing research.

## CONCLUSIONS

1. In the rocks surrounding the coal layer under investigation, organic matter is scattered as plant detritus and adsorbed on mineral components, especially on clay and limestone minerals. The lowest yields were from sandstone samples with higher ones from mudstone samples, particularly from the M1 mudstone sample with the highest chlorite content and with calcite and siderite. The highest yield of the total polar fraction was from the M1 mudstone. The high contents of polar substances may relate to the sorptive and catalytic properties of

clay minerals (especially chlorite), present in considerable amounts in the M1 mudstone.

2. Infrared analysis of the extracts obtained shows that, relative to the coal extract, the rock extracts contain generally more C–H bonds in the aliphatic structures and aromatic compounds with a lower degree of condensation; higher amounts of C=O groups which may be attributed here to carboxylic acids (1720 cm<sup>-1</sup>); and lower contents of quinone C=O groups (1660 cm<sup>-1</sup>) and also C–O groups (1270 cm<sup>-1</sup>).

3. The eluted polar fractions, relative to parent extracts contain by generally lower contents of aliphatic structures, higher quantities of aromatic rings and oxygenic groups, though some quinone groups and higher condensed structures probably remained in the non-eluted polar fraction.

4. A comparison of infrared spectra of extracts from the S1 and S2 sandstones from the roof and floor of the coal layer shows higher concentrations in the floor extract of macromolecular aliphatic and aromatic structures and also of oxygen groups of quinone type.

5. The extracts as well as eluted polar fractions obtained from mudstone samples show higher contents of aliphatic C–H bonds than the other samples of this type investigated here. A comparison of infrared spectra of the extracts obtained from mudstone samples (M1 and M2) indicates that in the extracts of the M1 sample there are more C=O groups in aliphatic carboxylic acids and quinone C=O groups and lower contents of C=O groups in aromatic or unsaturated carboxylic acids. There is also a higher quantity of aliphatic and a lower amount of aromatic C–H bonds than in the extract of the M2 mudstone.

6. The organic matter found shows features of type III kerogen (humic coal, the S1 sandstone and M2 mudstone) or type II kerogen of bacterial/terrestrial origin of primary biogenic matter (the S2 sandstone and M1 mudstone). Generally the environment of deposition was oxic as shown by high pristane/phytane ratios, especially in the case of one of sandstones (S1).

7. GC analysis shows that organic matter is at the end of diagenesis or early beginning of catagenesis. The highest maturity, shown by CPI and hopane diastereomers ratio and low Pr/Ph ratios in organic matter in the S2 sandstone, may be a result of input of older migrating bitumen. Because sandstones are commonly routes of petroleum migration it is not unusual to find such residual bitumen in rocks of this type.

8. The biodegradation of the organic matter seems to have been influenced by the mineral composition of the host rock. The higher content of chlorite in the M1 mudstone caused protection of organic material and lowered bacterial decay while the organic matter in porous sandstones was susceptible to extensive biodegradation.

## REFERENCES

- ALEXANDER R., CUMBERS K. M. and KOGI R. I. (1986) — Alkylbiphenyls in ancient sediments and petroleum. *Org. Geochem.*, **10**: 841–845.
- BELKA Z. (1993) — Thermal and burial history of the Cracow-Silesia region (southern Poland) assessed by conodont CAL analysis. *Tectonophysics*, **227** (1–4): 161–190.

- BOJKOWSKI K. (1967) — Stratigraphy of the Carboniferous of the Upper Silesia Coal Basin based on fauna (in Polish with English summary). *Rocz. Pol. Tow. Geol.*, **37** (1): 65–99.
- BRAY E. E. and EVANS E. D. (1961) — Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta*, **22**: 2–15.
- CONNAN J. (1984) — Biodegradation of crude oils in reservoirs. In: *Advances in Petroleum Geochemistry*. J. Brooks and D. Welte (1982), **1**: 300–335.
- DEMBOWSKI Z. (1972) — General information on the Upper Silesian Coal Basin (in Polish with English summary). In: *The Carboniferous of the Upper Silesian Coal Basin*. *Pr. Inst. Geol.*, **61**: 9–20.
- DIDYK B. M., SIMONEIT B. R. T., BRASSELL S. C. and EGLINGTON G. (1978) — Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. *Nature*, **272**: 216–222.
- DISNAR J. R. and HAROUNA M. (1994) — Biological origin of tetracyclic diterpanes, *n*-alkanes and other biomarkers found in Lower Carboniferous Gondwana coals (Niger). *Org. Geochem.*, **21**: 143–152.
- HAVEN H. L., de LEEUW J. W., RULLKOTTER J. and SINNINGLE DAMSTE J. S. (1987) — Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature*, **330**: 641–643.
- JURKIEWICZ J. A., MAKIEJEWA G. P. and DROZDOWSKAJA S. W. (1985) — Khimičeskij sostav slancev Turovskogo mestoroždenija. *BSSR. Khim. Tvjord. Topl.*, **4**: 32–37.
- KETT U. (1961) — Thermogravimetrische Untersuchungen zur Zersetzung von Steinkohlen, Dissertation. Bergakademie. Clausthal.
- KOWALSKA M., GULER H. and COCKE D. L. (1994) — Interactions of clay minerals with organic pollutants. *Sci. Total Environ.*, **141**: 223–240.
- NOBLE R., ALEXANDER R., KAGI R. I. and KNOX J. (1986) — Identification of some diterpenoid hydrocarbons in petroleum. *Org. Geochem.*, **10**: 825–829.
- OURISSON G., ALBRECHT P. and ROHMER M. (1979) — The hopanoids. Palaeochemistry and biochemistry of a group of natural products. *Pure Appl. Chem.*, **51**: 709–729.
- OZONKOWA H. (1979) — Geologia historyczna. Skrypt dla studentów geochemii i mineralogii. Katowice.
- PALMER S. (1993) — Effect of biodegradation and water washing on crude oil composition. In: *Organic Geochemistry. Principles and Applications* (eds. M. H. Engel and S. A. Macko): 511–534. Plenum Press. New York and London.
- PETERS K. E. and MOLDOWAN J. M. (1993) — *The biomarker guide*. New Jersey.
- RULLKOTTER J. and MARZI R. (1988) — Natural and artificial maturation of biological markers in a Toarcian shale from northern Germany. *Org. Geochem.*, **13** (4–6): 639–645.
- STOCH L. (1974) — *Minerały ilaste*. Wyd. Geol. Warszawa.
- STOPA S. Z. (1957) — Subdivision stratigraphique du Houiller dans le Bassin Houiller de la Haute Silésie (in Polish with French summary). *Biul. Inst. Geol.*, **115**: 195–262.
- STOPA S. Z. (1967) — Les problèmes de subdivision stratigraphique du Houiller Cracovio-Silésien à la mégaflore (in Polish with French summary). *Rocz. Pol. Tow. Geol.*, **37** (1): 7–39.
- WAPLES D. W. and MACHIHARA T. (1991) — Biomarkers for geologists — a practical guide to the application of steranes and triterpanes in petroleum geology. *Am. Ass. Petrol. Geol. USA*.