Middle Famennian (Late Devonian) interval with pyritized fauna from the Holy Cross Mountains (Poland): Organic geochemistry and pyrite framboid diameter study

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The pyrite framboid diameter and the extractable organic matter from the Middle Famennian rhythmic succession of limestones, nodular limestones and marly shales with pyritized fauna (KPG horizon) from the Holy Cross Mountains (Poland) were analyzed in order to constrain the water column structure during their deposition. In all samples investigated, small framboids (<5 µm) that may have formed in the water column occur but the majority of the framboids have larger diameters, characteristic for their formation within the sediments, below an oxic or dysoxic water column. This suggests that during deposition of the KPG horizon, the depositional environment was highly dysoxic, but not anoxic. Low concentration of the aryl isoprenoids and isorenieratane, and very high values of the AIR parameter point to the episodic photic zone euxinia and later post-depositional, partial degradation of the OM in suboxic conditions. Intermittent, but certainly short-lasting, anoxic conditions on the sea-floor, may also be supported by the lamination of the rock matrix and increased mortality of the juvenile ammonoids. The results of this study indicate that anoxic conditions prevailed in the shallow depths below the water-sediment interface, where pyritization following by dissolution of aragonitic shells of fauna occurred.

Keywords: biomarkers, pyritized fauna, framboids, isorenieratane, aryl isoprenoids

INTRODUCTION

The Holy Cross Mountains (HCM) is one of the best known and most thoroughly investigated areas of the late Devonian period in Europe (see Racki, 2005 and references therein). Upper Devonian rocks are easily accessible and a complete Upper Devonian sequence is exposed in the Kowala quarry near Kielce (Fig. 1a). Thus far, investigations have focused mainly on the major late Devonian biotic events, in particular those occurring near the Frasnian-Famennian (F-F) boundary (e.g., Joachimski et al., 2001; Racki et al., 2002; Bond and Zatoń, 2003; Bond et al., 2004; Pujol et al., 2006; Schwark and Empt, 2006) and the Devonian–Carboniferous transition (Marynowski and Filipiak, 2007). Geochemical investigations concerning the sedimentary conditions of organic matter, as well as its origin, were also conducted for the entire Devonian sequence of the HCM (Marynowski et al., 2000). One of the most interesting palaeontological-sedimentologic aspects of the Devonian of HCM is the occurrence of horizons with pyritized shelly faunas in basinal facies. These faunas include ammonoids, nautiloids, gastropods, bivalves and brachiopods (Racki and Szulczewski, 1996; Berkowski, 2002; Dzik, 2006). Similar horizon with pyritized fossils was recently described in the palaeontological (e.g., Dzik, 2002; Jagt-Yazykova et al., 2006) and geochemical-palaeoecologic aspects (Racki et al., 2004) from the Lower Frasnian of Kostomłoty, situated in the NW of the HCM.

In this report, we present the first geochemical study of the black shales and limestones, comprising also pyritized fauna, but from the Middle Famennian rhythmic basinal succession of the HCM (Kowala section, see Racki, 2005). Using biomarkers and pyrite framboid size distribution, we characterize the type of the organic matter (OM), marked by uniquely low degree of thermal maturity in this locality (see Joachiminski et al., 2001; Marynowski et al., 2000; Racki, 2005), and the redox conditions occurring in the water column, as well as in the early stage of diagenesis.

GENERAL GEOLOGICAL BACKGROUND

The investigated area is located in the southern limb of the Gałężice-Kowala syncline, in the southern part of the Kielce region of the Holy Cross Mountains, Poland.
Fig. 1. Simplified geological map of the western and central part of the Holy Cross Mountains showing the location of the Kowala Quarry (a) and schematic map of the Kowala Quarry (b). The arrow in (b) indicates the investigated part of NE wall of the quarry.

Fig. 2. North-eastern wall of the active Kowala Quarry (July 2004; see Fig. 1b), with circled numbers indicate sample position (a) and lithological section of the sample interval (b). Arrows indicate sample position, KPG - goniatitic level.

(Fig. 1). The Famennian section in the Kowala Quarry is divided into informal lithological sets H-2 to L (Racki and Szulczewski, 1996; Berkowski, 2002). For more detailed informations concerning geology and sedimentology of the Upper Devonian of the Holy Cross Mountains see Szulczewski (1971, 1995), Racki (1993) and Marynowski et al. (2000).
SAMPLES AND METHODS

Samples
The samples analyzed come from the pyritized fauna horizon (named here KPG), located on the north-eastern wall of the Kowala Quarry (Fig. 2a). The general thickness of the section investigated attains 8.6 m.

The investigated strata consist of rhythmic successions of limestones, nodular limestones and marly shales (Fig. 2b). In some layers numerous pyrite concretions occur. Thickness of the goniatitic level equals 177 cm (and embraces the following beds: KPG-2, KPG-1 and KPG 0) (Fig. 2b). Stratigraphically, the investigated section almost exactly fits the middle part of the Famennian, corresponding to the upper \textit{marginifera} conodont zone and lower \textit{prolobites} ammonoid zone (Fig. 3).

Elemental analysis and Rock-Eval pyrolysis
Concentrations of total organic carbon (TOC) were determined using a Leco Carbon Analyser CR-12. For determination of TOC, carbonates were removed from the samples by treatment with hydrochloric acid 25% and washed by water. Rock-Eval measurement were carried out using Rock-Eval 6 instrument.

Pyrite framboid size analysis
Measurements of pyrite framboid diameters were carried out on Philips XL30 ESEM/TMP environmental scanning electron microscope, using polished blocks. The framboid diameter of selected samples was measured directly from the screen (see Wignall and Newton, 1998 for detailed procedures). The observation and measurements were undertaken in the backscattered electron (BSE) mode. Wignall and Newton (1998; see also Wignall \textit{et al.}, 2005) recommend measuring 100 specimens per polished block in order to obtain a representative number for further statistical analysis. However, in the analysed samples the number of pyrite framboids varied widely, so it was not always possible to obtain 100 measurements.

Extraction and fractionation
Samples were Soxhlet-extracted with dichloromethane. The extracts were separated using pre-washed TLC plates coated with silica gel (Merck, 20 × 10 × 0.25 cm). Prior to separation, the TLC plates were activated at 120°C for 1 h. The plates were loaded with the \textit{n}-hexane soluble fraction and developed with \textit{n}-hexane/dichloromethane (V:V 97:3). Bands comprising aliphatic (Rf 0.7–1.0), aromatic (Rf 0.05–0.7) and polar + asphaltenes (Rf 0.0–0.05) fractions were collected.

The aliphatic and aromatic fractions were analysed in further detail.

Gas chromatography coupled with mass spectrometry (GC-MS)
The analyses were performed using an Agilent 6890 Series Gas Chromatograph interfaced with an Agilent 5973 Network Mass Selective Detector with an Agilent 7683 Series Injector. (Agilent Technologies, Palo Alto, CA). An Agilent Technologies Enhanced ChemStation G1701CA ver. C.00.00 was used for the data collection and the Wiley Registry of Mass Spectral Data 7th Edition software for the mass spectra processing. 0.5 µl of sample was injected into a cool on-column injector with electronic pressure control, the temperature of which, in “Track Oven” mode, was 3°C higher than that of the oven.

Helium 6.0 (Linde, Kraków) at a constant flow rate of 2.6 ml/min. was used as the carrier gas. Analyzed compounds were separated on two fused-silica capillary columns: J&W DB5-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness) and DB35-MS (60 m × 0.25 mm i.d., 0.25 µm film thickness).

The GC oven temperature was programmed from 40°C (isothermal for 1 min) to 120°C at a rate of 20°C/min and
Fig. 4. Fossils from the KPG horizon. Ammonoids: 1 - Tornoceras pseudobilobatum (Dybczyński) GIUS4-2851-KW-1/1; 2a, b - Polonoceras planum (Dybczyński) GIUS4-2852-KW-2/1; 3a, b - Protornoceras polonicum (Dybczyński) GIUS4-2854-KW-4/1; 4 - Protornoceras aphylliforme (Dybczyński) GIUS4-2853-KW-3/1; 5 - Protornoceras sp. (juvenile form) GIUS4-2855-KW-5/1; 6 - Pseudoclymenia sp. GIUS4-2856-KW-6/1; 7 - Cheiloceras sp. GIUS4-2868-KW-13/1; 8a, b - Felisporadoceras kielcense (Sobolew) GIUS4-2865-KW-15/1; 9a, b - Sporadoceras lagowiense (Sobolew) GIUS4-2869-KW-19/1; 10 - Gundolficeras bilobatum (Wedekind) GIUS4-2857-KW-7/1; 11 - Platyclymenia sp. GIUS4-2890-KW-40/1; 12 - Praeflexiclymenia tenuis (Sobolew) GIUS4-2891-KW-41/1; 13 - Orthoceratidae indet. GIUS4-3447-KW. Possible bactritids: 14 - Bactrites? sp. GIUS4-3448-KW. Bivalves: 15 - Guerichia sp. GIUS4-3449-KW. Brachiopods: 16a, b, c - Rozmanaria magna (Biernat and Racki) GIUS4-3450-KW; 17a, b - Pugnaria plana (Biernat and Racki) GIUS4-3451-KW; 18 - Barroisella sp. GIUS4-3452-KW. Gastropods: 20 - Gastropoda indet. GIUS4-3454-KW.
Pugnaria plana (Biernat and Racki). Inarticulate occurrence in the anoxic black-shales above in the sec-

flying in the surface waters (Fig. 4). Their mass-

epibiontic organisms, attached by byssus to the see-weeds

Orbiculoidea brachipods, on the other hand, are represented by two taxa:

alignment. However, in the KPG the

bedding planes is chaotic, without any directional

It is also supported by the fact, that their occurrence on

indeed pseudoplanktonic (see Wignall and Simms, 1990).

benthic organisms. It is possible that these bivalves were

occur as single specimens only, along with the other

Gastropods are preserved as inner moulds, and maybe

rabdite genera occur, such as

Obriculoidae sp. and Barroisella sp. (Fig. 4). These art-

iculate smooth-shelled rhychnonellid brachiopods are

characteristic for deep-water environments (Biernat and Racki, 1986).

Pyritized moulds of bivalves are represented by at least

two indeterminated taxa, supplemented by non-pyritized

suggested, that Guerichia bivalves could have lived as

epibiontic organisms, attached by byssus to the see-weeds

floating in the surface waters (Fig. 4). Their mass-

occurrence in the anoxic black-shales above in the section

(Annulata horizons; see Bond and Zatoń, 2003) lacking

any other benthic species may attest, that they were

indeed pseudoplanktonic (see Wignall and Simms, 1990).

It is also supported by the fact, that their occurrence on

the bedding planes is chaotic, without any directional

alignment. However, in the KPG the Guerichia bivalves

occur as single specimens only, along with the other

benthic organisms. It is possible that these bivalves were

facultative pseudoplanktonic (see Wignall and Simms, 1990).

Gastropods are preserved as inner moulds, and maybe

the representatives of the family Loxonematidae (Dr. W.

Krawczyński, pers. inf., 2006; see also Krawczyński et

al., 2003). Probably they may have lived as semi-infauna

near the sediment-water interface (Dr. W. Krawczyński, pers. inf., 2006).

Nectonic organisms are represented mainly by

ammonoids (goniatitids and clymeniids), as well as

nautiloids. The dominant groups are goniatitids, which

definitely attain higher diversity than clymeniids. Among

the goniatitids, the most numerous genera are

Protornoceras and Felisporadoceras; and among the

clymeniids the single representatives of the genera

Platyclymenia and Praeflexiclymenia occur (Fig. 4). Addi-

tionally, other goniatitid genera occur, such as

Tornoceras, Polonoceras, Pseudoclymenia, Gundolliceras, Chelloceras and Sporadoceras

(Rakociński 2006; Dzik, 2006, Fig. 4). Nautiloids are rep-

resented by indeterminate orthoceratids and supposed

bactritids (Bactrites? sp.) (Fig. 4).

The basis of the trophic chain was phytoplankton, e.g.,

prasinophytes and acritarchs occurring in the investigated

level (see Dąbrowska and Filipiak, 2006). The top of the

food chain, on the other hand, were certainly fishes, e.g.,

holocephalians described from the upper part of the com-

plex K (Ginter and Pichota, 2004).

BIOTIC CHARACTERISTICS OF THE KPG HORIZON

During the sedimentation of the KPG deposits, the

environment was characterized by rather calm sedimenta-

tion and soft, carbonate mud-type substrate (see

Szulczewski, 1971). Diversity of macrofauna in the KPG

horizon is not high. Quite numerous, but not poorly di-

version and soft, carbonate mud-type substrate (see

Biernat and Racki, 1986).

PYRITE FRAMBOIDS

General characteristics

Pyrite frambooids are densely-packed, spherical aggrega-

tes of pyrite microcrystals (see Wilkin et al., 1996; Wilkin et al., 1997; Wignall and Newton, 1998) (Fig. 5a).

Wilkin and Barnes (1996, 1997) proposed a four-stage model for their formation, from the nucleation of iron

monosulphide microcrysts, through greigite (FeS2), fol-

lowed by aggregation of greigite microcrysts to form

spherical frambooids, and finally with replacement of

greigite by pyrite to form pyrite frambooids. Frambooids

form at the early stages of diagenesis and are common

constituents of organic-rich sediments. They are very

numerous in the sediments deposited in oxygen-limited

environments (Raiswell and Berner, 1985; Wignall et al., 2005). Generally, pyrite frambooids form close to the

redox boundary, slightly above the bacterial sulphate-

reduction zone (see Wignall, 1994; Wignall and Newton, 1998; Wignall et al., 2005).

Investigations of recent, as well as fossil environments

showed that the framboid diameter distribution may be a

reliable indicator of the redox conditions (Wilkin et al., 1996; Wignall and Newton, 1998; Racki et al., 2004; Wignall et al., 2005; Bond and Wignall, 2005). Measurement of pyrite frambooid diameters allows characterization of the sedimentary conditions occurring in the basin during deposition (Wilkin et al., 1996). Under euxinic conditions, syngenetic frambooids form directly in the water column, reaching maximum diameters of approxi-

Quantification and identification

Abundance of selected compounds was calculated from comparison of internal standard (2-phenylindene) peak area with peak area of the individual hydrocarbons obtained from the GC-MS chromatograms. Peak identifi-
cation was carried out by comparison of retention times with standards, by comparison of mass spectra with those of the Wiley library and spectra published elsewhere.

Pyritization and quantification of pyrite frambooids was carried out in the following way:

1. Sample preparation for GC-MS analysis

Sample preparation was carried out by pyritization of bivalve shells (Gastropoda and Bivalvia). Pyritization was achieved by exposure to a series of sufficiently high temperatures for a period of time. The temperatures and times used were designed to achieve optimal conditions for pyritization of the shells. The sample preparation was carried out in a high-temperature, high-pressure pyritization apparatus.

2. GC-MS analysis

GC-MS analysis was performed on a gas chromatograph/mass spectrometer (GC-MS) system. The GC was equipped with an electron impact (EI) ion source and a quadrupole mass analyzer. The GC column outlet was connected directly to the ion source of the mass spectrometer. The GC column was packed with a 30-m long, 0.25-mm i.d., 0.25-μm film thickness, fused silica capillary column coated with a high-polarity stationary phase. The GC column was held at 25°C for 1 min, then programmed to 280°C at a rate of 3°C/min. The final temperature was held for 35 min. The GC column outlet was connected directly to the ion source of the mass spectrometer. The GC-MS interface was held at 280°C and the quadrupole analyzer at 230°C and 150°C, respectively. Mass spectra were recorded at m/z 45-550 (0–40 min) and m/z 50–700 (above 40 min). The mass spectrometer was operated in the electron ionization (70 eV). The abundance of selected compounds was calculated from comparison of internal standard (2-phenylindene) peak area with peak area of the individual hydrocarbons obtained from the GC-MS chromatograms. Peak identifi-
cation was carried out by comparison of retention times with standards, by comparison of mass spectra with those of the Wiley library and spectra published elsewhere.

3. Quantification

Quantification was carried out by comparison of retention times with internal standards. The abundance of selected compounds was calculated from comparison of internal standard (2-phenylindene) peak area with peak area of the individual hydrocarbons obtained from the GC-MS chromatograms. Peak identifi-
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approximately 5 µm before falling out of the water column. Crucially, they do not continue to grow after their accumulation on the basin floor and subsequent burial, since they are no longer close to the redox boundary (Wilkin et al., 1996). In contrast, in dysoxic environments, where framboids form in surficial sediments, size is largely governed by the local availability of reactants and the framboids are larger and more variable in size (Wilkin et al., 1996; Wignall and Newton, 1998). Wignall and Newton (1998), using the framboid diameters in the interpretation of the fossil sedimentary conditions (but see also Wilkin et al., 1996 for modern setting), paid attention to three significant parameters: mean values, standard deviation, and maximum framboid diameter. In sediments forming in an anoxic environment, Wignall and Newton (1998) observed that the mean values of framboid diameters are low, from 2.7–3.2 µm, and that framboids

Larger framboids on the other hand, form within the sediments, below an oxic or dysoxic water column (Wilkin et al., 1996; Wignall and Newton, 1998). Wignall and Newton (1998), using the framboid diameters in the interpretation of the fossil sedimentary conditions (but see also Wilkin et al., 1996 for modern setting), paid attention to three significant parameters: mean values, standard deviation, and maximum framboid diameter. In sediments forming in an anoxic environment, Wignall and Newton (1998) observed that the mean values of framboid diameters are low, from 2.7–3.2 µm, and that framboids
of more than 10 µm in diameter do not occur. Under conditions of lower dysoxia, an increase of the mean values, as well as the presence of single framboids of more than 10 µm in diameter was observed. Under upper dysoxic conditions, a rapid increase of framboid diameters was observed (Wignall and Newton, 1998; Wignall et al., 2005).

Pyrite framboid analysis on investigated samples

In all the samples investigated here, framboids are characterized by their wide range of diameters, from 2.5–25 µm. Their mean values in all samples range from 5.69 to 11.6 µm. In all samples, single large framboids (12.5–25 µm, see Fig. 6) occur.

Framboids are scattered in the rock matrix, and also occur as clusters within the fossils, e.g., nautiloid conchs (see Fig. 5, KPG 0). Besides framboids, diagenetic forms of pyrite (e.g., euhedral crystals, see Fig. 5, KPG 0) occur, but their frequency in particular samples differs; the samples KPG-6, KPG 1 and KPG 2 are rather poor with respect to pyrite; however, the samples KPG-2 and KPG 0 are enriched, and come from the goniatitic level where pyrite is very common.

Organic Geochemistry

Content of the organic carbon (TOC) in the investigated samples ranges from 0.4–1.0% (Table 2), constituting a significantly lower amount in comparison to the black shales of the Hangenberg Event (4–22.5% TOC, Marynowski and Filipiak, 2007), and some beds from the F-F boundary (to the 5% TOC, Joachimski et al., 2001), or Middle Frasnian black shales (up to 8% TOC, Marynowski et al., 2007). Nonetheless, the TOC values from 0.5 to 1.0% are elevated compared to the majority of the Upper Devonian sedimentary rocks of the HCM (see Marynowski et al., 2000; Joachimski et al., 2001; Marynowski and Filipiak, 2007; Marynowski et al., 2007). Hydrogen Index data (HI, see Table 2) and the HI vs. T_max plot (Fig. 7) indicates that samples consist of a mixture of type II kerogen. However, on the HI vs. OI plot (not shown), the samples correspond to the type II and I/II kerogen. Mean and high values of OI (Table 1) obtained for the samples analyzed suggest that the OM deposited in the basin was subjected to partial oxidation in the water column and shortly after deposition. The lowest values of OI and simultaneously the highest values of HI were measured for KPG 2 sample. Low T_max values obtained from Rock-Eval pyrolysis (Table 2) suggest relatively low levels of OM maturity.

In the fractional composition of the dissolved OM, the polar fraction dominates, except in sample KPG-6, which is enriched in the aliphatic fraction (Table 2).

n-alkanes and isoprenoids

The basic feature characterizing the investigated samples is the very similar distribution of n-alkanes, with a maximum at n-C15 and definite preponderance of short-chain n-alkanes (from n-C_{11} to n-C_{25}) over long-chain n-alkanes (from n-C_{25} to n-C_{35}). Examples of n-alkane dis-

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**Table 1. Macrofaunal diversity in the KPG horizon**

<table>
<thead>
<tr>
<th>Groups</th>
<th>Nr of families</th>
<th>Nr of genera</th>
<th>Nr of taxa</th>
<th>Nr of specimens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonoids</td>
<td>6</td>
<td>10</td>
<td>15</td>
<td>113</td>
</tr>
<tr>
<td>Nautiloids</td>
<td>2</td>
<td>2?</td>
<td>2?</td>
<td>(25)*</td>
</tr>
<tr>
<td>Brachiopods</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>Bivalves</td>
<td>2?</td>
<td>3</td>
<td>37</td>
<td>(8)**</td>
</tr>
<tr>
<td>Gastropods</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*Total number is difficult to estimate, because of frequent fragmentation of the specimens.
**The bivalves Guerichia has not been taken into consideration; question marks (?) indicate uncertainty in the identification.

![Fig. 7. Cross plot of Hydrogen Index vs. T_max (based on Armstrong et al., 2006).](image)
Despite the distinct preponderance of short-chain $n$-alkanes, which are characteristic for marine OM, in the range $n$-C$_{25}$–$n$-C$_{35}$, the preponderance of the $n$-alkanes with odd carbon numbers in the chain over the even $n$-alkanes, is observed (Fig. 8, see the enlarged fragment). The consequence of this is somewhat elevated value of the CPI$_{(25-31)}$ parameter, the values of which are higher than 1, ranging from 1.21 to 1.36. Such values are characteristic of leaf waxes input and indicate terrestrial OM contribution (Bray and Evans, 1961; Eglinton and Hamilton, 1967). The obtained pristane to phytane (Pr/Ph) values (in all samples investigated high values of the ratio Pr/Ph > 3 are observed; see Table 2) point to the oxidizing depositional environment with contribution from terrestrial OM (Didyk et al., 1978; ten Haven et al., 1987). However, as Brown and Kenig (2004) showed, in the Upper Devonian basinal deposits pristane may be also genetically linked with algae, resulting in the parameter Pr/Ph becoming an unreliable indicator of the depositional conditions and the source of the OM.

All the samples investigated do not show any influences of secondary processes, such as biodegradation, water washing or secondary hydrothermal oxidation. The high concentration of pristane and its domination over the $n$-alkanes (see Pr/n-C$_{17}$ Table 2), on the other hand, points to a relatively low degree of thermal maturity (Tissot and Welte, 1984), typical of the Kowala succession (see Marynowski et al., 2000; Joachimski et al., 2001).

### Table 2. Bulk geochemical data, percentage yields of fractions and basic molecular parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>TOC [%]</th>
<th>$T_{\text{max}}$ [°C]</th>
<th>HI</th>
<th>OI</th>
<th>Fractions</th>
<th>CPI$_{(\text{Total})}$</th>
<th>CPI$_{(25-31)}$</th>
<th>Pr/Ph</th>
<th>Pr/n-C$_{17}$</th>
<th>Ph/n-C$_{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPG-6</td>
<td>0.5</td>
<td>438</td>
<td>692</td>
<td>154</td>
<td>41</td>
<td>29</td>
<td>30</td>
<td>1.5</td>
<td>1.26</td>
<td>2.81</td>
</tr>
<tr>
<td>KPG-2</td>
<td>0.8</td>
<td>437</td>
<td>508</td>
<td>64</td>
<td>18</td>
<td>37</td>
<td>45</td>
<td>1.61</td>
<td>1.29</td>
<td>3.84</td>
</tr>
<tr>
<td>KPG 0</td>
<td>1.0</td>
<td>438</td>
<td>527</td>
<td>82</td>
<td>12</td>
<td>18</td>
<td>70</td>
<td>1.7</td>
<td>1.36</td>
<td>4.76</td>
</tr>
<tr>
<td>KPG 1</td>
<td>0.4</td>
<td>434</td>
<td>562</td>
<td>147</td>
<td>13</td>
<td>17</td>
<td>70</td>
<td>1.59</td>
<td>1.34</td>
<td>5.38</td>
</tr>
<tr>
<td>KPG 2</td>
<td>1.0</td>
<td>439</td>
<td>1001</td>
<td>56</td>
<td>23</td>
<td>37</td>
<td>40</td>
<td>1.56</td>
<td>1.21</td>
<td>4.02</td>
</tr>
</tbody>
</table>

TOC [%] - total organic carbon.

$T_{\text{max}}$ [°C] - maximum pyrolysis temperature.

HI - Hydrogen index.

OI - Oxygen index.

AL [%] - Aliphatic fraction.

AR [%] - Aromatic fraction.

POL [%] - Polar fraction.

CPI$_{(\text{Total})}$ - Carbon Preference Index.

CPI$_{(25-31)}$ - Carbon Preference Index.

Pr/Ph - Pristane to phytane ratio.

Pr/n-C$_{17}$ - Pristane to n-heptadecane ratio.

Ph/n-C$_{18}$ - Phytane to n-octadecane ratio.
Triterpanes and steranes

The most abundant hopane is C_{30}-17α(H),21β-hopane, but C_{30}-17β(H),21β-hopane, C_{30}-17β(H),21α-hopane and C_{30}-17β(H),21α-hopane are also present in relatively high concentrations (Fig. 8). Values for the ratio of the C_{29} and C_{30} βα-hopane to the sum of βα + αβ-hopane (Peters et al., 2005) in the total sample set is 0.65 ± 0.03, which is characteristic for immature OM (Table 3). On the other hand between C_{27} hopanes, the more thermodynamically stable 18α-22,29,30-trisnorhopane (Ts) significantly dominated over less stable 17α-22,29,30-trisnorhopane (Tm), which is not consistent with low maturity of the samples (Table 3). However, it is know from published data that in the case of Ts/Tm ratio the facies influence usually covers the maturity trends (see Bakr and Wilkes, 2002 and references therein).

The distribution of homohopanes (C_{31} to C_{34} αβ-hopanes) is characterized by strong predominance of C_{31}(S+R) homologues and low to trace concentrations of the other homologues in the range of C_{32} to C_{35}(S+R)-homohopanes (Fig. 9). Such distribution is characteristic for the OM deposition in oxic and suboxic conditions (Peters et al., 2005).

In the all samples analyzed, gammacerane, an indicator of water column stratification (Sinninghe Damsté et al., 1995) was not detected or was detected only in trace amounts (see gammacerane/C_{30}-17α-hopane ratio in Table 3).

Similarly to the Hangenberg black shales, almost all investigated samples (excluding sample KPG-6) contain steranes, diasteranes, 3β-alkyl steranes, diaster-13(17)-enes, monoaromatic and triaromatic steroids. In the sample KPG-6 only steranes, diasteranes, monoaromatic and triaromatic steroids are present. The immature character of the samples is reflected by the predominance of steranes with biological configuration (20S + 20R) and unstable compounds, characteristic for early stages of diagenesis (Brassell et al., 1984; Peakman and Maxwell, 1988). Among regular steranes, C_{29} steranes, compounds characteristic for green algae (Schwark and Empt, 2006) and terrestrial OM (Huang and Meinschein, 1978; Peters et al., 2005), dominate (Table 3). The C_{30} steranes to C_{29} steranes ratio is generally lower than average values of this ratio described from many Upper Devonian locations, including the Kowala F-F boundary section. Average values of C_{29}/C_{28} steranes ratio from the Kowala F-F section were 0.25–0.35 (Schwark and Empt, 2006) while that calculated from KPG section varies between 0.11 to 0.21 (Table 3). Low values of C_{30}/C_{29} steranes ratio in the KPG section are most probably connected with terrestrial OM input into the KPG samples, which caused the increased concentration of C_{29} steranes.

Regular steranes to 17α-hopanes and triaromatic ster-
oids to monoaromatic hopanoids ratios varies between the samples. Generally, samples with increasing levels of organic carbon contain a higher concentration of steranes (Tables 2 and 3, Fig. 6). This relationship is characteristic of sediments from the F-F shelf-basin in the HCM (Marynowski et al., 2000; Marynowski and Filipiak, 2007), which resulted from increased algal inputs to the kerogen. Other steroid biomarkers, similar to that identified in Hangenberg black shale, are also present in the KPG shales, including: C28–C30 methylsteranes with a base peak at m/z 231, C29–C31 steranes with a base peak at m/z 245 and C30–C32 steranes with a base peak at m/z 259 (Marynowski and Filipiak, 2007).

Isorenieratane and aryl isoprenoids

Isorenieratane, 2,3,6-/3,4,5-trimethyl-substituted diaryl isoprenoid and their diagenetic and catagenetic products including aryl isoprenoids are products of the photosynthetic brown strain of the green sulfur bacteria (Chlorobiaceae), which are rigorously anaerobic and for their metabolism require light and H2S (Summons and Powell, 1987; Requejo et al., 1992; Hartgers et al., 1994; Koopmans et al., 1996a; Clifford et al., 1998). However, both isorenieratane and 2,3,6-/3,4,5-trimethyl-substituted diaryl isoprenoid identified in the Kowala Quarry near the F-F boundary (Joachimski et al., 2001), Middle Frasnian transitans/punctata interval (Marynowski et al., 2007) and in the uppermost Famennian section (Marynowski and Filipiak, 2007), are present only in one sample (KPG 0) and with very low concentration (Figs. 6 and 10).

The abundance of aryl isoprenoids in the samples is low (Table 3, Fig. 6), especially in comparison to the Middle Frasnian transitans/punctata section where concentrations of aryl isoprenoids were on average ~17 µg/g TOC (Marynowski et al., 2007), and the Hangenberg event succession where concentrations of aryl isoprenoids vary significantly, but reach even 120 µg/g TOC (Marynowski and Filipiak, 2007). Values of the AIR, calculated from the ratio of C_{13,17}/C_{18,22} (Schwark and

Fig. 9. Mass chromatograms of hopanoid (m/z 191) and steroid (m/z 217) hydrocarbons of the two samples from KPG section showing the similar distribution of these compounds between samples. The DB5-MS column was used.
Intermittent anoxia in the Middle Famennian sequences of Poland

Fig. 10. Summed mass chromatogram m/z 133 + 134 of the KPG 0 sample showing the distribution of isorenieratane (filled triangle), 2,3,6-/3,4,5-TM substituted diaryl isoprenoid (open triangle) and their derivatives including aryl isoprenoids (numbers identify individual carbon number pseudohomologues). The DB35-MS column was used.

During the deposition of the KPG horizon, the pyrite framboid frequency distribution, and the occurrence of pyritized fossils, concretions and incrustations indicates that the depositional environment was highly dysoxic (Brett et al., 1991). This is also supported by the low diversity of benthic fauna (brachiopods, bivalves and gastropods). It is well known (see Wignall, 1993; Wignall, 1994), that in dysoxic environments the overall diversity of benthic organisms is low, and in anoxic environments, their diversity drops to zero (Wignall, 1993). The presence of single specimens of the bivalves (*Guerichia*), so common in the higher oxygen-depleted black shales of the Annulata horizons (see Berkowski, 1993; Bond and Zatoń, 2003) may indicate that the conditions were suitable for them to settle the sea-floor. The analyses conducted suggest that generally the water column was well oxygenated. The first evidence of the OM oxidation are elevated OI values. Shortly after the OM deposition, due to protective effect of clays, OM was isolated from oxidizing conditions. Oxygen deficiency occurred only sporadically, reaching the photic zone and persisting for a very short time. Taking into account the fact that sedimentation of the analysed rocks coincided with the greatest regressive pulse in the Famennian, caused by glacieustasy (Johnson et al., 1985), it is hard to presume that anoxia existed in the water column; it persisted only below the photic zone. The evidence against anoxic conditions in the water column is not only the low frequency of small (<5 µm), but also the presence of larger (>10 µm) frambois, as well as the low concentration of the aryl isoprenoids and isorenieratane (Figs. 6 and 10), and very high values of the AIR parameter pointing to the episodic photic zone euxinia and later post-depositional, partial degradation of the OM in suboxic conditions (Table 3). Episodic, but certainly short-lasting, anoxic conditions on the sea-floor, may be supported by the preserved lamination of the non-bioturbated rock matrix in

**DISCUSSION**

In all samples investigated, small framboids (<5 µm) that may have formed in the water column (see Wilkin et al., 1996; Wignall and Newton, 1998) occur, but the majority of the framboids have larger diameters, characteristic of formation within the sediments, below oxic or dysoxic water column (Wilkin et al., 1996). In the samples investigated, other forms of pyrite also occur, such as euhedral crystals, which are responsible for the fossil pyritization, concretion and druse formation. These forms of pyrite formed within the sediment during the early stages of diagenesis (Brett et al., 1991; see also Taylor and Macquaker, 2000; Borkow and Babcock, 2003). That pyritization occurred at early stages of diagenesis may be supported by the fact that the majority of fossils occur in the form of pyritized moulds, e.g., ammonoids, nautiloids, bivalves and gastropods. The first three groups possess ornamentation on their moulds, which attests that pyritization had undergone before their aragonitic shells have been dissolved. However, the fact that the ornamentation has not been preserved in gastropods suggests that their delicate, thin aragonitic shells underwent dissolution almost simultaneously with the progression of pyritization. Among the faunal assemblage from this horizon, the exception are brachiopods. They, alike the previous groups, are also filled with pyrite, but their shells did not undergo any dissolution, because they were built by more resistant low-Mg calcite. In *Guerichia* bivalves, the original aragonitic shells (see Horowitz and Potter, 1971) were replaced by calcite.
The occurrence of intermittent anoxia in the water column is observed in many Palaeozoic and Mesozoic sedimentary basins, and the main cause of breaks in its occurrence is the transgressive-regressive oscillations of sea-level (Simons and Kenig, 2001; Marynowski and Filipiak, 2007). The occurrence of the episodic anoxia may also be evidenced by the high mortality of juvenile ammonoids (see Westermann, 1996; Jagt-Yazykova et al., 2006). The juvenile forms, unlike the adult ones, usually lived in deeper parts of the water column (Westermann, 1996), thus they were much more vulnerable to oxygen-depleted conditions occurring in the near-bottom zones. On the other hand, their increased mortality may be caused by the reproductive r-strategy of ammonoids (e.g., Ward, 1987; Wilkes, 1994; Klug, 2001), and their good state of preservation in the KPG horizon may in part be caused by the favourable fossilization conditions through pyritization and calm sedimentation of the muddy deposits.

The samples analyzed are characterized by very similar composition of the soluble hydrocarbons and do not show any influence of secondary processes (see above). The OM occurring in the sedimentary rocks of the investigated section has a relatively low degree of thermal maturity, confirmed by the presence of diaster-13(17)-enes, which were also identified in the Hangenberg shale (Marynowski and Filipiak, 2007). Additionally, relatively high concentrations of \( \beta \)-hopanes (see maturity parameters in Table 3) and \( \alpha \)-alpha-steranes (Fig. 8) occur in the samples.

The presence of organic compounds of terrestrial origin with the CPI\textsubscript{25–31} values higher than 1 (Table 2) has also been detected in the samples. The presence of terrestrial OM in the section is confirmed by finds of fragments of coalified terrestrial plants occurring in the same goniatic level, or in other parts of the complex. Most probably, these fragments belong to the genus Archaeopteris (see Dąbrowska and Filipiak, 2006).

CONCLUSIONS

During the sedimentation of the KPG deposits, oxic to highly dysoxic conditions prevailed in the environment. Photic zone anoxia occurring in the water column was present episodically. This might have had an influence on the increased mortality of the ammonoid juveniles. Anoxic conditions prevailed in the shallow depths below the water-sediment interface, in the sulphate reduction, where pyritization following by dissolution of aragonitic shells of fauna occurred. These processes occurred almost simultaneously. The OM occurring in the investigated sedimentary rocks is characterized by a relatively low degree of thermal maturity, at the beginning of the oil window stage. The analyzed samples are characterized by mixture of III-type of kerogene which suggests dominance of marine OM, but the presence of organic compounds of terrestrial origin has also been detected.

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