Organic geochemical characteristics of black shales across the Ordovician-Silurian boundary in the Holy Cross Mountains, Central Poland

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Abstract

Black shales in the Holy Cross Mountains area of Poland provide a record of environmental change across the Ordovician-Silurian boundary. The changing depositional conditions have generated a variation in organic matter contents above and below the boundary. Investigating the organic constitution of these black shales has the potential to reveal how their organic matter contents were generated and how suitable these rocks and their lateral equivalents may be for exploitation as shale gas reservoirs. One outcrop at the Holy Cross Mountains with a continuous section across the Ordovician-Silurian boundary occurs near the village of Bardo Stawy in the Kielce region, and contains sandy-silty mudstones, as well as grey and black shales. Organic geochemical analyses of samples at Bardo Stawy reveals low Total Organic Carbon (TOC) contents for Ordovician samples and higher TOC values for Silurian samples. Organic biomarkers indicate that the Ordovician rocks were deposited in a shallow-marine shelf setting, while the Silurian rocks were deposited in a deeper marine environment. The progressive increase in TOC from the uppermost Ordovician to the lowermost Silurian rocks reflects increasingly oxygen-poor depositional conditions during the post-glacial transgression. Following the deposition and preservation of organic matter in the Ordovician and Silurian rocks, these rocks were buried and subjected to thermal maturation. Rock Eval and

biomarker thermal maturity parameters all indicate that the organic matter is mature and lies within the oil window. The Ordovician and Silurian shales have direct relevance to recent attempts to discover and exploit shale gas reservoirs in Poland. Our data and interpretations suggest that the relatively low TOC values (<2%) and low maturities for gas generation render these rocks unsuitable for commercial shale gas production. The progressive improvement in conditions for preserving organic matter across the Ordovician-Silurian boundary does, however, leave the possibility that more suitable deposits occur in Early Silurian rocks in other parts of the basin.

1. Introduction

During the last ten years, there has been a substantial interest in the Ordovician and Silurian shale deposits in Europe as reservoirs for unconventional petroleum, particularly in Poland (Poprawa, 2010a). Silurian black shales, in particular, were investigated during exploration for shale oil and shale gas (Poprawa, 2010b; Poprawa and Kiersnowski, 2008). TOC content is variable within the Baltic Basin, north Poland, but a number of prerequisites for unconventional reservoirs exist (Poprawa, 2010a). Unconventional petroleum investigation initially focussed on Silurian black shales because of their relatively high TOC, laterally extensive nature, raised maturity and great thickness (Wieclaw et al., 2010). The first well in Europe that targeted an unconventional reservoir was drilled in 2011 in the Baltic Basin, north-western Poland (Boyer et al., 2011). The Early Ordovician to Early Silurian time interval represents a period of black shale deposition under stratified and anoxic bottom water conditions in many areas of North Africa, the Middle East and Europe, Fig. 1 (Berry, 2010; Leggett, 1980; Thickpenny and Leggett, 1987; Trela and Podhalanska, 2010; Wilde, 1987) including Poland (Melchin et al., 2013; Page et al., 2007). During the Ordovician-Silurian transition, there were considerable changes in the atmosphere, ocean, biosphere and, hence, in the general marine depositional conditions (Underwood et al., 1997) inextricably linked with the Late Ordovician (End Hirnantian) glacial event (Melchin et al., 2013; Sheehan, 2001). Glaciation events

have major influence on the productivity and preservation of organic matter due to the changes in oceanic ventilation and circulation that cause oxygenation of the seawater (Berry and Wilde, 1978; Berry, 2010; Wilde, 1987). During the Ordovician-Silurian transitional period, there was a substantial change in organic matter distribution, production, and preservation on the East European Craton, particularly in Poland (Lesniewicz, 2012; Wieclaw et al., 2010). The Ordovician-Silurian boundary in Poland has been studied from several different perspectives including sedimentology (Bednarczyk and Stupnicka, 2000; Dzik and Pisera, 1994; Modlinski and Szymanski, 2001; Trela et al., 2001), palynology (Kremer, 2001; Masiak et al., 2003; Podhalanska, 2003; Trela et al., 2001), petroleum geology (Kiersnowski and Dyrka, 2013; Lesniewicz, 2012) and geochemistry (Sawlowicz and Porebska, 1998). The Holy Cross Mountains (HCM), which is located in the transition zone between Baltica and the West European Platform (Fig. 1), represents a location where Ordovician-Silurian boundary rocks are exposed, either in complete successions or as intercalations (Teller, 1988). Until now, there has been no detailed organic geochemical study of the Ordovician-Silurian boundary in the HCM. Some organic geochemistry has been performed on a few chert samples from the Silurian of the Zalesie section in the HCM (Bauersachs et al., 2009). Our current study aims to define the distribution of organic matter across the Ordovician-Silurian boundary and provides new insights into organic matter preservation at this location. The essential role of the organic matter content in defining the shale oil and shale gas potential of black shale deposits allows determination of the suitability of these rocks as shale oil and shale gas targets.

1.1. General Geology

1.1.1. Ordovician

The Ordovician-Silurian transitional sedimentary deposits are exposed in Poland only within the eastern part of the HCM (Fig. 2C) and in the Sudety Mountains, which lie west of the HCM (Podhalanska, 2003; Teller, 1988). A gradational boundary across the Ordovician-Silurian contact in the southern HCM was recognised using fossil records (Masiak et al., 2003). A complete succession

of Ordovician and Silurian strata is preserved at Bardo Stawy (Dzik and Pisera, 1994) and a less complete succession is found at Zalesie Nowe (Masiak et al., 2003) although the precise Ordovician-Silurian boundary at these locations has not yet been determined (Kremer, 2001). Upper Ordovician deposits in the Bardo Stawy and Zalesie sections are composed of varied lithologies. These deposits comprise the Zalesie Formation, the upper parts of which are the called Zalesie Beds (Fig. 2A). The Zalesie Formation (Upper Ordovician) comprises sandstones and siltstones, dolomites and limestones, mudstones and marly mudstones (Kremer, 2001; Masiak et al., 2003). Only the uppermost Zalesie Formation rocks are exposed at the Bardo Stawy where they are six metres thick (Zalesie Beds) and are composed of green/grey sandstones and yellowish silty mudstones with shales (Masiak et al., 2003; Trela et al., 2012). These rocks were deposited during the Early Hirnantian (Latest Ordovician) regression caused by a drop in sea level that resulted from the incorporation of water in the ice caps on Gondwanaland located at the South Pole (Trela, 2007; Trela and Podhalanska, 2010). The close of the Hirnantian coincides with the appearance of light brown graptolitic shales and siltstones at the base of the Rembow Member (Fig.2A) which represent the start of a marine transgression that continued into the Early Silurian (Trela and Podhalanska, 2010). Latest Ordovician rocks in the Bardo Stawy section are well exposed in valleys and small streams, whereas they are not difficult to access in the Zalesie section because of vegetation cover.

1.1.2. Silurian

The Bardo Stawy section (Upper Ordovician-Lower Silurian) is characterised by a continuous lithological transition (Trela et al, 2012). Black siliceous shale, grey argillaceous shale, and laminated black radiolarian cherts of the Rembow Member represent the lowermost Silurian deposits in the HCM (Kremer and Kazmierczak, 2005). The grain size change from sandy/silty to muddy deposits; and the colour change from yellow, or beige, to dark grey may also; demonstrate the appearance of reduced conditions in the Early Silurian environment (Masiak et al., 2003). The lithological change is

consistent and coincides with the start of the proposed marine transgression at that time (Trela, 2003b). Lower Silurian sediments at Bardo Stawy are mainly graptolitic brown and black shales, as well as laminated radiolarian shales, with intercalations of sandy and marly mudstones and sandstones (Masiak et al., 2003; Trela et al., 2012). These Lower Silurian shale beds eventually pass into the Zbrza Member of the Bardo Formation (Fig. 2A). A decrease in grain size, a darkening of the colours of the sediments and a reduction in abundance of quartz grains and clasts in younger sediments suggest that the sedimentation rate progressively declined during the transition from the Ordovician to Silurian (Masiak et al., 2003). These deposits are well exposed in the stream escarpments and valleys in the Bardo Stawy section.

2. Experimental

2.1. Samples

For our investigation, 11 shale samples were collected in the Bardo Stawy outcrop from the Upper Ordovician and Lower Silurian units (Table 1 & Fig. 2B). The Ordovician-Silurian transition in this outcrop was sampled every 20 cm, across a two-metre span of the section. The samples were taken from the Zalesie Formation (Zalesie Beds) and Bardo Formation (Rembow Member). The boundary between Ordovician and Silurian in the Bardo Stawy section is marked by the first appearance of the graptolite *Akidograptus ascensus* which marks the base of the *persculptus* biozone and occurs at the junction between the sandy mudstones of the Zalesie Formation and the cherty shales of the Bardo Formation (Masiak et al., 2003). The Ordovician samples are composed of pale yellow, grey and dark grey silty/sandy shales and argillaceous shales. The Silurian samples consist of dark grey and black shales. About 5-10 cm of weathered rock was removed before sampling. One sample had two distinct lithologies (grey shale and silty yellow shale) and subsamples were collected and labelled as OR7a and OR7b.

2.2. Sample preparation and screening

Coherent shale samples were rinsed with *n*-pentane to remove surface contamination, and then crushed to a fine powder using a pestle and mortar. Aliquots of the powdered samples were analysed for total organic carbon (TOC) using a Carlo Erba Elemental Analyzer NC2500. Carbonate was removed prior to TOC analysis by acid treatment for 24 hours followed by drying in an oven for 2 hours. Decalcified samples were then run for 6 minutes by flash combustion. About 100 mg aliquots of each sample were also analysed by a Delsi-Nermag Rock-Eval 6 unit in which the sample was heated up to 550 °C in a helium atmosphere. The oven was hold at 300 °C for 3 minutes and then increased at a rate of 25 °C/ min. In this process, the amount of free hydrocarbons (S1), the amount of hydrocarbons thermally cracked from kerogen (S2), the amount of carbon dioxide (S3) that was expelled from pyrolysis, and the temperature at which the maximum amount of S2 hydrocarbons generated (T_{max}) were measured.

For extraction of hydrocarbons, known amounts (ca. 1.5 g) of powdered sample were subjected to solvent extraction. An internal standard prepared from squalane and p-terphenyl were added to each sample and used for semi-quantitation. The powdered samples were placed in test tubes and a solvent mixture of dichloromethane (DCM)/methanol (95:5 v:v) was added. The mixture was then sonicated for 3 minutes, centrifuged for 5 minutes, and the supernatant was removed; the extraction process was repeated five times. After extraction, activated copper turnings were added into each sample to remove elemental sulfur and then the combined supernatants were concentrated under a stream of dry nitrogen gas. The concentrated extracts were fractionated by column chromatography using activated alumina powder in which aliphatic and aromatic fractions were eluted using hexane and DCM:hexane (1:1 v/v), respectively, and the polar fraction was eluated using DCM:methanol (1:1 v/v). The aliphatic and aromatic fractions were concentrated (<0.5 ml) using dry nitrogen gas stream and were then transferred to 300 µL pre-weighed insert vials where they were allowed to dry before their weights were recorded.

2.3. Gas chromatography-mass spectrometry (GC-MS)

GC-MS analysis was carried out on the aliphatic and aromatic fractions of the samples using an Agilent Technologies 7890A gas chromatograph (GC) coupled to a 5975C Mass Spectrometer (MS). The GC injector was operated in a splitless mode (1 μ l) with a column flow rate of 1.1 mL/min. A J&W scientific DB-5MS capillary column (30 m, 250 μ m i.d., 0.25 μ m film thickness) was used for compound separation and helium employed as a carrier gas. The GC oven temperature was initially held at 40 °C for 2 minutes, and then raised to a 310 °C at a rate of 5 °C min⁻¹ where the atmosphere was held for 14 minutes. Mass spectra were acquired in electron impact mode (70 eV) in the scan range of 50-500amu.

2.4. Pyrolysis-GC-MS

About 2-3 mg of solvent extracted residues was placed in pyrolysis quartz tubes using quartz wool to hold the sample in place. Pyrolysis tubes were heated by the CDS Analytical 1500 pyroprobe in its platinum coil, which was heated to 650 °C at a rate of 20 °C ms⁻¹ and held for 15 seconds. The pyroprobe unit was interfaced to an Agilent Technology 6890 gas chromatograph coupled to 5973 mass spectrometer (GC-MS) and the CDS Analytical 1500 interface was heated at 300 °C and held for 5 minutes. The GC injector was held at 270 °C and operated in a split mode (10:1) with column flow rate of 1.1 mL min⁻¹. Compound separation achieved using a J&W DB-5MS UI column (30 m length, 0.25 mm internal diameter and 0.25 μ m film thickness). The oven was held at an initial temperature of 35 °C for 2 minutes then ramped at a rate of 5 °C min⁻¹ to 300 °C and held at this temperature for 8 min. Mass spectra were obtained in electron impact mode (70 eV) using a scan range of 45 to 550 amu.

3. Results

3.1. Organic Carbon Contents

The Upper Ordovician- Lower Silurian samples in the HCM are poor in TOC (values range from 0.07% to 1.02%). The Ordovician samples have very low TOC content, ranging from 0.07% to 0.11% (mean 0.08%), and the Silurian samples, however, have generally an order of magnitude higher TOC, ranging from 0.29% to 1.02% (mean 0.63%) (Table 2). These TOC values were corrected to their original contents according to the equation $[TOCo = TOCm + (TOCm * (Tmax - 435)/30)]$ for the samples that have Tmax higher than 435 °C (Cornford et al., 2001). Based on the TOC values the source rock quality of the Ordovician samples is “poor” (< 0.5%) and the quality of the Silurian black shales is “poor to fair” (0.5% to 1.0%) with only one sample (BS3) showing a “good” value (1.0% to 2.0%) (Peters, 1986; Peters and Cassa, 1994). Owing to their low TOC values, the Ordovician samples were not analysed further by programmed pyrolysis (Rock-Eval). The TOC content increases from the Ordovician towards the Silurian boundary (Table 2). Trela and Podhalanska (2010) have found similar enrichment in TOC in the Lower Silurian shales in the Debniak 1 well (20 km north of our studied section) and the Wilkow IG1 well (20 km north-west of studied section) in the Lysogory region.

3.2. *n*-Alkanes and isoprenoid hydrocarbons

n-Alkanes and isoprenoids are similarly distributed in both Ordovician and Silurian samples (Fig. 3) though some detailed differences can be noticed. The Ordovician samples contain *n*-alkanes in the range of *n*-C₁₅ to *n*-C₂₀, except for the OR6 sample, which contains *n*-alkanes up to *n*-C₃₃. With the exception of OR6, the distribution of *n*-alkanes is unimodal in all Ordovician samples with a consistent maximum at *n*-C₁₇. The OR6 sample has a bimodal distribution with maxima at C₁₇ and C₂₆ with a prominence of C₂₁ to C₂₉ *n*-alkanes. Trace amounts of *n*-alkylcyclohexanes from C₁₅ to C₁₉ with a slight predominance of odd-over-even carbon atoms were also detected. The Ordovician samples are characterised by Carbon Preference Index (CPI) (Bray and Evans, 1961) and Odd-over-

Even Predominance (OEP) (Scalan and Smith, 1970) values ranged from 0.99 to 1.61 and 0.95 to 1.16, respectively (Table 2), which are as would be expected for high maturity samples from a time where no significant land plants existed. Isoprenoid compounds are abundant in the samples and are represented by pristane, phytane, and their C_{17} and C_{18} counterparts. The pristane/phytane ratio (Pr/Ph) in the Ordovician samples ranges from 1.53 to 4.98. Pr/ n - C_{17} values are higher than one and Ph/ n - C_{18} values are very low ranging from 0.18 to 0.94. Terrigenous versus Aquatic Ratio (TAR) and n - C_{17} / n - C_{23} ratios for the samples ranged from 0.07 to 3.01 and 0.44 to 5.2, respectively (Table 2).

The ranges of n -alkanes vary between the Ordovician and Silurian samples (Fig. 3). The n -alkane distribution pattern in the Silurian samples is characterised by an abundance of C_{13} - C_{33} n -alkanes with maxima at n - C_{17} . The n -alkane distribution is unimodal in all of the Silurian samples, but the SB1 sample is distinguished by a broad unimodal distribution, with abundant C_{15} to C_{30} n -alkanes and n - C_{21} as the most prominent n -alkane (Fig. 3). The CPI and OEP values of the Silurian samples are lower than those observed for the Ordovician samples, and ranged from 0.84 to 1.13 and 0.88 to 1.01, respectively, (Table 2). Relative to the Ordovician samples, the Silurian samples are characterised by a higher abundance of isoprenoids and a prominence of pristane over phytane in all samples. Compared to the Ordovician samples, lower Pr/Ph values are observed in the Silurian samples, with a range from 1.68 to 3.46. The Pr/ n - C_{17} values are higher than one in all the samples and Ph/ n - C_{18} values are low, except for sample SB5 which has a higher value (Table 2). Low TAR values and high n - C_{17} / n - C_{23} values are recorded in all Silurian samples.

3.3. Hopanes

Hopanes are present in trace amounts in the Ordovician samples, whereas they are prominent in all Silurian samples. The hopane series exists as C_{27} and C_{29} to C_{35} 17α - 21β -hopane homologue (22R and 22S epimers) in all studied samples. Identified homohopane compounds were presented in

Table 3. The C₃₀ hopane is the most abundant hopane in all samples apart from SB5, which has both C₂₉ and C₃₀ hopane hydrocarbons as the most prominent peaks (Fig. 4). Homohopanes exist in trace amounts in most of the samples including Silurian samples (Fig. 4). In addition to the hopanes, tricyclic terpanes exist in the Ordovician samples in trace amounts. The tricyclic terpanes are markedly present in all Silurian samples, where they are more abundant than the hopanes with distributions dominated by C₂₀ to C₂₈ compounds. This higher relative abundance of tricyclic terpanes compared to hopanes is not so prominent in the Ordovician samples with the exception of the OR10, which exhibits tricyclic relative responses similar to those in the Silurian samples (Fig. 4).

3.4. Steranes

The steranes exist as regular steranes and diasteranes in all samples. Regular steranes exhibit C₂₁ to C₂₂ and C₂₇ to C₂₉ compounds of $\alpha\alpha\alpha$ and $\alpha\beta\beta$ configurations with both 20R and 20S epimers apparent. Low molecular weight steranes (C₂₁ pregnane and C₂₂ homopregnane) exist as $\alpha\alpha$, $\alpha\beta$ and $\beta\alpha$ configurations with S and R epimers present. Detailed identifications of the sterane hydrocarbons can be found in Table 3. Pregnane is more prominent than the homopregnane in all samples. C₂₇ to C₂₉ diasteranes exist in almost all of the samples as $\beta\alpha$ and $\alpha\beta$ configurations (20R and 20S epimers). The C₂₇ regular sterane occurs as the highest peak in all the samples (Fig. 5). The Ordovician samples are characterised by a high abundance of C₂₇ regular steranes with traces, or the complete absence, of the C₂₈ and C₂₉ regular steranes and by a low abundance of pregnane and homopregnane steranes and diasteranes (Fig. 5). The Silurian samples display C₂₇ regular steranes as the most prominent peak but relative to the Ordovician samples they have a notably higher responses for pregnane, homopregnane, and diasteranes (Fig. 5).

3.5. Pyrolysates

The results of the Py-GC-MS analysis show that the kerogen in the Ordovician samples produces only low or trace amounts of organic compounds upon pyrolysis. The Ordovician samples release small amount of *n*-alkenes/*n*-alkanes in a range from C₉ to C₁₈ with a maximum at *n*-C₁₆ (Fig. 6)

Benzene, toluene, *n*-alkyl-benzenes, and *n*-di-alkyl-benzenes are also present in the pyrolysates from the Ordovician samples in low abundance but in a relatively higher proportion than the *n*-alkenes and *n*-alkanes. Aromatic compounds (naphthalene, methylnaphthalene, phenanthrene, and dibenzothiophene) exist in low amounts in the pyrolysates of all Ordovician samples (Fig. 6). Weathering is known to remove aromatic compounds from sedimentary rocks (Marynowski et al., 2011a). The pyrolysis-GC-MS responses for the Silurian samples demonstrate that the kerogen in these samples is capable of generating hydrocarbons. The pyrolysates from the Silurian samples contain *n*-alkenes/*n*-alkanes doublets ranging from C₆ to C₁₈, with maxima at C₁₀ to C₁₂. In contrast to the pyrolysis products from the Ordovician samples, ion chromatograms of m/z 91 and 92 of the Silurian pyrolysates are dominated by higher amounts and longer side chain alkyl-benzenes, as well as by responses from benzene and toluene. Naphthalene, phenanthrene, dibenzothiophene, and their alkylated counterparts are also prominent in pyrolysates of the Silurian samples (Fig. 6).

4. Discussion

4.1. Origin of organic matter

Terrigenous organic matter in the Ordovician and Early Silurian samples is not expected owing to the absence of terrestrial biomass during this part of Earth history (Grantham, 1986). Both Ordovician and Silurian samples in the HCM contain biomarkers that suggest a marine source for the organic matter owing to (i) the dominance of low molecular weight *n*-alkanes (<*n*-C₂₃) (Spiro et al., 1983), (ii) the unimodal distribution of *n*-alkanes in almost all of the samples (excepting samples OR6 and SB1) (Ficken et al., 2000; Gelpi et al., 1970; Tissot and Welte, 1984), (iii) high *n*-C₁₇/*n*-C₂₃ ratio (apart from OR6 and SB5) (Peters et al., 2005; Riboulleau et al., 2007), and (iv) a high relative abundance of C₂₃ and low relative contents of C₁₉ and C₂₀ tricyclic terpanes in all samples (Ahmed et al., 2014; Peters et al., 2005; Zumberge, 1984). The organic matter in OR6 and SB5 also has marine characteristics but with slight differences compared to other samples. The following characteristics

were observed in the Ordovician OR6 sample: (i) abundant medium to high molecular weight *n*-alkanes (*n*-C₂₂ to *n*-C₂₉); (ii) a low OEP; (iii) a prominent response from C₂₆ *n*-alkane; and (iv) a CPI value of 1.08. The *n*-alkane distribution of the Silurian SB1 sample, on the other hand, is characterised by: (i) a broad unimodal distribution, with maxima at *n*-C₂₁; (ii) a CPI value of 0.96; and (iii) a small OEP indicating a marine origin of organic matter. Such variations indicate that the progressive change from shallow Ordovician to deeper Silurian conditions was not accompanied by a monotonous change in organic matter content and was occasionally interrupted by variation in organic matter source. The high content of tricyclic terpanes in the Ordovician and Silurian samples (Fig. 4) demonstrates a marine origin for the organic matter, as tricyclic terpanes are absent in terrestrially-sourced organic matter (Philp and Gilbert, 1986).

Existence of C₁₅-C₂₂ *n*-alkanes (Fig. 3) with a low OEP (Table 2) in the samples, particularly *n*-C₁₅, *n*-C₁₇, and *n*-C₁₉ in the Ordovician samples, and existence of trace amounts of *n*-alkylcyclohexanes with a slight odd-over-even predominance around C₁₇ alkylcyclohexane (Douglas et al., 1991; Fowler, 1992; Fowler et al., 1986) are characteristic features of organic matter derived from *Gloeocapsomorpha prisca* algae (Hoffmann et al., 1987; Peters et al., 2005; Reed et al., 1986).

Bacteriohopanepolyols, which are bacterial membrane lipids, have been considered as the precursor of hopanoid biomarkers (Ourisson and Albrecht, 1992; Ourisson et al., 1979; Ourisson and Rohmer, 1992), consistent with the high relative abundance of homohopanes (C₃₁-C₃₄) in all samples (Fig. 4), particularly in the Silurian samples (Peters and Moldowan, 1991). Tricyclic compounds originated from algae and bacteria during the Ordovician (Moldowan et al., 1983; Ourisson et al., 1982; Zumberge, 1987). The relative abundance of regular steranes can be used as a biomarker indicator of contributing organisms and it has been suggested that the C₂₇ sterane is sourced from marine planktons while the C₂₉ sterane is derived from land plants (Huang and Meinschein, 1979; Volkman, 1986) or from microalgae (Volkman, 2003). As would be expected the ternary plot of steranes in the Ordovician samples reveals an abundance of C₂₇ steranes (Fig. 7), which imply an exclusively algal

source of organic matter while the same plot for the Silurian samples demonstrates marine-derived organic matter from both algal and bacterial sources (Fig. 7).

4.2. Paleodepositional environments

The Pr/Ph ratio and the homohopane index in the Table 2 (Didyk et al., 1978; Peters et al., 2005; Powell, 1988) suggest that the depositional environment of the organic matter was mostly suboxic, intermittently, and became anoxic for periods as a result of reintroduction of deep anoxic waters to shelf areas during Late Hirnantian sea level rise (Hammarlund et al., 2012). The interpretation of the depositional setting as generally oxic/suboxic is supported by the predominance of C₃₁ homohopane homologue and the low content of the C₃₅ homohopane (Peters and Moldowan, 1991). In addition, the Late Ordovician and Early Silurian sediments may have contained phosphate in their pore spaces, as indicated by the high content of C₂₃ tricyclic terpanes and C₃₁ and C₃₂ extended hopanes in the Silurian samples (Fig. 4) (Zumberge, 1987). A few studies in the HCM region suggest enrichment of the environment with phosphorous as a result of microbial communities (mats) and nutrient-rich influxes from an upwelling system (Glenn et al., 1994; Kremer, 2005; Kremer and Kazmierczak, 2005; Trela, 2003a). The phosphate abundance has been suggested to form from macroaggregates on the sea floor in shallow marine environments (Kremer, 2005).

The marine depositional environment and its changes across the transition of the Ordovician to the Silurian in the samples were inferred from the TOC and biomarker data (Fig. 8). Previous investigations suggested an oxic/suboxic depositional environment for the Ordovician and less oxygenated conditions for the Silurian in the HCM, with short-term reducing conditions, in either open marine or estuarine/bay environments (Kremer, 2001; Masiak et al., 2003; Podhalanska, 2003; Trela et al., 2001). Low values of the DBT/phenanthrene ratio from pyrolysates of the samples (Table 2) are consistent with the preservation of kerogen within a marine depositional environment in the Ordovician and Silurian (Hughes et al., 1995). The distribution and abundance of the methyl-

phenanthrenes in the Silurian samples (Fig. 6) also indicate a marine depositional environment (Budzinski et al., 1995).

The HCM area was located at the southern edge of Baltica (Fig. 1) at the end of the Ordovician (Podhalanska and Trela, 2007). At this time, the Rheic Ocean had regressed owing to the Hirnantian glaciation event (Trela, 2007) and shallow water conditions dominated in the study area (Fig. 9A). The Ordovician sediments were deposited in intra-shelf waters (Fijalkowska-Mader et al., 2010) with alternating suboxic/anoxic to oxic conditions (Trela et al., 2012). Melting of the ice caps and the resulting marine transgression in the Latest Hirnantian eventually led to deeper water conditions in the Early Silurian (Fig. 9B) and the introduction of nutrient rich waters via an upwelling system driven by the southeast trade winds (Kremer, 2005). Enhanced productivity brought about by nutrient supply would have generated oxygen depletion in the water column and therefore enhanced organic matter preservation within the pelagic or hemipelagic environment (Sawlowicz and Porebska, 1998). Enhanced preservation is consistent with TOC increase, biomarker ratios, and lithology change across the boundary (Fig 8 and Table 2). The proposal that depositional conditions changed from relatively oxic to relatively reducing across the Ordovician-Silurian boundary owing to a sea level rise (Berry, 2010; Hammarlund et al., 2012; Trela, 2007; Zhang et al., 2011), during which black graptolitic and organic rich shales were deposited, can be tested using biomarker data and the Pr/Ph ratio and homohopane index (Fig. 8 and Table 2) that represent clear evidence of such changes (Fig. 9B).

The biomarker data in this study imply that more reduced depositional conditions during the transgression (Trela, 2003a; Trela, 2003b) are consistent with the lithological changes across the boundary; from silty/sandy claystones of the Ordovician to the black laminated shales of the Silurian (Kremer, 2001; Kremer and Kazmierczak, 2005). Our interpretations of changing conditions in the Late Ordovician and Early Silurian (Fig. 9 A&B) in the HCM are consistent with those for the wider Ordovician-Silurian paleoenvironments. For instance, a drastic change in the

depositional environment, bottom water condition, fossil fauna, and organic matter production and preservation was observed during the transition from the Late Ordovician to the Early Silurian, not only in Poland (Kremer, 2001; Masiak et al., 2003; Podhalanska, 2003; Sawlowicz and Porebska, 1998; Trela et al., 2001), but also in other parts of the world (Armstrong et al., 2009; Lünig et al., 2006; Melchin et al., 2013; Vecoli, 2008).

A petrological study of the Ordovician and Silurian samples (Masiak et al., 2003) reveals clay-rich rocks with little variation in mineral content across the Ordovician-Silurian boundary at Bardo Satwy. A high content of C_{31} homohopane (Hakimi and Abdullah, 2013) accompanied by decreasing homohopane ratios (Fig. 4), abundance of diasteranes (Fig. 5), ratio of C_{26}/C_{25} tricyclic terpanes and ratio of C_{29}/C_{30} hopanes are all consistent with the clay-rich character of the rocks (Peters et al., 2005; Waples and Machihara, 1991). Low ratios of DBT/Phenanthrene from the pyrolysates, Fig. 6, are also consistent with clay-rich rocks (Hughes et al., 1995).

4.3. Weathering effects on the samples

Published work implies that TOC % in rocks reduces by about 70 to 95 % following weathering (Marynowski et al., 2011a; Wildman et al., 2004). Even after taking into account a 70 to 95% loss of TOC by weathering, the original TOC content of our samples is still far less than 2 % for the Ordovician samples, whereas SB2 and SB3 Silurian samples would have original TOC percentages of about 2 %.

Weathering preferentially removes short chain alkanes, steranes, and some aromatic compounds, particularly methylated naphthalenes and phenanthrenes, but has lesser effects on hopanes (Clayton and King, 1987; Marynowski et al., 2011a; Marynowski et al., 2011b; Marynowski and Wyszomirski, 2008; Petsch et al., 2005; Wildman et al., 2004).

The detection of low responses for short chain alkanes and alkyl- naphthalene and phenanthrenes (Fig. 6) in several samples can be related to surface weathering by which these compounds were

partially removed (Fig. 3). Thermal maturation indicators are also influenced by weathering (see below) (Table 2 and Fig. 8).

4.4. Maturity

In order to investigate the maturity of the samples, $T_{\max}$ values from programmed pyrolysis and several biomarker parameters were used. All samples were found to be mature for petroleum generation. Programmed pyrolysis $T_{\max}$ values of the Silurian samples range from 439 to 440 °C indicating a maturity consistent with the beginning of oil window (Peters, 1986; Peters and Cassa, 1994). Isomerisation of C_{32} hopane at the C_{22} position and isomerisation C_{29} sterane at the C_{20} position, as well as T_s/T_m ratios and the C_{31} hopane abundance indicate a mature state for the organic matter in the samples (Peters and Moldowan, 1991; Peters et al., 2005; Seifert and Moldowan, 1980). The C_{32} hopane index ($22S/(22S+22R)$) produces high values for all samples (0.44 to 0.64) indicating mature organic matter in both Ordovician and Silurian samples (Table 2). A mature state for the organic matter in all samples can also be inferred from the C_{29} ($20S/(20S+20R)$) sterane index, which range from 0.54 to 0.65 (Peters et al., 2005). As T_m is unstable during diagenesis and decreases with maturity, the T_s/T_m ratio and $T_s/(T_s+T_m)$ index can also be used as maturation indicators (Seifert and Moldowan, 1978). The $T_s/(T_s+T_m)$ index values (0.40-0.62) and the T_s/T_m values (0.67-1.66) indicate that both Ordovician and Silurian samples are mature (Table 2). The maturity data in the studied samples is consistent with the previously published maturity data from acritarchs (dark brown to black colour) (Fijalkowska-Mader et al., 2010) in the HCM. Maturity parameters exhibit some differences between the samples (Fig. 8 and Table 2) that is most likely related to differential weathering effects on the various biomarkers. For instance, steranes and some aromatic compounds are highly sensitive to weathering (Marynowski et al., 2011a; Marynowski et al., 2011b; Wildman et al., 2004).

5. Shale gas potential characteristics

The shale gas potential of organic-rich shale can be assessed using several industry standards. These main standards are TOC, thermal maturity, thickness, mineralogy, kerogen type, gas-in-place, porosity, and permeability (Boyer et al., 2006; Jarvie et al., 2007). To be considered as good shale gas target a rock must satisfy a number of main prerequisites including : (1) TOC > 2.0 %, (2) maturity >0.8-1.1% Ro, (3) thickness > 15 m, (4) clay content < 30%, and (5) kerogen type II/III. Some additional requirements such as porosity >5%, permeability > 100 md, and overpressure are also taken into account (Boyer et al., 2006; Curtis and Zumberge, 2010; Jarvie et al., 2007; Kiersnowski and Dyrka, 2013; Zou et al., 2010).

For the HCM samples, the TOC content of both Ordovician and Silurian samples is far less than the 2 % cut-off value (average TOC content 0.09% and 0.82 % respectively). Yet the HCM rocks do have some positive qualities. The maturity of all the samples is adequate for the generation of oil and maybe some gas ; the Ordovician and Silurian samples are at an early-peak maturity level that is insufficient for major gas generation. The kerogen type indicates a marine depositional environment and type II organic matter. Hence, our data and interpretations suggest that the relatively low TOC values (< 2%) and early maturities render these rocks unsuitable for commercial shale gas production. However, progressive improvement in conditions of preserving organic matter across the Ordovician-Silurian boundary does leave open the possibility that more suitable deposits of Early Silurian age may exist in other parts of the basin.

6. Conclusions

The study of the Ordovician-Silurian boundary in the HCM provides important information for the future unconventional petroleum exploration in this area. A substantial change during the transition from the Ordovician to Silurian in terms of organic matter content and depositional environment is inferred. The marine-derived organic matter was poorly preserved in the Ordovician samples

because of oxic/suboxic conditions, whereas the Silurian samples are characterised by higher TOC content (than the Ordovician) preserved under reducing bottom water conditions. Weathering has affected, to some extent, the TOC % and biomarker content of the samples. The studied samples are thermally mature with some potential for hydrocarbon generation. The changing conditions were probably related to deglaciation and sea level rise at the end of Ordovician (Latest Hirnantian) leading to higher organic matter productivity and enhanced organic preservation. While the shale samples at Bardo Stawy have poor shale oil or shale gas potential, the general improvement in conditions for organic matter production and preservation as the Ordovician transitions into the Silurian boundary suggests the possibility of more suitable deposits in lateral equivalents elsewhere in Poland.

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Tables

Table 1: selected samples and their sampling distance in the Bardo Stawy outcrop section in the HCM, central Poland

Sample	Distance	Age	Sample	Distance	Age
SB0	00 cm (Top)	Silurian	OR6	120 (Top)	Ordovician
SB1	20		OR7a	140	
SB2	40		OR7b	140	
SB3	60		OR8	160	
SB4	80		OR9	180	
SB5	100 (bottom)		OR10	200 (Bottom)	

Table 2: sample locations and their calculated biomarker parameters of the solvent extracts of the Ordovician and Silurian samples in the studied section.

Sample	OR10	OR9	OR8	OR7b	OR7a	OR6	SB5	SB4	SB3	SB2	SB1	SB0
Age (Periods)	Ordovician						Silurian					
Location	Bardo Stawy						Bardo Stawy (Rembow member)					
Distance (cm)	200	180	160	140	140	120	100	80	60	40	20	0
TOC (%)	0.08	0.08	0.09	0.06	0.07	0.11	0.47	0.29	1.02	0.77	0.37	0.85
Tmax °C	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	439	441	<u>n.d.</u>	440
HI	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	40	51	<u>n.d.</u>	53
OI	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	138	173	<u>n.d.</u>	175
S1	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	0.03	0.03	<u>n.d.</u>	0.02
CPI ^a	1.61	1.17	1.07	1.34	0.99	1.08	1.10	0.84	1.02	0.96	0.96	1.13
OEP ^b	1.08	1.07	1.03	1.14	1.16	0.95	0.88	0.9	1.04	0.96	1.01	1.01
Pr/Ph	3.48	4.20	3.45	4.98	4.55	1.53	1.68	3.46	3.22	2.89	2.83	3.41
Pr/ <i>n</i> -C ₁₇	1.06	2.10	2.34	1.21	0.66	1.28	6.62	2.31	1.71	1.20	1.06	2.5
Ph/ <i>n</i> -C ₁₈	0.31	0.43	0.55	0.26	0.18	0.94	1.35	0.58	0.53	0.41	0.31	0.72
TAR ^c	0.28	0.16	0.18	0.22	0.07	3.01	1.02	0.15	0.16	0.10	0.07	0.61
<i>n</i> -C ₁₇ / <i>n</i> -C ₂₃	2.50	1.46	1.75	3.24	5.2	0.44	0.32	2.91	2.36	3.22	2.28	0.93
C ₂₃ /C ₂₁ tricyclic	0.76	0.66	0.83	0.91	0.77	0.33	1.20	1.35	1.55	1.12	1.25	0.98
Homohopane index ^d	0.06	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	<u>n.d.</u>	0.08	0.09	0.09	0.13	0.12	0.43	0.14
C ₂₉ /C ₃₀ αβ hopane	0.90	1.01	0.81	0.83	0.83	0.95	0.77	0.73	0.74	0.58	0.53	0.69
C ₃₂ 22S/(22S+22R)	0.51	0.57	0.55	0.44	0.57	0.64	0.59	0.62	0.63	0.61	0.56	0.54
C ₂₉ ααα 20S/(20S+20R)	0.51	0.25	0.31	0.38	0.41	0.48	0.51	0.51	0.52	0.52	0.54	0.5
Ts/(Ts+Tm)	0.40	0.42	0.53	0.53	0.52	0.48	0.62	0.62	0.62	0.56	0.50	0.46
Regular Sterane %												
C ₂₇	<u>97.41</u>	<u>97.33</u>	<u>98.26</u>	<u>98.40</u>	<u>96.67</u>	<u>89.79</u>	<u>54.54</u>	<u>45.13</u>	<u>31.18</u>	<u>49.73</u>	<u>68.31</u>	<u>61.72</u>
C ₂₈	<u>1.00</u>	<u>1.46</u>	<u>0.66</u>	<u>0.59</u>	<u>2.03</u>	<u>3.81</u>	<u>22.66</u>	<u>23.49</u>	<u>30.97</u>	<u>15.93</u>	<u>10.49</u>	<u>8.56</u>
C ₂₉	<u>1.59</u>	<u>1.20</u>	<u>1.08</u>	<u>1.01</u>	<u>1.30</u>	<u>6.40</u>	<u>22.80</u>	<u>31.38</u>	<u>37.86</u>	<u>34.35</u>	<u>20.76</u>	<u>29.72</u>
Diasterane/Sterane ^e	2.80	1.24	1.33	2.28	3.37	2.18	2.45	1.61	1.67	1.13	1.86	0.86
DBT ^f /phenanthrene	0.40	0.11	0.14	0.11	0.18	0.09	0.44	0.34	0.26	0.25	0.47	0.36

Footnotes

^aCarbon Preference Index (Bray and Evans, 1961) (CPI) = {(C₂₅+C₂₇+C₂₉+C₃₁+C₃₃)/ (C₂₄+C₂₆+C₂₈+C₃₀+C₃₂)+ (C₂₅+C₂₇+C₂₉+C₃₁+C₃₃)/ (C₂₆+C₂₈+C₃₀+C₃₂+C₃₄)} / 2

^bOdd over Even Predominance (Scalan and Smith, 1970) (OEP) = (C₂₁+6C₂₃+C₂₅) / (4C₂₂+4C₂₄)

^cTerrigenous over Aquatic Ratio (Peters et al, 2005) (TAR) = (C₂₇+C₂₉+C₃₁) / (C₁₅+C₁₇+C₁₉) *n*-alkanes

^dC₃₅ Homohopane index = C₃₅ / (C₃₁+C₃₂+C₃₃+C₃₄+C₃₅)

^eC₂₉ βα Diasterane / C₂₉ ααα sterane

^fDibenzothiophene (DBT)

n.d. : no data

Table 3: identified peaks and their nomenclatures in the m/z 191 and 217 chromatograms of the studied samples in Bardo Stawy

Peak label	Carbon number	Compound nomenclature
Hopanes		
1	C ₂₇	18 α -22,29,30-Trisnorhopane (Ts)
2	C ₂₇	17 α -22,29,30-Trisnorhopane (Tm)
3	C ₂₉	17 α (H), 21 β (H)-Hopane
3a	C ₂₉	18 α - 30-Norneohopane
3b	C ₃₀	17 α (H)-Diahopane
4	C ₃₀	17 α (H), 21 β (H)-Hopane
5	C ₃₁	17 α (H), 21 β (H)-Hopane (S+R)
6	C ₃₂	17 α (H), 21 β (H)-Hopane (S+R)
7	C ₃₃	17 α (H), 21 β (H)-Hopane (S+R)
8	C ₃₄	17 α (H), 21 β (H)-Hopane (S+R)
9	C ₃₅	17 α (H), 21 β (H)-Hopane (S+R)
Steranes		
10	C ₂₁	5 α (H), 14 α (H)-Pregnane (S)
11	C ₂₁	5 α (H), 14 α (H)-Pregnane (R)
12	C ₂₁	5 α (H), 14 β (H)-Pregnane (S)
13	C ₂₁	5 α (H), 14 β (H)-Pregnane (R)
14	C ₂₂	5 α (H), 14 β (H)-Homopregnane (S)
15	C ₂₂	5 β (H), 14 α (H)-Homopregnane (S)
16	C ₂₂	5 β (H), 14 α (H)-Homopregnane (R)
17	C ₂₂	5 α (H), 14 α (H)-Homopregnane (S)
18	C ₂₂	5 α (H), 14 β (H)-Homopregnane (R)
19	C ₂₇	13 β (H), 17 α (H)- Diasterane (S)
20	C ₂₇	13 β (H), 17 α (H)- Diasterane (R)
21	C ₂₇	13 α (H), 17 β (H)- Diasterane (S+R)
22	C ₂₈	13 β (H), 17 α (H)- Diasterane (S+R)
23	C ₂₈	13 α (H), 17 β (H)- Diasterane (S+R)
24	C ₂₉	13 α (H), 17 β (H)- Diasterane
25	C ₂₇	5 α (H), 13 α (H), 17 α (H)- Sterane (S)
26	C ₂₉	13 β (H), 17 α (H)- Diasterane (S)
27	C ₂₇	5 α (H), 13 β (H), 17 β (H)- Sterane (S+R)
28	C ₂₇	5 α (H), 13 α (H), 17 α (H)- Sterane (R)
29	C ₂₉	13 β (H), 17 α (H)- Diasterane (R)
30	C ₂₈	5 α (H), 13 α (H), 17 α (H)- Sterane (S)
31	C ₂₈	5 α (H), 13 β (H), 17 β (H)- Sterane (S+R)
32	C ₂₈	5 α (H), 13 α (H), 17 α (H)- Sterane (S)
33	C ₂₉	5 α (H), 13 α (H), 17 α (H)- Sterane (S)
34	C ₂₉	5 α (H), 13 β (H), 17 β (H)- Sterane (S+R)
35	C ₂₉	5 α (H), 13 α (H), 17 α (H)- Sterane (R)

Figure captions

Figure 1: Paleogeographic reconstruction for the Late Ordovician (450 Ma) displaying the Baltic continent and the approximate location of the HCM (solid square) during the Late Ordovician, which had a shallow water environment and was influenced by an upwelling system, resulted from SE trade winds. The paleogeographic map was redrawn from R. C. Blakey maps available at <http://cpgeosystems.com/mollglobe.html> and the names and labels were taken from Rasmussen and Harper (2011).

Figure 2: General lithostratigraphic column (A) and simplified geological map (C) of the HCM displaying geographical location of the Bardo Stawy and sample stratigraphic locations within the sampled interval (B). SB and OR denote Silurian and Ordovician samples, respectively. The lithostratigraphic column was compiled from (Kremer, 2005; Masiak et al., 2003; Modlinski and Szymanski, 2001; Trela, 2006; Trela and Salwa, 2007) and the geological map was modified from Fijalkowska-Mader et al. (2010).

Figure 3: Partially reconstructed chromatogram (m/z 57) showing the distribution of *n*-alkanes and isoprenoids in the solvent extracts of the Ordovician (OR) and Silurian (SB) samples in the HCM. The numbers above the peaks represent carbon atom numbers, Pr: Pristane, Ph: Phytane, and IS is the internal standard.

Figure 4: Partially reconstructed chromatogram (m/z 191) displaying the tricyclic terpanes and homohopane distribution in the extracts of some representative samples of the Ordovician (OR) and Silurian (SB) in the HCM. Carbon numbers on the peaks represent tricyclic terpane series, numbers denote homohopanes- refer to Table (3) for compound names- and IS is internal standard.

Figure 5: Partially reconstructed chromatogram (m/z 217) illustrates the regular steranes and diasteranes distribution in the extracts of some representative samples of the Ordovician (OR) and Silurian (SB) samples of the HCM, Poland. Note the prominent existence of C_{27} regular sterane in the Ordovician samples and high abundance of diasteranes in the Silurian samples. Refer to table (3) for peak identifications.

Figure 6: Pyrograms of aromatic compounds in the pyrolysates of representative samples of the Ordovician and Silurian periods illustrates n -alkanes (m/z 57), naphthalene and alkyl-naphthalenes (m/z 128+142+156), phenanthrene (m/z 178), methyl-phenanthrenes (m/z 192), dibenzothiophene (m/z 184), and methyl-dibenzothiophenes (m/z 198). Structures refer to their identified compound peaks.

Figure 7: Ternary plot of regular steranes ($\alpha\alpha\alpha$ S isomers) in the solvent extracts of Ordovician (OR) and Silurian (SB) samples in HCM showing sources of organic matter. Note the particular distribution of the Ordovician samples in the C_{27} corner. The diagram is modified from Huang and Meinschein (1979).

Figure 8: Stratigraphical trends of TOC percentage and some biomarker ratios displaying the change across the transition of the boundary from Ordovician into Silurian. For the legend of lithostratigraphy, refer to Figure 1.

Figure 9: Schematic model illustrates the depositional conditions, sea level, and upwelling during the Late Ordovician (A) and Early Silurian (B) for the samples in the HCM, central Poland. During the Hirnantian (A) sea level was low leading to oxic depositional conditions of the Ordovician sediments that might have been replenished by the oxygen minimum water, whereas during the Rhuddanian (B), sea level has been raised and depositional conditions were changed to suboxic/anoxic and hence shale deposition.

Figures

FIGURE (1)

FIGURE (2)

FIGURE (3)

FIGURE (4)

FIGURE (5)

FIGURE (6)

FIGURE (7)

FIGURE (8)

FIGURE (9)