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Geochemical and faunal proxies in the Westphalian A (Langsettian) marine horizon of the Lublin Coal Basin

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The uppermost Westphalian marine horizon (*Dunbarella* horizon) is especially important for correlation of Carboniferous deposits in the Lublin Coal Basin and in other basins of the Northwest European Carboniferous Basin. The *Dunbarella* horizon is characterized by cyclic sedimentation and consequent faunal spectrum variability, typical for Westphalian marine horizons of northwestern Europe. Palaeontological study of the *Dunbarella* horizon showed the presence of macrofauna representing different palaeoenvironments, from marine to brackish (non-marine) and freshwater conditions. The vertical sea level fluctuations and changes in seawater salinity resulting in palaeontological record changes do not link with geochemical proxies. TOC, redox-sensitive trace element concentrations, and V/Cr, Ni/Co and V/(V + Ni) ratios generally suggest that the *Dunbarella* horizon sediments were deposited under predominantly oxic conditions (with local exceptions during the initial phase of the *Dunbarella* ingression; Kopina 1 borehole).

Key words: inorganic geochemistry, palaeoredox conditions, *Dunbarella* horizon, Lublin Coal Basin.

INTRODUCTION

The Northwest European Carboniferous Basin (NWECB) is a large sedimentary basin extending from Ireland in the west to Poland in the east. It developed north of the Variscan Rheno-Hercynian belt (Kombrink, 2008). Geology of the NWECB has been extensively studied by many authors because of its economic importance the Pennsylvanian coal-bearing (mainly Westphalian) series (e.g., Calver, 1968; Leeder, 1988; Narkiewicz, 2007; Kombrink, 2008). Nowadays, the most prospective area for coal deposits of the NWECB is the Lublin Coal Basin (LCB) located in Poland, in the eastern part of the basin.

The most important part of the coal-bearing Carboniferous series of LCB is the Lublin Formation (Pennsylvanian, Westphalian A and B) containing the main multi-seam coal deposits (Porzycki and Zdanowski, 1995).

Only one coal mine operates in the LCB, and it encompasses ~0.8% of the total coal basin area. Currently, due to the investor interest, intensive geological research of the deposits has been conducted. Within the Lublin Coal Project, the Prairie Mining Limited Company has focused on the development and operation of a new coal mine in the Lublin Coal Basin. One of the most important stages of the geological research is the identification of the *Dunbarella* marine marker horizon that can be found in the lower part of the Lublin Formation. Therefore, it constitutes the most important section for correlation and exploration of the deposits in the LCB. Furthermore, since the *Dunbarella* marine marker horizon has its equivalents in other coalfields of the Northwest European Carboniferous Basin, it is a significant marker horizon for the whole region. The identification of this faunal horizon is essential for the recognition of coal deposits in the LCB.

Palaeontological studies of the *Dunbarella* horizon have been presented by many authors. So far, detailed palaeontological study is the only method for its identification (Musiał et al., 1995; Musiał and Tabor, 2001; Krzeszowska, 2015 and references cited therein).

Laterally extensive marine horizons that occur within paralic sequences (e.g., *Dunbarella* marine horizon) are generally regarded as reliable correlative stratigraphic markers in the Pennsylvanian coalfields. These horizons are represented typically by goniatite-bearing black shales characterized by high U and Mo levels, and interpreted as deposited during times of anoxia (Fisher and Wignall, 2001; Kombrink, 2008; Kombrink et al., 2008; Pearce et al., 2010). Enrichment in redox-sensitive trace elements, and high TOC and S contents allow identification of the oxygen-restricted environments (e.g., Kombrink, 2008; Fisher and Wignall, 2001; Zatoń et al., 2009; Pearce et al., 2010; Racka et al., 2010; Marynowski et al., 2012).

Therefore, the main goals of the study were to (1) determine the palaeoredox conditions of the *Dunbarella* marine horizon, (2) compare the geochemical data with the palaeontological record, and (3) test, whether inorganic geochemistry can be used for identification and correlation of the *Dunbarella* marine horizon.

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GEOLOGICAL SETTING

The Lublin Coal Basin is located in south-east Poland. The Lviv-Volhynia Coal Basin is its continuation in Ukraine. It is situated at the contact zone of two major geological units: the Precambrian East European Platform and the Early Paleozoic West European Platform. The LCB is an extended province stretching from south-east to north-west, 20 to 40 km wide and 180 km long (Fig. 1). The sub-Carboniferous basement consists of Proterozoic crystalline rocks and Lower and Upper Paleozoic deposits. The Carboniferous strata, which lie discordantly on the older substrate, are represented by Middle Mississippian to Lower Pennsylvanian deposits (Fig. 2). They are overlain by a sequence of Permo-Mesozoic and Cenozoic rocks. The thickness of the overburden varies from 350 to >1200 m (e.g., Porzycki and Zdanowski, 1995; Zdanowski, 1999).

The main hard coal-bearing series of the LCB, as well as the other basins of the NWECB, consists of the Westphalian deposits (representing mostly the Lublin Formation in the LCB). These are paralic deposits with multiple marine fauna horizons (mainly in the Westphalian A), which pass into brackish and then into continental deposits. The marine horizons are important marker horizons within a monotonous mudstone-claystone sequence of fluvial or lacustrine sediments. They form relatively thin (up to several metres in thickness) deposits being a record of marine or brackish sedimentary conditions (Leeder, 1988; Suess et al., 2007). The *Dunbarella* marine horizon, which is the subject of this study, is the most important marker horizon in the LCB (in Poland). It marks the boundary between the Westphalian A and B and between paralic and limnic sedimentation (Musiał et al., 1995; Krzeszowska, 2015). This marker horizon correlates with the Clay Cross Marine Band (England), the Katharina horizon (Germany and the Netherlands) and the Quaregnon horizon (Belgium). These are very important correlation horizons in northwestern and central Europe due to their very large extent, their common presence, and the fact that they are located within a sequence very rich in coal resources (Calver, 1968; Musiał et al., 1995; Kombrink, 2008; Krzeszowska, 2015). A distinctive feature of this horizon is cyclic sedimentation and associated variability of the fauna spectrum typical of the Westphalian marine fauna horizons (Krzeszowska, 2015). The cyclic sedimentation and consequent faunal spectrum variability in the profiles of marine horizons have been reported from the basins of northwestern and central Europe (Calver, 1968; Kombrink, 2008).

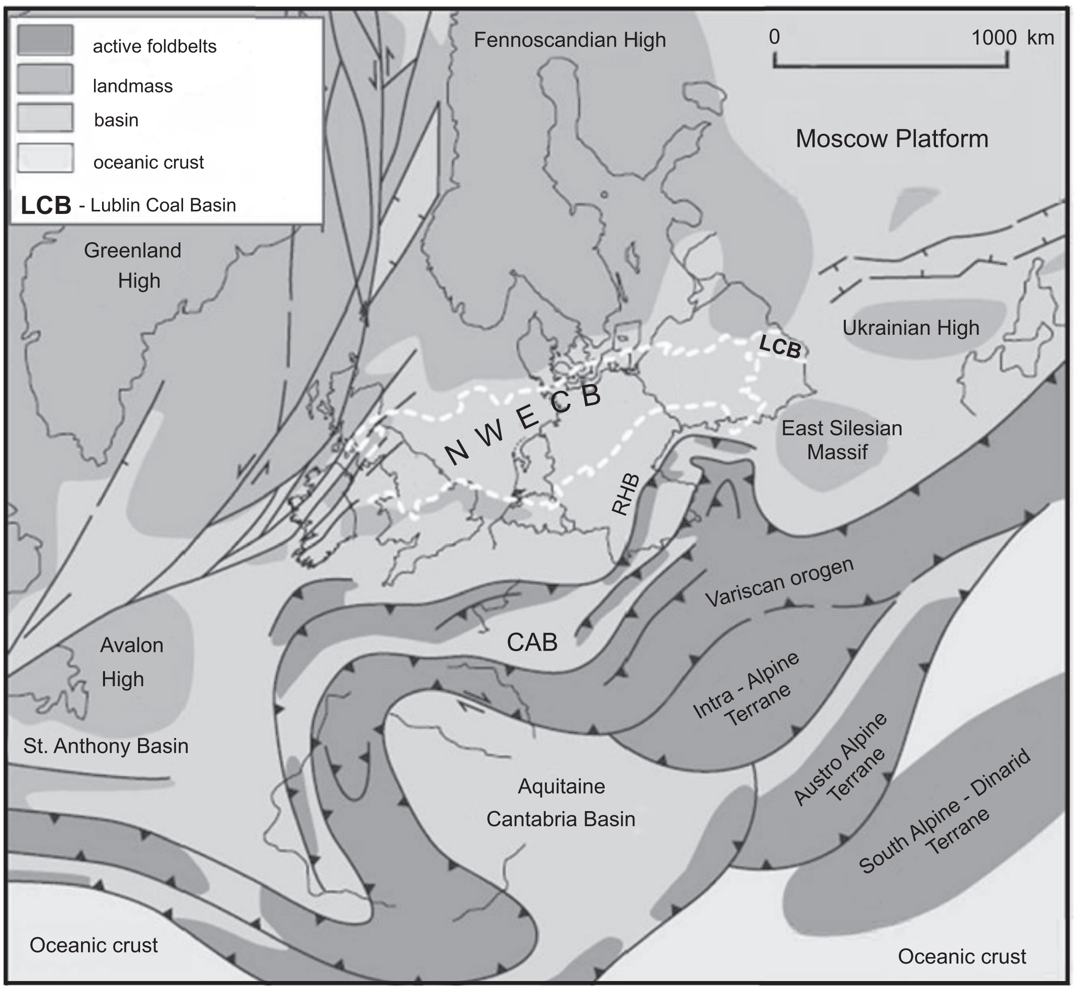

Fig. 1. Location of the Lublin Coal Basin (LCB) within the Northwest European Carboniferous Basin (NWECB)

The dashed white line indicates the present-day contours of the NWECB; RHB – Rhenohercynian Basin, CAB – Central Armorican Basin (Kombrink, 2008, redrawn after Ziegler, 1989)

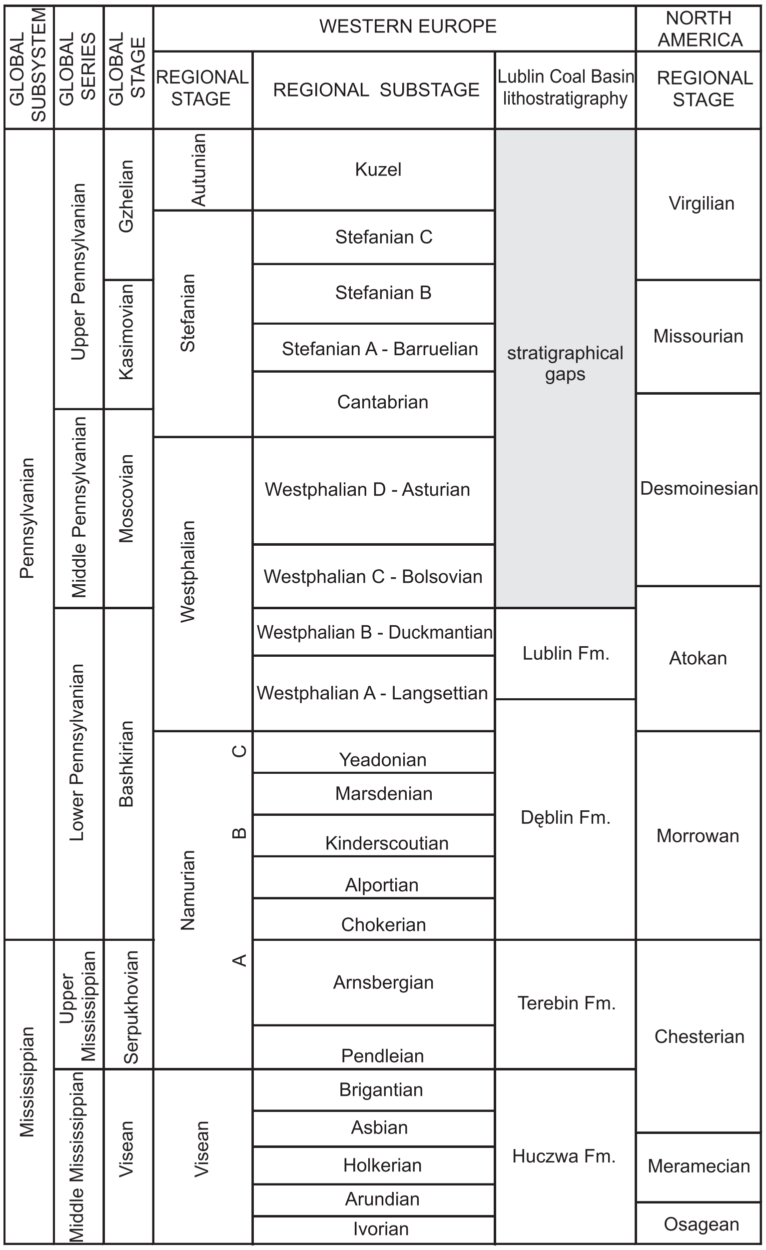

Fig. 2. Divisions of the Carboniferous succession in the Lublin Coal Basin and its correlation with the North America Regional Stage (simplified) (after Porzycki and Zdanowski, 1995; Dusar, 2006; Heckel and Clayton, 2006; Richards, 2013)

MATERIALS AND METHODS

The material studied comes from core samples from the Kopina 1, Borowo, Kulik and Syczyn 7 boreholes, located in the central part of the Lublin Coal Basin (Figs. 3 and 4). The study is based on data from 41 samples taken from the *Dunbarella* marine marker horizon.

The *Dunbarella* horizon is composed of grey claystones, locally sandy claystones or mudstones with thin carbonate and siderite interlayers (Fig. 5).

Sampling for the geochemical study followed a detailed palaeontological study of the horizon (Krzeszowska, 2015). Samples (claystones and sandy claystones) representing 0.2 m intervals of the profiles with different faunal record were selected for the geochemical study (Fig. 5).

The samples represent intervals of the *Dunbarella* horizon characterized by the following features (after Calver, 1968):

– abundant typical marine fauna represented mainly by bivalve and same goniatites and gastropods, with varying occurrence of brachiopods (mainly *Lingula*),
– abundant brackish fauna or fauna with high salinity tolerances, represented mainly by bivalves, with varying occurrence of brachiopods (mainly *Lingula*),
– abundant fauna represented mainly by brachiopods (*Lingula*),
– freshwater fauna or indeterminate remains of freshwater fauna,
– few faunal specimens, including primarily brachiopods and bivalves or indeterminate remains.

Sample preparation and analytical procedures were performed by the AcmeLab Analytical Laboratory (currently Bureau Veritas Commodities Canada Ltd), Vancouver, Canada, and the Oil and Gas Institute – National Research Institute (Kraków, Poland). Major and trace elements (U, TH, Mo, V, Cr, Co, Ni, Zn, Cu, Pb, Fe and Al) were analysed using inductively coupled plasma mass spectrometry (ICP/MS) following 4-acid digestion (HF + $HClO_4$ + HCl + $+HNO_3$). Contents of total sulphur (S) were obtained using a LECO analyser. Total organic carbon (TOC) was determined by Rock-Eval pyrolysis. Table providing chemical data, including methods and detection limits for each sample (Appendix 1*).

RESULTS AND DISCUSSION

TOC-Fe-S RELATIONSHIPS

The relationship between TOC (total organic carbon) vs. Fe vs. S has been extensively used to assess palaeoredox conditions in marine systems (e.g., Berner and Raiswell, 1984; Raiswell and Berner, 1986; Leventhal, 1987; Raiswell and Al-Biatty, 1989; Szczepanik et al., 2007; Algeo and Maynard, 2008; Zatoń et al., 2009; Racka et al., 2010; Marynowski et al., 2012; Wójcik-Tabol, 2015).

Total organic carbon, and total sulphur (S) and iron (Fe) contents are generally low in the *Dunbarella* horizon (Fig. 6, Table 1 and Appendix 1). Increased TOC, S and Fe contents were observed mainly in the lower part of the horizon in the Kopina 1 borehole (samples K2, K3 and K4).

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1374

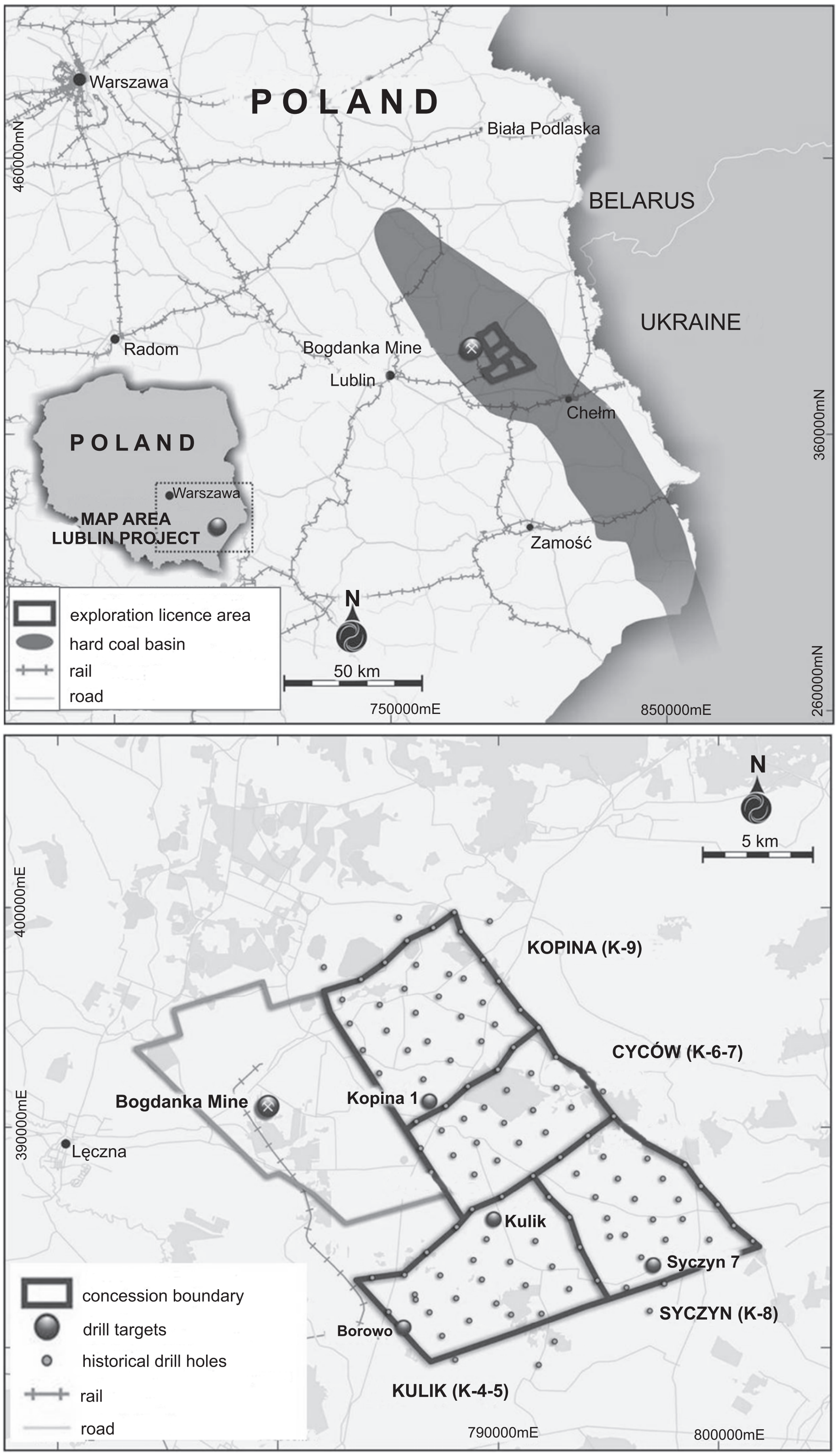

Fig. 3. Location of the sampled boreholes: Kopina 1, Kulik, Borowo, Syczyn 7 carried out under the Lublin Coal Project (http://www.pdz.com.au)

Degree of pyritization (DOP) is often applied to determine the palaeoredox conditions (Hatch and Leventhal, 1992; Cruse and Lyons, 2000; Rimmer, 2004; Algeo and Maynard, 2008). DOP is defined as the pyrite iron/pyrite iron + reactive iron ($\%Fe_{pyrite}/\%Fe_{pyrite}+_{reactive}Fe$) (Berner, 1970) ratio. Raiswell et al. (1988) have suggested that sediments with DOP less than 0.46 indicate aerobic conditions, DOP values between 0.46 and 0.75 indicate dysoxic or restricted conditions, and DOP values >0.75 suggest anoxic (inhospitable) conditions for the sediment deposition.

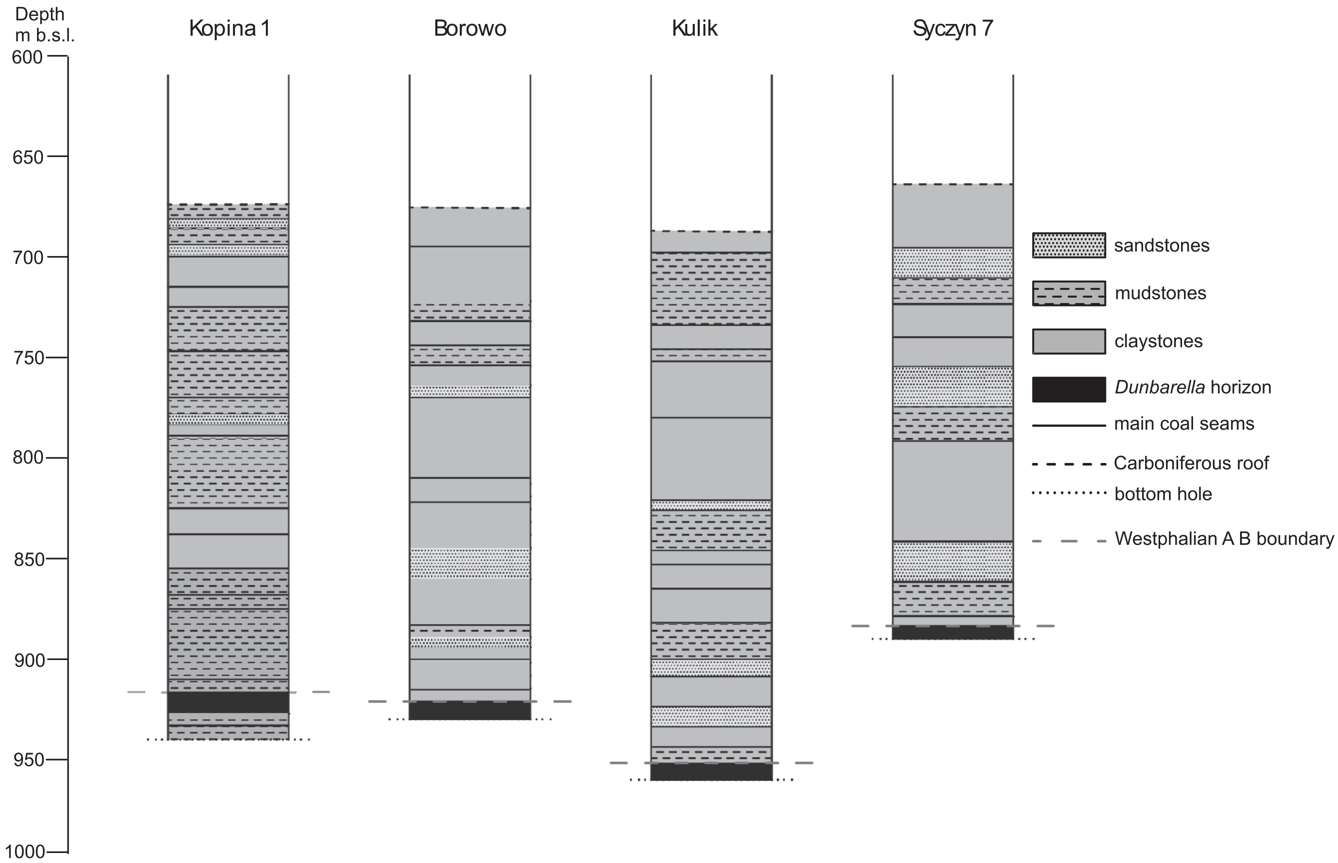

Fig. 4. Location of the *Dunbarella* horizon within the simplified Carboniferous profiles of the Kopina 1, Borowo, Kulik and Syczyn 7 boreholes (LCB) (after Krzeszowska and Kokowska-Pawłowska, 2017: fig. 2 ibidem, simplified)

Calculation of DOP values requires determination of reactive iron, but Algeo and Maynard (2004, 2008) proposed making a rough assessment using DOP_t values (in place of true DOP). DOP_t is based on the ratio of pyrite Fe (based on total S) to total Fe. This index can be used in place of true DOP, if pyrite S composes the bulk of total S, and reactive Fe composes the bulk of total Fe (Algeo and Maynard, 2008). Although DOP_t values are systematically lower than true DOP values, there is a strong relationship between the two parameters, and DOP_t can be used as an estimator of true DOP (Algeo and Maynard, 2008).

DOP_t values for aerobic conditions are typically <0.3 for restricted conditions between 0.3 and 0.6, while for inhospitable conditions it is usually >0.6 (Algeo and Maynard, 2008).

In this study, DOP_t values (in place of true DOP) have been analysed. DOP_t values for most of the samples are low indicating aerobic or restricted conditions (Fig. 7 and Table 1). The samples from the lower part of the horizon in the Kopina 1 borehole (K2, K3, K4) show higher DOP_t values which indicate anoxic conditions.

REDOX-SENSITIVE TRACE ELEMENT

Redox-sensitive trace element (TEs) concentrations (such as U, V, Mo, Cr, Co, Ni, Cu, Zn and Pb) have been frequently used as indicators of redox conditions in modern and ancient sedimentary systems (e.g., Calvert and Pedersen, 1993; Jones and Manning, 1994; Wignall, 1994; Algeo, 2004; Rimmer, 2004; Tribovillard et al., 2006; Algeo and Maynard, 2008; Pearce et al., 2010; Racki et al., 2012; Wójcik-Tabol, 2015). The most useful trace elements for palaeoenvironmental analyses are U and Mo, because they:

- demonstrate conservative behaviour under oxic conditions and have long residence times in seawater,
- exhibit nearly consistent concentrations in seawater globally,
- are present in low concentrations in plankton, so enrichments in sediments generally comes from seawater, especially under oxygen-depleted conditions (Algeo and Tribovillard, 2009).

TEs commonly exhibit considerable enrichment in laminated, organic-rich facies, especially those deposited under euxinic conditions (Algeo and Maynard, 2008). On the other hand, inferences regarding palaeoenvironmental conditions based on trace element concentrations are commonly unreliable if single element distributions are used, because their concentrations are influenced by many factors and mechanisms (Tribovillard et al., 2006). Many authors consider not only the concentration of elements but also the degree of enrichment or depletion of a trace element to reconstruct palaeoenvironmental conditions (e.g., Wedepohl, 1991; Rimmer, 2004; Brumsack, 2006; Tribovillard et al., 2006; Kombrink, 2008; Algeo and Tribovillard, 2009). The method of geochemical normalization and calculation of enrichment factors (EFs) is as follows:

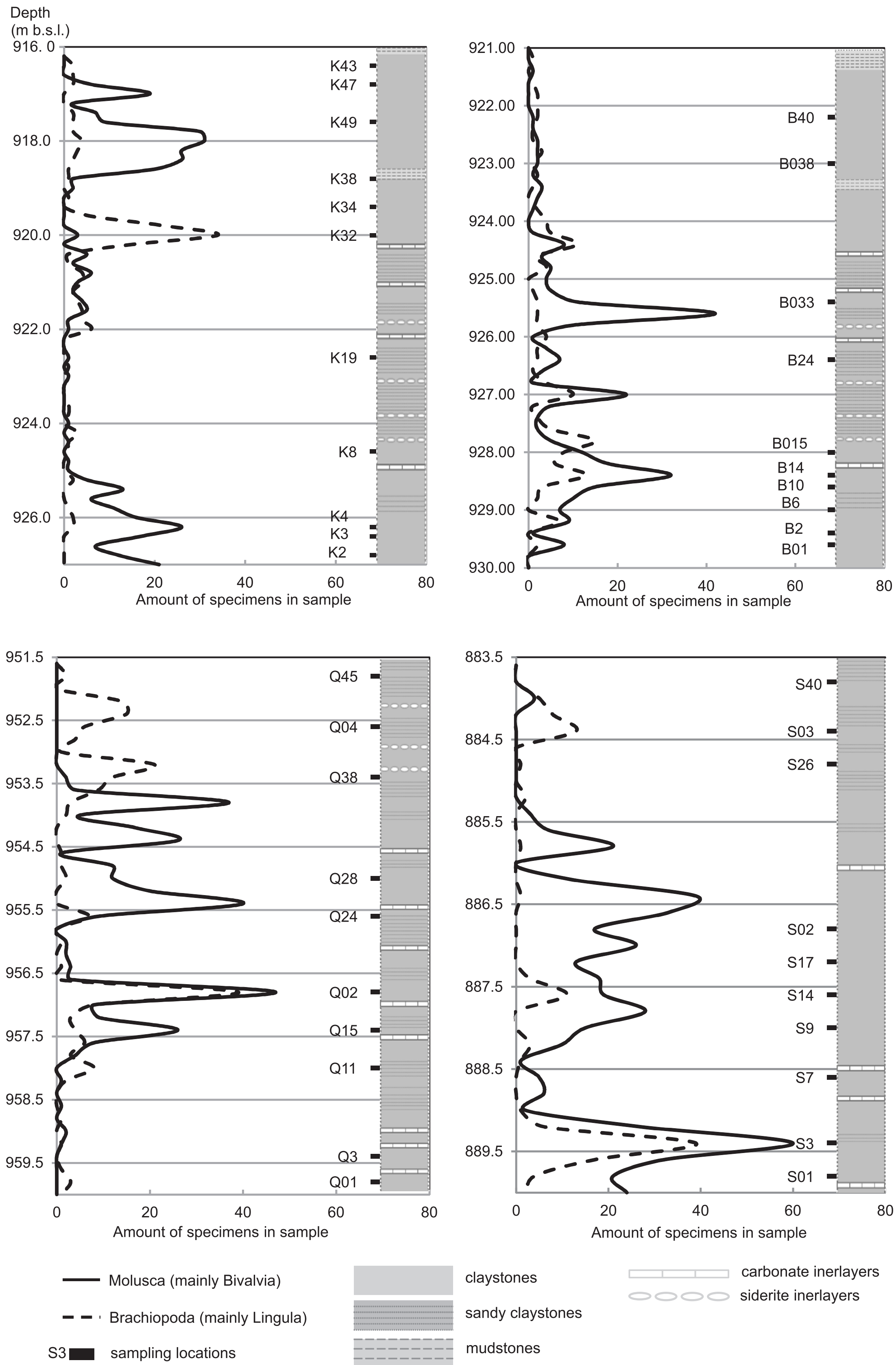

Fig. 5. Mollusc/brachiopod dynamics and sampling location within the *Dunbarella* marine marker horizon (LCB)

A – Kopina 1, B – Borowo, C – Kulik, D – Syczyn 7; after Krzeszowska (2015: fig. 5 ibidem)

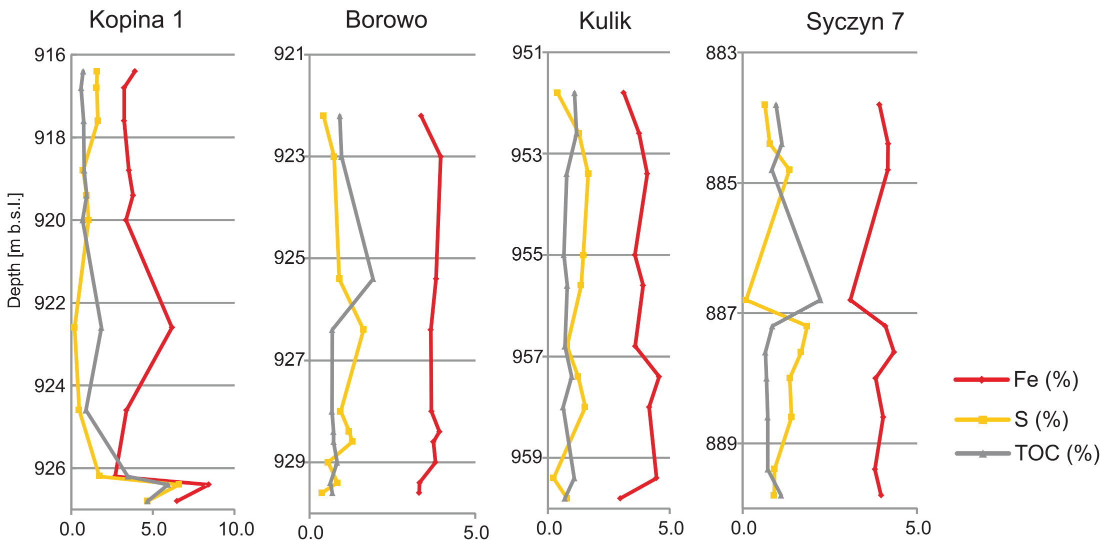

Fig. 6. Vertical distribution of TOC, S and Fe within the *Dunbarella* marine horizon in the Lublin Coal Basin

Table 1

Major palaeontological and geochemical data for samples from the *Dunbarella* horizon

Bore-hole	Sample	Depth (m b.s.l.)	Major palaeontological data: Genus dominated	Major palaeontological data: Main genus accompanying	TOC %	S %	Fe %	DOP_t	U_{aut}	EF_U	EFmo	V/Cr	Ni/Co	V/(Ni=V)
Kopina 1	K43	916.4	No fauna		<1	1.58	3.90	0.41	0.00	1.51	0.95	<2	<5	0.58-0.67
	K47	916.8	*Edmondia Sanguinolites*	*Lingula*		1.56	3.24	0.48		1.73	1.10			
	K49	917.6	*Posidonia*	*Edmondia Sanguinolites Dunbarella Anthracoceras*		1.63	3.24	0.50	0.27	1.88	1.24			
	K38	918.8	Remains of freshwater fauna			0.72	3.53	0.20	0.00	1.40	0.23			
	K34	919.4	No fauna			0.94	3.78	0.25		1.41	0.17			
	K32	920.0	*Lingula*			1.05	3.35	0.31		1.39	0.21			
	K19	922.6	No fauna		1.84	0.20	6.17	0.03		1.11	0.58			
	K8	924.6			<1	0.48	3.38	0.14		1.12	0.32			
	K4	926.2	*Posidonia Euchondria Dunbarella*	*Dunbarella Anthracoceras Gastrioceras*	3.46	1.72	2.69	0.64	5.60	2.76	20.93		6.74	
	K3	926.4			5.93	6.60	8.42	0.78	1.87	1.88	2.37		<5	
	K2	926.8	*Carbonicola Naiadites*	*Curvirimula Anthracosia*	4.67	4.65	6.47	0.72	1.20	1.57	1.81			
Borowo	B40	922.2	Remains of freshwater fauna		<1	0.42	3.37	0.12	0.57	1.40	0.32	<2	<5	0.60-0.69
	B038	923.0	No fauna		0.74	3.96	0.19	0.60	1.41	0.40				
	B033	925.4	*Edmondia Sanguinolites*	*Posidonia Anthracoceras*	1.92	0.90	3.82	0.24	0.38	1.57	0.49			
	B24	926.4	*Posidonia*	*Edmondia Sanguinolites*	<1	1.63	3.66	0.45	0.00	1.43	0.43			
	B015	928.0	*Lingula*	*Posidonia*		0.94	3.68	0.26	0.27	1.66	0.32			
	B14	928.4	*Posidonia Dunbarella*	*Polidevcia Anthracoceras*		1.20	3.92	0.31	0.03	1.39	1.43			
	B10	928.6				1.29	3.74	0.34	0.00	1.22	0.29			
	B6	929.0				0.56	3.80	0.15		1.14	0.35			
	B2	929.4				0.84	3.32	0.25		1.17	0.27			
	B01	929.6				0.37	3.31	0.11		1.34	0.43			

Tab. 1 cont.

Bore-hole	Sample	Depth (m b.s.l.)	Major palaeontological data		Major geochemical proxies									
			Genus dominated	Main genus accompanying	TOC %	S %	Fe %	DOP_t	U_{aut}	EF_U	EF_{Mo}	V/Cr	Ni/Co	V/(Ni=V)
Kulik	Q45	951.8	Remains of freshwater fauna		1.09	0.39	3.11	0.13	0.53	1.56	0.34	<2	<5	0.57-0.70
	Q04	952.6	*Lingula*		1.17	1.27	3.74	0.34	0.00	1.30	0.40			
	Q38	953.4	*Lingula*		<1	1.65	4.07	0.41	0.27	1.62	0.76			
	Q28	955.0	*Edmondia*	*Posidonia Dunbarella Sanguinolites Anthracoceras Lingula*		1.45	3.57	0.41	0.00	1.46	0.61			
	Q24	955.6				1.36	3.90	0.35		1.50	0.63			
	Q02	956.8	*Polidevcia, Phestia Lingula*	*Posidonia Dunbarella Anthracoceras*		0.78	3.58	0.22		1.35	1.07			
	Q15	957.4	*Polidevcia, Phestia*	*Posidonia Dunbarella Anthracocera Lingula Edmondia*		1.24	4.56	0.27		1.59	3.29			
	Q11	958.0	*Lingula*			1.53	4.15	0.37		1.19	0.35			
	Q3	959.4	No fauna		1.08	0.23	4.45	0.05		1.14	0.21			
	Q01	959.8	Few faunal specimens – *Lingula*		<1	0.78	2.97	0.26		1.09	0.49			
Syczyn 7	S40	883.8	Remains of freshwater fauna		<1	0.64	3.92	0.16	0.60	1.47	0.28	<2	<5	0.59-0.73
	S03	884.4	*Lingula*		1.12	0.78	4.17	0.19	0.10	1.51	0.53			
	S26	884.8	No fauna		<1	1.34	4.16	0.32	0.67	1.57	0.56			
	S02	886.8	*Dunbarella Posidonia*	*Edmondia Sanguinolites*	2.23	0.10	3.09	0.03	1.20	2.33	0.35			
	S17	887.2	*Dunbarella Posidonia*	*Anthracoceras*	<1	1.85	4.09	0.45	0.00	1.59	1.31			
	S14	887.6	*Edmondia Sanguinolites*	*Dunbarella Anthracoceras Lingula*		1.68	4.34	0.39	0.07	1.54	1.04			
	S9	888.0				1.35	3.81	0.35	0.00	1.30	0.36			
	S7	888.6	*Posidonia*	*Phestia Dunbarella*		1.40	4.03	0.35		1.42	0.51			
	S3	889.4	*Posidonia Phestia*	*Dunbarella Anthracoceras Lingula*		0.91	3.79	0.24	0.03	1.50	0.49			
	S01	889.8	*Posidonia Phestia Dunbarella*	*Anthracoceras Gastrioceras*	1.10	0.90	3.97	0.23	0.00	1.51	0.70			

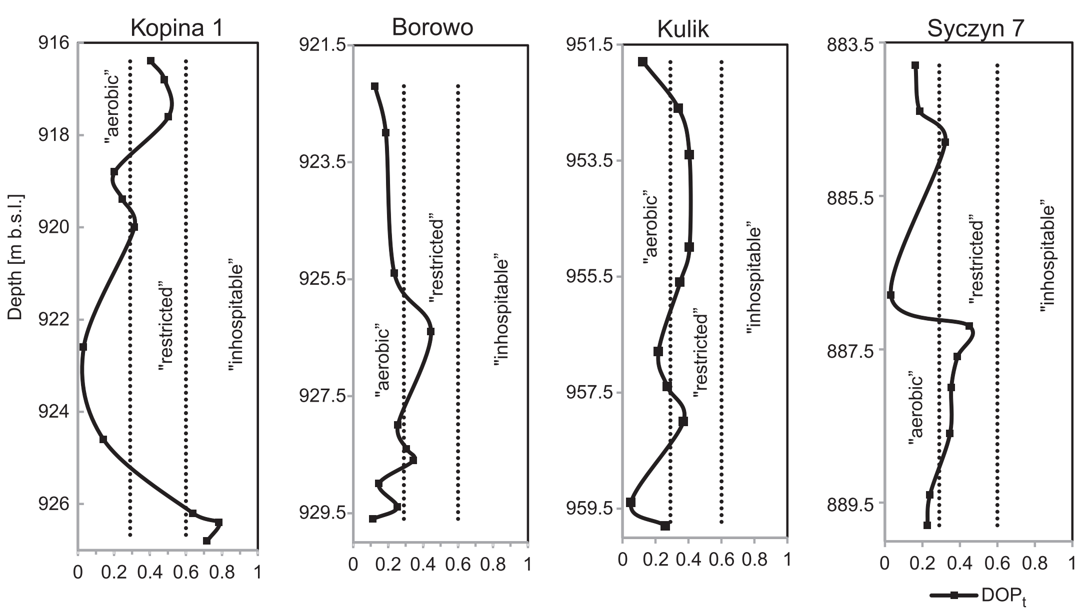

Fig. 7. Vertical variability of the estimate of degree of pyritization (DOP_t) within the *Dunbarella* marine horizon. The boundaries for aerobic, restricted and inhospitable conditions (based on DOP_t) were established according to Algeo et al. (2008)

$$EF = \frac{\frac{El_s}{Al_s}}{\frac{El_{av}}{Al_{av}}}$$

where: El_s – element concentration in the sample, Al_s – Al concentration in the sample, El_{av} – element concentration in average crustal rocks or average shale, and Al_{av} – Al concentration in average crustal rocks or average shale.

U is the most important redox-sensitive trace element for reconstruction of the sedimentary environment (e.g., Leeder, 1988; Fisher and Wignall, 2001; Rimmer, 2004; Kombrink, 2008; Algeo and Tribovillard, 2009; Pearce et al., 2010; Wójcik-Tabol, 2015). The U content of sediments is a combination of authigenic and detrital components, and authigenic U is a suitable indicator of redox conditions (Jones and Manning, 1994). Authigenic uranium can be calculated as $U_{aut} = U_{tot}$ - Th/3, with Th/3 as an estimate of the detrital uranium fraction in mudstones (Wignall and Myers, 1988). Reducing conditions may precipitate uranium to enrich the sediment in authigenic (non-detrital) uranium. Its values <5 indicate oxic conditions, while values 5–12 and >12 indicate dysoxic and suboxic to anoxic conditions, respectively (Jones and Manning, 1994). Algeo and Tribovillard (2009) proposed to use enrichment factors (EF) for rapid assessment of the authigenic fraction of U (similarly for Mo), indicating that the detectable authigenic enrichment corresponds to EF>3, and the substantial enrichment to EF>10.

The U contents of the samples from the *Dunbarella* marine horizon range from 3.5 to 11.6 ppm (Fig. 8 and Appendix 1). Only three samples showed values >6 ppm, which suggest marine deposition under reducing conditions (Leeder et al., 1990; samples from the lower part of the horizon in the Kopina 1 borehole and from the middle part of the horizon in the Syczyn 7 borehole). Most of the samples have low EF_U values, calculated relative to average shale (Wedepohl, 1991) (1.09–2.76), and the lack of authigenic U. This indicates oxic sedimentary environment (Fig. 8, Table 1 and Appendix 2).

Mo concentration, which (next to U) has been reported as the most important indicator in distinguishing oxic, suboxic and anoxic facies (Algeo and Lyons, 2006; Algeo and Rowe, 2012; Marynowski et al., 2017), shows significant variability in the samples from the *Dunbarella* horizon. The EF_{Mo} values range from 0.17 to 20.93 (Table 1), but high Mo concentrations were observed only in the samples from the lower part of the horizon in the Kopina 1 borehole (samples K2, K3 and K4) and from the middle part of the horizon in the Kulik borehole (sample Q15), suggesting oxygen-depleted sedimentary facies.

Algeo and Tribovillard (2009) analysed patterns of covariation between Mo and U in modern and ancient anoxic marine systems. To compare enrichments of these elements, they proposed using enrichment factors (EF_{Mo}, EF_U) that are useful for rapid assessment of the authigenic fraction of Mo and U. Algeo and Tribovillard (2009) stated that EF_{Mo} *versus* EF_U crossplots (Fig. 9), in which the Mo/U molar ratio (~7.5–7.9) of seawater is a guide to interpreting relative enrichments of Moauth *versus* Uauth, can be applied for palaeoenvironmental analyses. Oxic facies show little or no Mo and U enrichments, suboxic facies exhibit modest enrichment with $Mo_{aut.}/U_{aut.}$ (clearly lower than the seawater ratio), while anoxic facies exhibit strong enrichment accompanied by progressively higher $Mo_{aut.}/U_{aut.}$ ratios (Algeo and Tribovillard, 2009).

Most of the samples from the *Dunbarella* horizon show low $U_{aut.}$ enrichment and lack of $Mo_{aut.}$ enrichment, corresponding to the seawater Mo/U molar ratio of <0.2, indicating oxic conditions (Fig. 9 and Appendix 2). Samples showing low $U_{aut.}$ and $Mo_{aut.}$ enrichments (EF_U and EF_{Mo} between 1–3) yielding seawater Mo/U molar ratio of ~0.2–0.7, suggest variable redox conditions, probably ranging from oxic or suboxic. Only one sample (from the lower part of the horizon in the Kopina 1) has distinctly higher $Mo_{aut.}$ enrichment and moderate $U_{aut.}$ enrichment, representing the Mo/U molar ratio greater than that of seawater, which strongly suggests anoxic facies.

In addition to U and Mo, other redox-sensitive trace metals can be useful as palaeoredox proxies. V, Cr and Co tend to be more soluble under oxidizing conditions and less soluble under reducing conditions, resulting in authigenic enrichments in oxy-

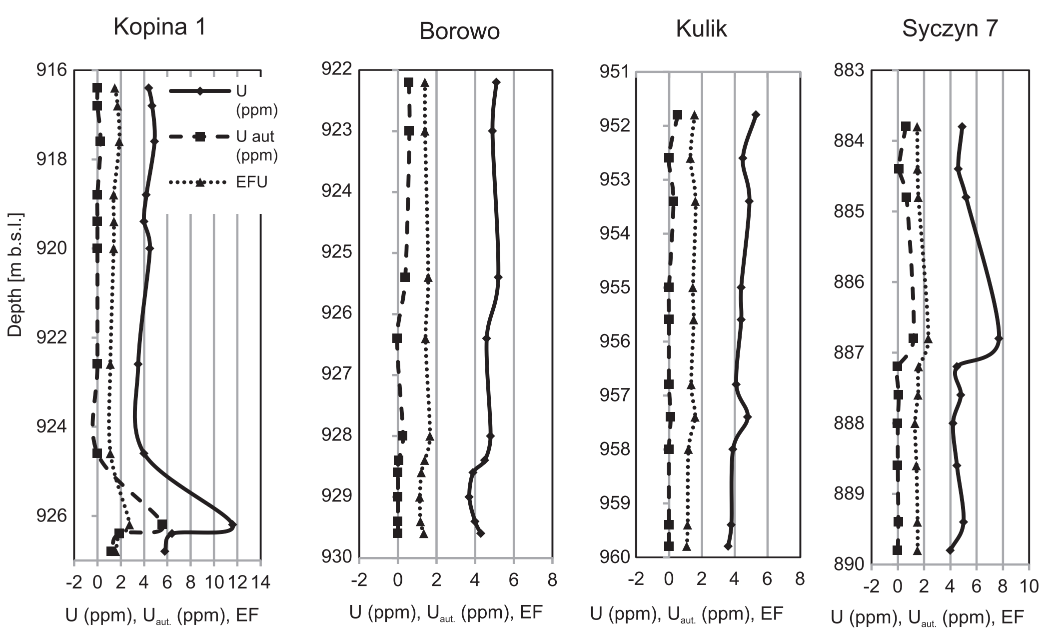

Fig. 8. Vertical distribution of uranium in the *Dunbarella* marine horizon

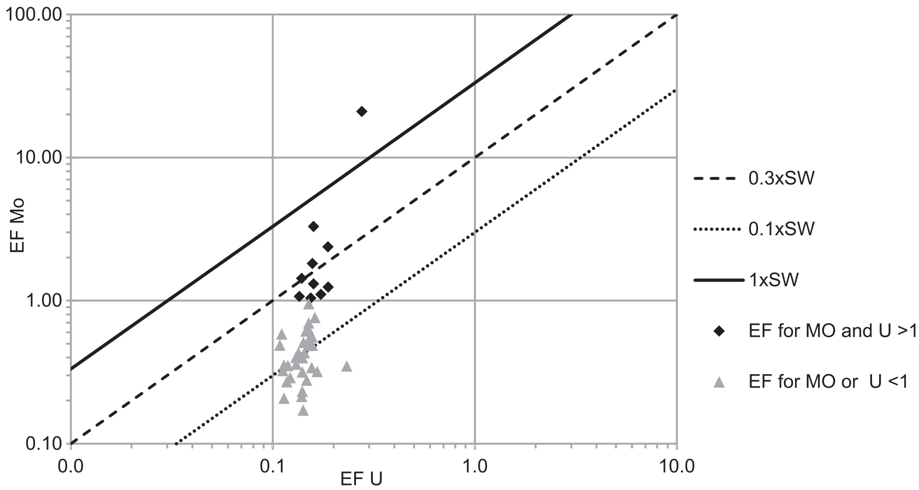

Fig. 9. Crossplot of enrichment factors EFMo vs EF_U for samples from the *Dunbarella* horizon (LCB)

The lines show Mo/U molar ratios equal to the seawater value (1×SW) and to fractions thereof 0.3×SW and 0.1×SW by Algeo and Tribovillard (2009)

gen-depleted sedimentary facies (Tribovillard et al., 2006). All the redox-sensitive trace elements examined in this study (except for Mo) exhibited low EFs (calculated relative to average shale – Wedepohl, 1991) varying from 0.38 to 3.01, with the mean values for the elements ranging from 0.87 to 1.77 (Fig. 10 and Appendix 1).

TRACE ELEMENT INDICES

V/Cr, Ni/Co and V/(V + Ni) trace element indices have been suggested to evaluate palaeoredox conditions in many studies (e.g., Dill et al., 1988; Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer, 2004; Algeo and Maynard, 2008;

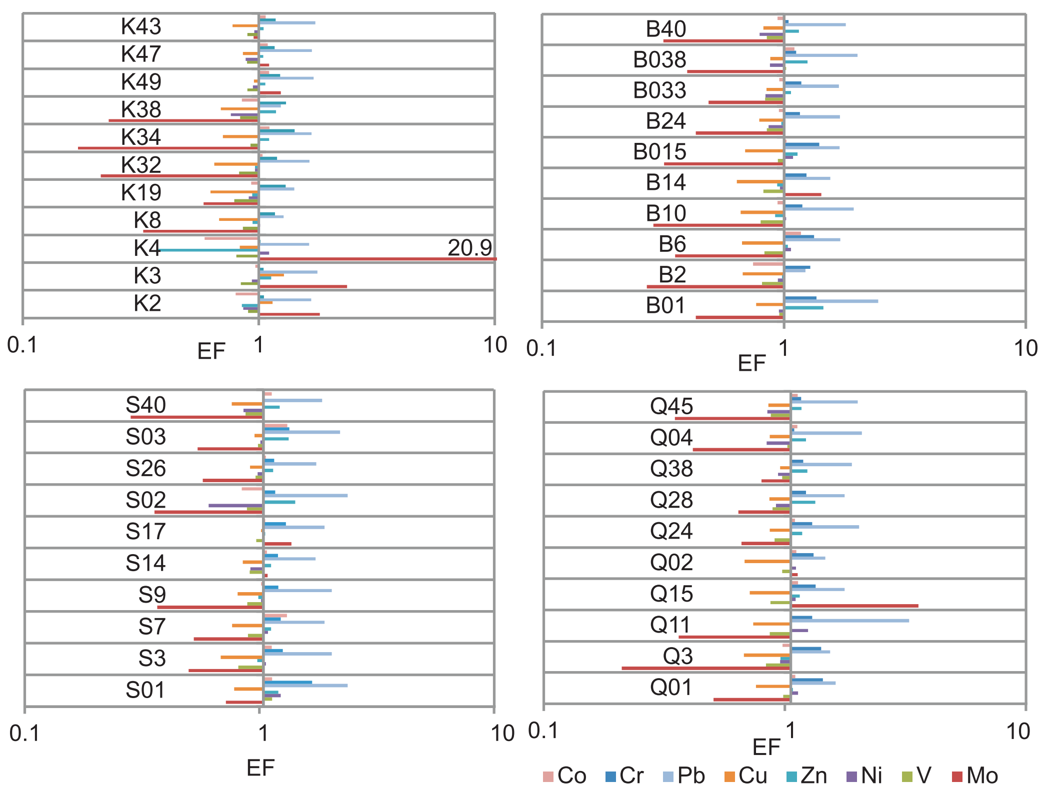

Fig. 10. Enrichment factors (EF) for samples from the *Dunbarella* horizon of the LCB

Racka et al., 2010; Marynowski et al., 2012; Racki et al., 2012; Wójcik-Tabol, 2015). Jones and Manning (1994) proposed to use V/Cr ratios to estimate the palaeoredox depositional conditions, with V/Cr <2 indicating oxidizing condition, 2< V/Cr <4.25 indicating a dysoxic sedimentary environment, and V/Cr >4.25 indicating a reducing environment. The Ni/Co ratios <5 indicate oxic environments, Ni/Co ratios between 5 and 7 suggest dysoxic environments, while higher ratios (Ni/Co >7) suggest anoxic conditions (Jones and Manning, 1994; Rimmer, 2004). Hatch and Leventhal (1992) used V/(V + Ni) ratios as a parameter distinguishing oxic and anoxic bottom waters by suggesting that a high V/(V + Ni) ratio (>0.84) indicates the presence of H_2S in the water column (euxinic conditions), a ratio between 0.46 to 0.84 represents anoxic to dysoxic conditions, and a ratio <0.46 represents oxic conditions.

The V/Cr ratios in samples from the *Dunbarella* horizon are generally uniform and relatively low (0.9–1.4), suggesting oxic environments, while Ni/Co ratios varying from 2.6 to 6.7 for a sample from the lower part of the horizon in the Kopina 1 borehole (sample K4) indicate dysoxic environments (Fig. 11). V/(V + Ni) ratios for all studied samples range between 0.57 and 0.73, which suggests dysoxic to anoxic conditions that do not correspond with the other trace element indicators analysed above (Fig. 12). Similar results were reported, inter alia, for the Devonian–Mississippian black shales (Rimmer, 2004; Rimmer et al., 2004), Middle Jurassic mudstones (Szczepanik et al., 2007; Zatoń et al., 2009), and Upper Famennian of the Holy Cross Mountains (Racka et al., 2010), since the V/(V + Ni) ratios predicted lower oxygen conditions than either Ni/ Co or V/Cr.

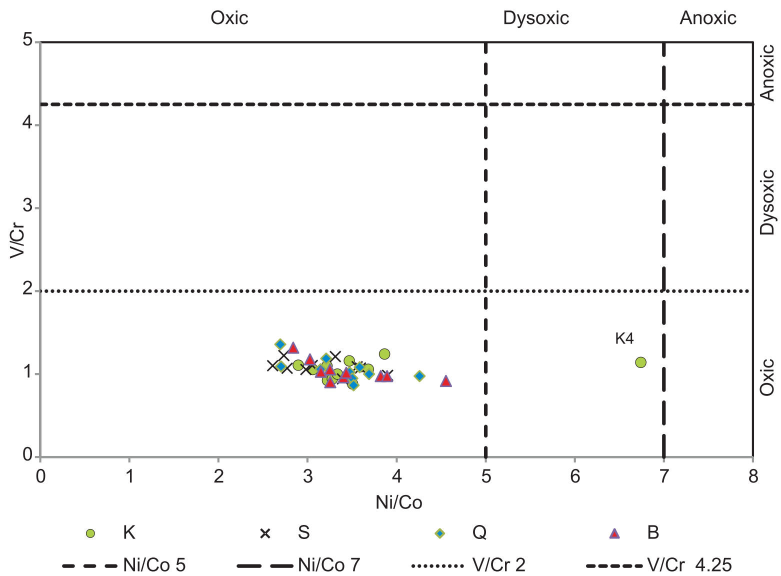

Fig. 11. Crossplots of Ni/Co vs V/Cr redox indices

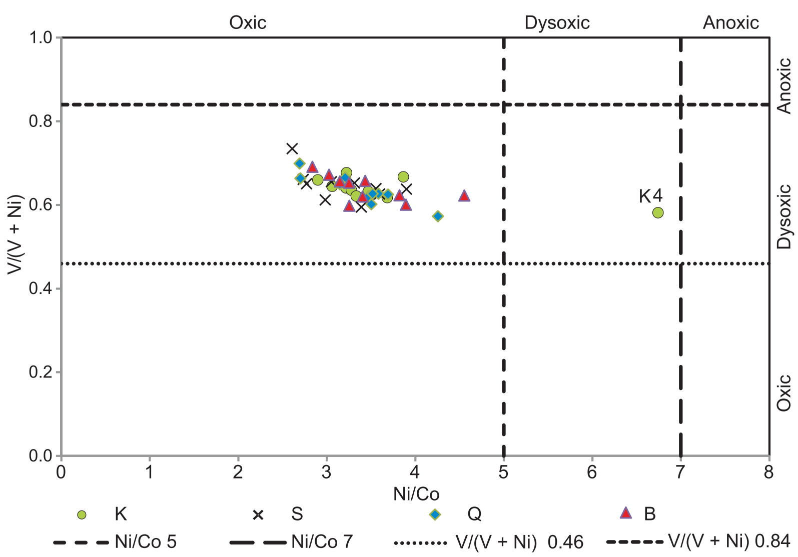

Fig.12. Crossplots of Ni/Co vs V/(V+Ni) redox indices

GEOCHEMICAL PROXIES VS. PALAEONTOLOGICAL RECORD

Detailed palaeontological study of the *Dunbarella* faunal horizon in the Lublin Coal Basin (Poland) has shown the presence of abundant macrofauna – mostly molluscs, brachiopods, and some representatives of crinoids, arthropods and fish (Krzeszowska, 2015). The distribution of fauna in the analysed horizon within the investigated boreholes fluctuates in terms of both abundance and taxonomy, and cyclic sedimentation typical of marine Westphalian horizons was observed.

Palaeontological study of the *Dunbarella* showed the presence of intervals with a different palaeontological record. The samples studied represent deposits containing:

– typical marine fauna (e.g., *Dunbarella, Posidonia, Anthracoceras, Gastrioceras*), occasionally accompanied by bivalve taxa of high salinity tolerance (*Edmondia, Sanguinolites*),
– brackish or high salinity-tolerant faunas (*Lingula, Edmondia, Sanguinolites*),
– freshwater fauna (e.g., *Carbonicola, Naiadites*) or indeterminate remains,
– no fauna (Table 1).

All the analysed samples represent similar lithologies (claystones and sandy claystones).

Vertical variations in the palaeontological record refer to sea level and salinity changes. Cyclic sedimentation and consequent variability of the faunal spectrum in marine horizons are related to changes in environmental conditions, marine ingressions, and periodic sea freshening. Several processes have been proposed to control the cyclic sedimentation: autogenic changes in facies and allogenic changes that are mainly related to periodical sea level fluctuations (>100 m) generated by glacial episodes of the Gondwana tectonic subsidence and climate (Calver, 1968; Ludwig, 1994; Hampson et al., 1999; Joachimski et al., 2006; Suess et al., 2007; Rygel et al., 2008; Waksmundzka, 2013).

The geochemical investigations, presented for the first time for the *Dunbarella* horizon, focus mainly on geochemical proxies to determine the palaeoredox conditions. Previous studies of the horizons containing remains of freshwater fauna in the aspect of the water salinity (e.g., Th/K_2O, P_2O_5/Al_2O_3 and Rb/K) provided predominantly ambiguous results (Krzeszowska and Kokowska--Pawłowska, 2017).

Most of the *Dunbarella* marine horizon in the analysed boreholes is represented by intervals containing marine bivalves accompanied by goniatites. The most important species for stratigraphy are *Dunbarella papyracea* and *Anthracoceras vanderbeckei* – the marker species for the *Dunbarella* faunal horizon.

Goniatite-bearing intervals with marine bivalves can indicate a relatively deep-water environment (Kombrink, 2008). If intervals with goniatites form in oxygen-restricted conditions, it can result in enrichment in U, Mo and other redox-sensitive trace elements, and high TOC and S contents (Fisher and Wignall, 2001; Kombrink, 2008). Therefore, they can be recognized using geochemical methods. Geochemical studies on Upper Carboniferous marine bands have shown that marked enrichments in redox-sensitive trace elements, and high TOC and S contents were observed in same goniatite levels, for example, in the *Gastrioceras listeri* Marine Band (Westphalian A, Middlecliff Quarry, England), the Vanderbeckei Marine Band (Westphalian A and B boundary, Rowe borehole, West Midlands, England), the Namurian Goniatites Marine Band of the Geverik well (Netherlands) (Fisher and Wignall, 2001; Kombrink, 2008; Kombrink et al., 2008; Pearce et al., 2010).

The major environmental proxies (DOP_t, V/Cr, Ni/Co, TOC, TOC, U and Mo) in most of the samples representing intervals with goniatite in the *Dunbarella* horizon indicate oxic conditions during deposition. Similar results were presented for the Westphalian marine bands (Domina, Veldhof and Aegir) of the Netherlands. Those marine bands represent predominantly a Lingula facies characterized by low organic carbon contents (1–2 wt.%), and mostly lacking significant trace element enrichments (Kombrink, 2008; Kombrink et al., 2008).

Anoxic conditions are suggested only by geochemical indicators calculated for samples from the lowest part of the Kopina 1 borehole. Samples K3 and K4 show generally higher TOC, DOP_t and Ni/Co values than those from other parts of the *Dunbarella* horizon. In addition, the U and Mo enrichment, the presence of authigenic U, and the Mo/U molar ratios (especially in sample K4) also suggest oxygen-restricted conditions. It is also worth noting that the deposits (sample K2) directly underlying the above-mentioned samples (K3, K4) contain freshwater fauna and show similar geochemistry, suggesting oxygen-restricted conditions.

The samples with brackish and high salinity-tolerant faunas generally show major environmental indices values indicating oxic conditions during deposition, as well as the sample with freshwater fauna or non-assignable remains, and those the lack of fauna.

Palaeontological data allow identification of intervals with similar geochemical characteristics, representing marine, offshore or brackish, and freshwater sedimentation. Thus, the palaeontological study seems to be the only method to dentify the *Dunbarella* horizon.

CONCLUSIONS

Palaeontological study of the *Dunbarella* marine marker horizon showed the presence of macrofauna representing different palaeoenvironments, from marine and brackish (non-marine) to freshwater conditions (cf. Krzeszowska, 2015). Vertical variations of faunal assemblages are related to rapid and probably short-term sea level and salinity changes controlled by marine ingressions and periodic basin freshening.

Geochemical parameters are relatively similar throughout the *Dunbarella* horizon. They do not show as large fluctuations as the palaeontological record does. The proxies (TOC, Dop_t, redox-sensitive trace element concentrations, $Mo_{aut.}/U_{aut.}$, V/Cr, Ni/Co) suggest mostly permanently oxygenated conditions.

Oxygen-restricted conditions are suggested only by the values of geochemical indicators calculated for samples from the lowest part of the Kopina 1 borehole section.

Two complementary, palaeoecological (based on the faunal spectrum) and geochemical studies were applied to determine palaeoenvironmental conditions of the *Dunbarella* horizon. They have allowed confirming significant changes in palaeo-salinity and relatively constant redox conditions during deposition of the analysed horizon. To make a complete reconstruction of sedimentary environments, an integrated approach, including palaeoecology, geochemistry and sedimentology, should be used.

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