Organic carbon accumulation events in the mid-Cretaceous rocks of the Pieniny Klippen Belt (Polish Carpathians) — a petrological and geochemical approach

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New petrological and geochemical data lead to a consistent depositional model of the $C_{org.}$-rich sedimentation within the Pieniny Basin during the mid-Cretaceous. Considerable terrestrial runoff into the Pieniny Basin occurred during the late Albian. Detrital macerals accumulated under aerobic conditions on the shelf and continental slope. Fertilization of surface water induced primary productivity; aerobic degradation of organic matter led to the development of an oxygen-minimum zone within mid-water. The oxygen-minimum zone spread over almost all of the Pieniny Basin (Albian/Cenomanian). At the same time, a stagnant pool developed in the Grajcarek Basin. During the mid-Cenomanian the O_2 minimum zone retracted and covered only the shelf and upper/middle slope. Stagnant pools might have formed in the depressions. Turbidity currents flowed down the slope and deposited calciturbiditic sequences with organic detritus in the Branisko and Pieniny basins. At the end of the Cenomanian, isolated anoxic or even H_2S-bearing basins existed on the shelf. The slope was still occupied by the oxygen-minimum zone. In the deepest part of the sea-floor a stagnant basin formed.

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INTRODUCTION

Black shale sedimentation was widespread in Europe and other parts of the world during the Cretaceous, from the Aptian until the Turonian in particular (eg. the Pacific: Thiede *et al.*, 1982; the North Europe: Jenkyns, 1985; the South Europe: Arthur and Premoli Silva, 1982; Baudin *et al.*, 1998; the Atlantic: Brumsack, 1980, 1986; Venezuela: Alberdi-Genolet and Tocco, 1999) and peaked during global Oceanic Anoxic Events (OAEs, *cf.* Schlanger and Jenkyns, 1976). Development of anoxic facies in black shales was explained using three models: detrital, productivity and stagnant anoxic. The "Detrital Anoxic Event" model suggests that supply of terrestrial organic matter and sedimentation rate are high to produce the anoxity (Erbacher and Thurow, 1990). The "Productivity Anoxic Event" model suggests that nutrient input (by upwelling or by river) leads to elevated surface water productivity (Erbacher and Thurow, 1995; Hay, 1995). The oxygen used to oxidise organic remains led to development of a mid-water oxygen-minimum zone. If oxygen-minimum zone grew larger, there would develop a "Stagnant Anoxic Event" (Brumsack and Thurow, 1986; Erbacher and Thurow, 1995), due to stagnant or sluggish water circulation (*op. cit.*).

The extreme warming in the mid part of the Cretaceous represents one of the best examples of "greenhouse" climate conditions in the geological record (De Graciansky *et al.*, 1987; Hoefs, 1997). Globally averaged surface temperatures in the mid-Cretaceous were over 10°C higher than today (De Boer, 1982). The oceans of the Cretaceous may have been similar to the modern Pacific Ocean, both with large marginal seas (Chamley and Robert, 1982; Hay, 1995). It is possible that the Tethys was a hypersaline area, where water became more saline and dense because of evaporation. Meridional seaways that connected regions with surface waters having similar density but different temperatures and salinities may have played a special role in the Cretaceous oceans (Hay, 1995, 1997).

Episodes of increased accumulation of organic matter in the Cretaceous deposits coincide with transgression periods (Schlanger and Cita, 1982). The oxygen content of sea-water was low and the water circulation was sluggish during the greenhouse period (Hay, 1995). As a result, remineralization of

organic matter and thus recycling of nutrients was hampered. Moreover, an increased loss of nitrate caused by denitrification in oxygen deficient waters might have led to "starved basin" development (Brumsack, 1980; Brumsack and Thurow, 1986).

Black shale deposition in the Central Atlantic and western Tethys was attributed to stagnant pools of warm saline bottom water (Brass *et al.*, 1982). It may also have been caused by O_2 depletion, being the response to periodic development of a positive fresh-water balance (large land runoff, low evaporation, flow of nutrient-rich surface water out to the open ocean) and estuarine circulation (Rohling and Hilgen, 1991). Additionally, increasing runoff from land brought nutrients and fertilized the oceans. This is indicated by the widespread occurrence of siliciclastics along the margins of the western Tethys (Weissert, 1990).

The Cretaceous rock formations of the Pieniny Klippen Belt (PKB) have been the focus of scientific interest for many years, with research into their lithology, palaeontology/biostratigraphy and sedimentology (Birkenmajer, 1960; 1977, 1979; Aleksandrowicz *et al.*, 1968; Sikora, 1971; Książkiewicz, 1972; Gasiński, 1988). The layers of black shale intercalated within the Cretaceous strata of the PKB have been interpreted by Birkenmajer and Jednorowska (1984, 1987) and Gasiński (1988, 1991) as records of anoxic events. These authors suggested that local oxygen deficiency episodes are equivalents of the global Oceanic Anoxic Events, as, during Mesozoic time, the Pieniny Basin belonged to the northern branch of the Tethys Ocean.

This paper presents the results of a multidisciplinary approach that combines sedimentological, petrological and geochemical methods in order to propose a consistent depositional model for the mid-Cretaceous organic carbon-rich ($C_{org.}$-rich) sediments within the Pieniny Basin.

GEOLOGICAL SETTING

The Pieniny Klippen Belt (PKB) represents a long and narrow arch-like structure situated in the Palaeo-Alpine Accretionary wedge between the Inner and the Outer Carpathians (Fig. 1; Birkenmajer, 1979).

The facies division distinguishable between Jurassic sequences points to various depositional realms. The shallow, threshold-like one is called the Czorsztyn Succession. This developed on an elevation of the northern ridge (the Czorsztyn Ridge) of the Pieniny Basin. The Niedzica and Branisko successions were formed on the southern slope of the Czorsztyn Ridge. The deepest part of the PKB Basin was occupied by deep water facies of the Pieniny Succession (Fig. 2; Birkenmajer, 1977).

Unification of the lithofacies occurred there during mid-Cretaceous time. Deposition of marls and marly shales dominated across the entire Pieniny Basin. This model of bathymetry has been based on the foraminiferal assemblage distribution (Gasiński, 1991; Birkenmajer and Gasiński, 1992).

Cretaceous oceanic anoxic event records have been recorded within the Pieniny rock successions as grey and brownish-black, organic carbon-rich sediments. The Aptian-Albian formations: Kapuśnica, Pomiedznik and Wronine, comprise

marly shales with occasional sandstone intercalations. The Jaworki Formation is dated as Cenomanian–Turonian. It includes several lithostratigraphic units (Figs. 2 and 3) developed mainly as pelagic marls (i.e.: Skalski Member), shales (Magierowa Member), and calciturbidite deposits (Macelowa, Trawne, Snežnica members). Planktic foraminiferal biostratigraphy enables their assignation to the following zones: the *Rotalipora subticinensis–R. ticinensis, Planomalina buxtorfi–R. appenninica, R. reicheli–R. greenhornensis* and the latest *R. cushmani* up to the Early *Helvetoglobotruncana helvetica* zones (after Gasiński, 1983, 1988; Birenmajer and Jednorowska, 1984, Fig. 2).

METHODOLOGY AND MATERIALS

The Wronine Formation, characteristic of the Grajcarek Succession, occurs in the following exposures: the Szczawnica Rzeźnia (the samples signed RZ) and the Sztolnia Stream (SZT). The Pomiedznik Formation, typical of the Czorsztyn Succession, occurs on the right bank of the Grajcarek River, below the church in the village of Jaworki (JK). The archival material collected from the Halka Klippe (HL) — today flooded under water of the Czorsztyn Lake — has been also studied. The Kapuśnica Formation (the Branisko and Niedzica successions) were exposed and sampled on the left slope of the Dunajec River, beneath the dam (KP), in the Zawiasy Klippe in Krościenko (ZAW) and in the Grajcarek Stream in Jaworki (JG). The Trawne Member — a biostratigraphical analogue of the upper part of the Kapuśnica Fm. was sampled within the Branisko Succession, in the Trawne Stream (TR 1) and in the Pasieczny Stream (PA) profiles. The Skalski Member is exposed along the road from Jaworki through to Bukowiny Hill (BUK, Niedzica Succession) and in the Trawne Stream (TR 2–5, Branisko Succession). The Snežnica Member from the Niedzica Succession was sampled in the Skalski Stream in Jaworki (PSK samples). The Snežnica Member occurs also within the Pieniny Succession (the Macelowa Mount section — MC). The Magierowa Member (MG) recognized only within the Pieniny Succession, was collected in the stratotype profile: the Magierowa Klippe in the hamlet of Sromowce Niżne.

Microstructures were determined in 55 samples using microscopic observation (*Nikon ECLIPSE, E 600 POL*; transmitted and reflected light). Organic petrology was studied in polished thin section (30 samples) under fluorescent light (*Olympus OPl 3, Fl Mk II*). The quality of organic matter was evaluated in 36 samples using Rock-Eval pyrolysis. Other Rock-Eval parameters such as the Hydrocarbon Index (HI) and T_{max} were defined in Espitalie (1985). Trace-element contents were measured in 28 samples using *ICP-OES* spectrometry and INAA analysis (Ag, Al, Ca, Cd, Cu, Mn, Mo, Ni, Pb, V, Y, Zn, As, Ba, Co, Cr, Fe, Na, Th, U, W, La, Ce). The pulverized material was analyzed by *ICP-OES* after dissolution in a $HCl–HNO_3–HClO_4–HF$ solution. Trace-element contents were shale-normalized to give an estimation of their relative enrichment. The used enrichment factor is (Wedepohl, 1970, 1991):

(trace-element content/Al content)$_{sample}$ / (trace-element content /Al content)$_{shale}$
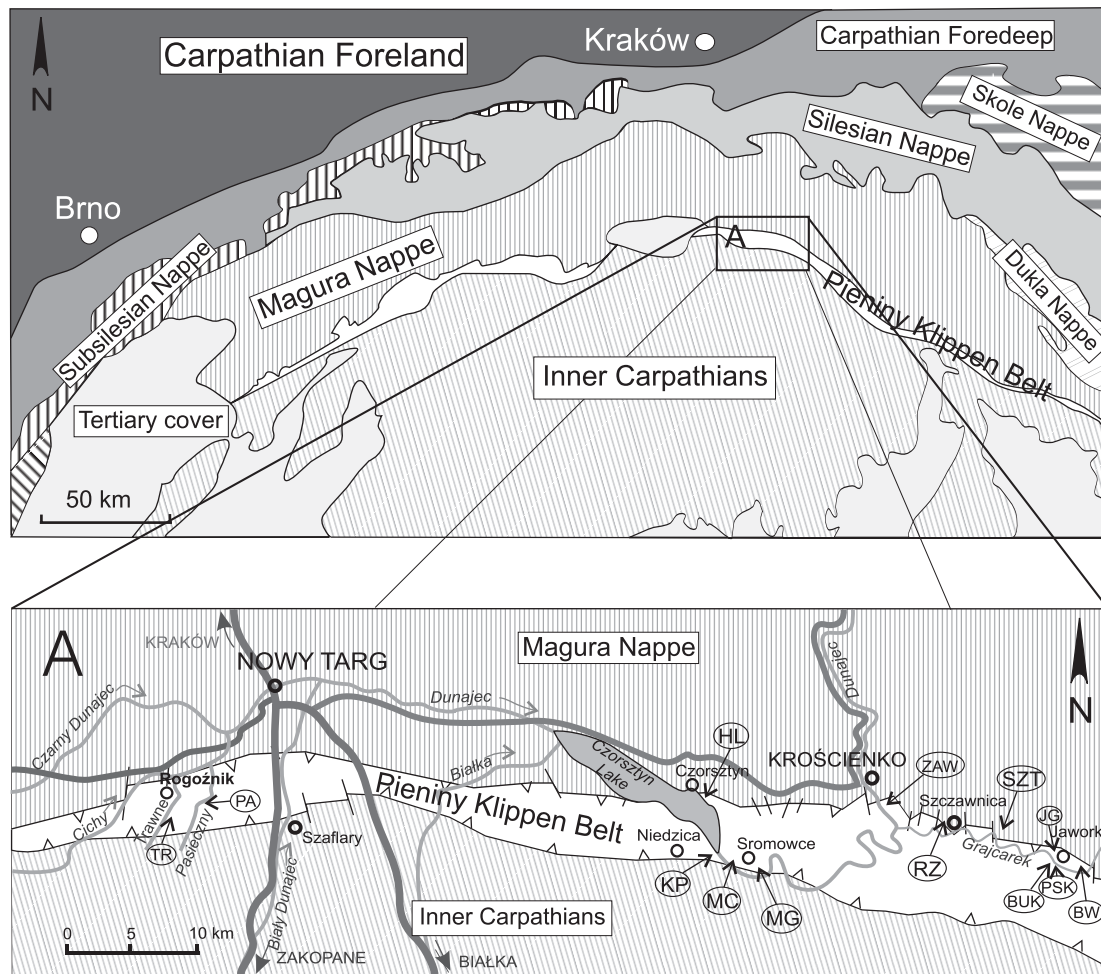
Fig. 1. Location of the investigated Polish part of the Pieniny Klippen Belt (A) against the schematic geological map of the Carpathians (after Żytko *et al*., 1989; Birkenmajer, 1979, modified)

Location of studied sections containing black shales: BUK — Bukowiny Hill, BW — Biała Woda Valley, HL — Halka Klippe, JG — Jaworki Grajcarek and Jaworki Church, KP — Niedzica Water Dam, MC — Macelowa Mount, MG — Magierowa Rock, PA — Pasieczny Stream, PSK — Skalski Stream, RZ — Szczawnica Rzeźnia, SZT — Sztolnia Stream, TR — Trawne Stream, ZAW — Zawiasy Klippe

Isotopic determinations (organic and anorganic carbon) were carried out on a *MI-1305* mass spectrometer with detecting system. The stable isotope composition was expressed as $\delta^{13}C$ values relative to the PDB standard.

RESULTS AND DISCUSSION

The absolute concentrations of the selected major and trace elements are shown both on the table (Table 1) and on the graph (Fig. 4A, B). They are compared to the values of the enrichment factor. Most of the samples are sulphur-depleted; some S concentrations are very low. The samples investigated were collected from surface outcrops. Due to weathering processes, the sulphur content was probably drastically reduced. Most sulphides (FeS$_2$) have been altered to oxides.

THE ALBIAN POMIEDZNIK AND KAPUŚNICA FORMATIONS

The oldest event of organic matter deposition studied is biostratigraphicaly dated as late Albian (OAE 1c; *Rotalipora subticinensis–R. ticinensis* LCRZ, after Gasiński, 1988). This was investigated within the Pomiedznik Fm. (JK samples) and the Kapuśnica Fm. (KP) of the Czorsztyn and Branisko successions, respectively, and additionally within the Trawne Member (samples TR 1, PA 2) of the Branisko Succession (Fig. 3).

The JK samples from the Pomiedznik Fm. represent hemipelagic sediments — marls and marly shales. These green rocks contain black blots and intercalations of black marls. The Kapuśnica Fm. consists of black and dark grey shales with intercalations of cherty limestone and of fine-grained sandstone (Birkenmajer, 1979). The microfauna assemblages contain oligotaxic planktonic foraminifers and radiolarians coexisting with calcareous benthos (Fig. 5A; Gasiński, 1988). The lower
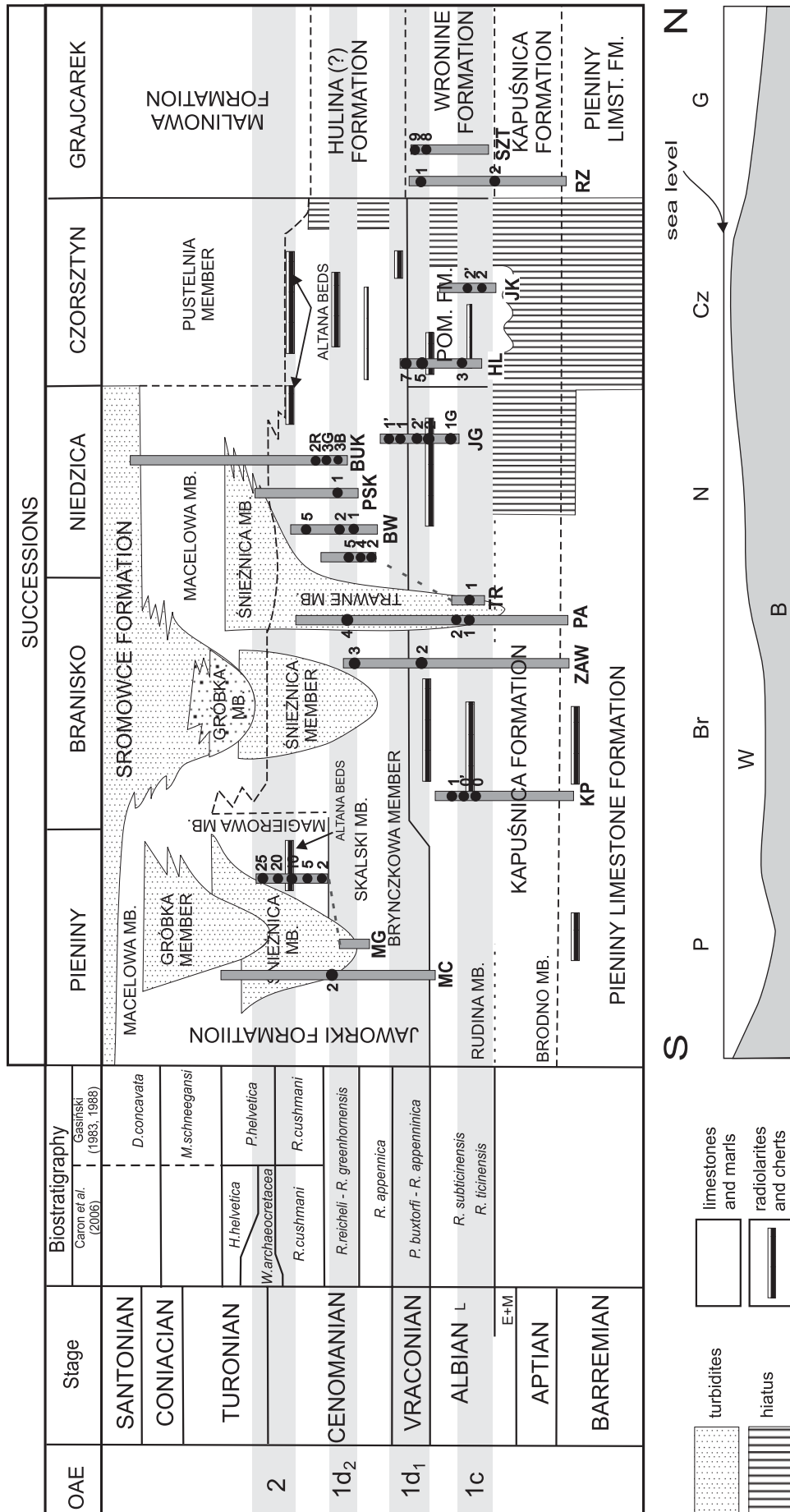
Fig. 2. Correlation of the Upper Cretaceous lithostratigraphic units in the Pieniny Klippen Belt Basin, Poland (lithostratigraphy after Birkenmajer and Jednorowska, 1987; biostratigraphy after Gasiński, 1983, 1988 and Caron *et al.,* 2006; palinspastic reconstruction after Birkenmajer, 1979 modified)

Successions: P — Pieniny, Br — Branisko, N — Niedzica, Cz — Czorsztyn, G — Grajcarek; W — water column, B — basement; for other explanations see Figure 1

Fig. 3. Lithostratigraphic columns of studied sections and position of collected samples (arrowed) and horizons of black shales (OAE) * —after Birkenmajer and Myczyński (1977)

For other explanations see Figure 1

T a b l e   1

Chemical composition of the Pieniny samples

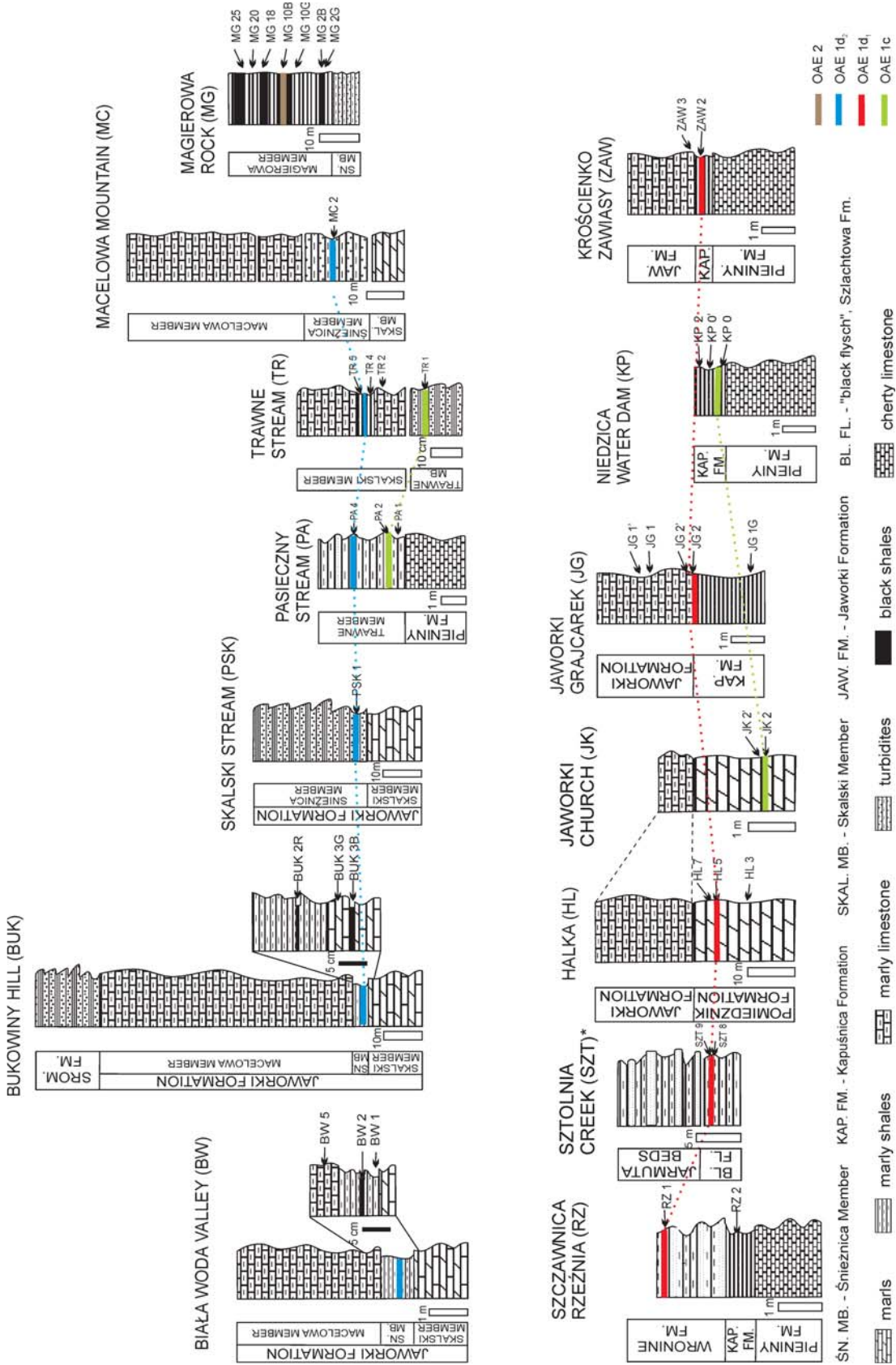|	Sample	Ag	Cd	Cu	Mn	Mo	Ni	Pb	Zn	Al	Ca	V	Y	As	Ba	Co	Cr	Fe	S	Th	U	La	U/Th	V/V+Ni
				[ppm]						[%]		[ppm]						[%]		[ppm]				
OAE1c	JK 2	<0.3	0.5	44	717.1	<1	61.8	14.8	69.7	2.8	21.4	62.4	39	14	920	17	71	1.86	0.07	6.6	2.2	34	0.33	0.50
	enrich. factor		12.16	3.09	3.24		2.87	2.13	1.92		43.08	1.52	3.01	6.32	5.01	2.83	2.49	1.21		1.9	2.17	2.69	1.14	0.35
	KP O'	<0.3	0.6	31.2	272.5	<1	49.5	16.9	99.3	0.6	19.5	33.5	17.6	12	2000	5	42	1.32	0.15	1.4	2.5	10	1.79	0.40
	enrich. factor		68.08	10.23	5.74		10.7	11.33	12.74		183.2	3.8	6.33	24.23	50.86	3.88	6.88	4.02		1.88	11.52	3.69	6.13	0.26
	KP 1	<0.3	<0.3	43.1	550.6	<1	60.9	22.4	55.7	3.1	15.8	64.3	27.8	4	240	10	61	1.98	0.24	6.2	1.5	36	0.24	0.51
	enrich. factor			2.73	2.25		2.56	2.91	1.38		28.73	1.41	1.94	1.67	1.18	1.5	1.93	1.17		1.61	1.34	2.57	0.83	0.36
	TR 1	<0.3	<0.3	53.5	947.9	5	75.9	21.1	105.4	11	2	139.1	22.4	23	490	19	114	4.27	0.82	12.9	3	42	0.23	0.65
	enrich. factor			0.96	1.09	2.01	0.9	0.77	0.74		1.02	0.86	0.44	2.67	0.68	0.8	1.02	0.71		0.94	0.75	0.84	0.80	0.49
	PA 2	<0.3	0.4	38.2	825.6	<1	93.7	14.9	76.2	3.5	14.3	88.8	23	7.6	1500	19	106	3.07	0.15	8.8	2.8	31	0.32	0.49
	enrich. factor		7.78	2.15	2.98		3.48	1.71	1.68		23.03	1.73	1.42	2.75	6.54	2.53	2.98	1.6		2.02	2.21	1.96	1.09	0.33
	HI 5	<0.3	<0.3	34.8	497.1	<1	104.6	27.7	61	2.1	21.2	52	19.8	73	2400	61	54	3.54	2.02	4.6	3.1	34	0.67	0.33
	enrich. factor			3.26	2.99		6.48	5.31	2.24		56.91	1.69	2.04	43.95	17.44	13.53	2.53	3.08		1.76	4.08	3.58	2.32	0.21
	JG1	<0.3	<0.3	192.1	438.8	2	92	29.5	80.8	5.6	2.7	132.4	24.1	3.9	310	24	113	3.94	0.05	12.7	2.5	74	0.20	0.59
	enrich. factor			6.75	0.99	1.58	2.14	2.12	1.11		2.72	1.61	0.93	0.88	0.84	2	1.98	1.29		1.82	1.23	2.92	0.68	0.43
	JG1'	<0.3	<0.3	100	1573.5	<1	73.5	16.5	64.1	4.4	11.3	74.3	30.2	1.4	250	17	75	4.45	0.03	10.1	1.8	79	0.18	0.50
	enrich. factor			4.47	4.52		2.17	1.51	1.12		14.48	1.15	1.48	0.4	0.87	1.8	1.68	1.85		1.85	1.13	3.97	0.61	0.35
	JG2	0.8	4.8	94.3	1049.1	<1	210.7	57.5	499.1	2.9	16.9	185.3	28.4	25.4	1150	165	114	3.03	1.43	6.2	5.4	58	0.87	0.47
	enrich. factor	34.9	112.68	6.4	4.57		9.46	7.98	13.24		32.85	4.35	2.11	11.07	6.05	26.5	3.87	1.91		1.72	5.15	4.43	2.99	0.31
OAE1d	JG2'	<0.3	<0.3	62	1631.1	<1	43.2	17.3	43.1	3.2	18.1	65.6	22.8	3.2	270	14	52	1.98	0.16	6.3	1.6	53	0.25	0.60
	enrich. factor			3.81	6.44		1.76	2.17	1.04		31.88	1.4	1.54	1.26	1.29	2.04	1.6	1.13		1.58	1.38	3.66	0.87	0.44
	JG1G	<0.3	<0.3	69.1	1273.8	<1	63.1	29.7	77.1	3.2	19.6	72.2	24	13.4	220	19	60	2	0.39	6.6	2.3	60	0.35	0.53
	enrich. factor			4.25	5.03		2.57	3.73	1.85		34.53	1.54	1.62	5.29	1.05	2.77	1.84	1.14		1.66	1.99	4.15	1.20	0.37
	ZAW 3	0.9	<0.3	59	324.1	<1	73.8	18.8	109.7	3.6	16.9	81.9	33.7	41.8	1000	13	87	2.33	0.05	7.4	3.4	44	0.46	0.53
	enrich. factor	31.6		3.22	1.14		2.67	2.1	2.35		26.46	1.55	2.02	14.68	4.24	1.68	2.38	1.18		1.65	2.61	2.7	1.58	0.37
	SZT 9	<0.3	<0.3	63.6	1007.1	6.5	85.1	38.3	134.6	7.3	5.4	119.8	21.9	49.6	340	22	87	4.18	1.12	10.6	2.7	37	0.25	0.58
	enrich. factor			1.71	1.74	3.94	1.52	2.11	1.42		4.17	1.12	0.65	8.59	0.71	1.4	1.17	1.05		1.17	1.02	1.12	0.87	0.42
	RZ 1	<0.3	<0.3	37.5	1723.7	<1	53.7	21.7	112.3	5.3	7.3	104.4	20.3	26.3	540	15	85	3.56	0.67	11.7	3.5	37	0.30	0.66
	enrich. factor			1.39	4.11		1.32	1.65	1.63		7.76	1.34	0.83	6.27	1.55	1.32	1.58	1.23		1.78	1.83	1.54	1.03	0.50

Tab. 1 continued

Group	Sample	Ag [ppm]	Cd [ppm]	Cu [ppm]	Mn [ppm]	Mo [ppm]	Ni [ppm]	Pb [ppm]	Zn [ppm]	Al [%]	Ca [%]	V [ppm]	Y [ppm]	As [ppm]	Ba [ppm]	Co [ppm]	Cr [ppm]	Fe [%]	S [%]	Th [ppm]	U [ppm]	La [ppm]	U/Th	V/V+Ni	V/Cr
OAE1d₂	BUK 2R	<0.3	<0.3	23	920.2	<1	44.3	17.4	47.2	2.3	25.6	55.4	24.3	3.7	240	8	55	2.35	0.03	5	1	24	0.20	0.56	1.01
	enrich. factor			1.97	5.06		2.51	3.04	1.58		62.74	1.64	2.28	2.03	1.59	1.62	2.35	1.87		1.75	1.2	2.31	0.69	0.40	0.70
	BUK 3B	1.5	1.2	104.3	602.6	<1	50.8	123.4	68.9	2.8	21.8	157.5	19.9	13.1	760	20	70	2.1	0.23	5.8	4	25	0.69	0.76	2.25
	enrich. factor	67.7	29.18	7.33	2.72		2.36	17.73	1.89		43.89	3.83	1.53	5.92	4.14	3.33	2.46	1.37		1.67	3.95	1.98	2.37	0.62	1.56
	BUK 3G	<0.3	<0.3	87.6	737.1	<1	38	15.8	55	2.3	23.3	96	23.7	2.6	250	9	79	1.79	0.03	5.6	1.6	27	0.29	0.72	1.22
	enrich. factor			7.49	4.05		2.15	2.76	1.84		57.1	2.84	2.22	1.43	1.66	1.82	3.38	1.42		1.96	1.92	2.6	0.98	0.57	0.84
	PSK 1	0.3	<0.3	30.4	462	<1	47.8	20.4	68	3.7	14.7	79	19.1	5.2	410	11	80	2.29	0.05	9.8	3	27	0.31	0.62	0.99
	enrich. factor	10.3		1.62	1.58		1.68	2.22	1.41		22.4	1.45	1.11	1.78	1.69	1.38	2.13	1.13		2.13	2.24	1.61	1.05	0.46	0.68
	BW 2	<0.3	<0.3	66.3	472.3	<1	53.6	44.4	89.8	5.1	13.8	88.4	21.8	6.1	350	13	87	2.53	0.04	9.6	3.8	32	0.40	0.62	1.02
	enrich. factor			2.56	1.17		1.37	3.5	1.36		15.25	1.18	0.92	1.51	1.05	1.19	1.68	0.91		1.51	2.06	1.39	1.36	0.46	0.70
	TR 2	<0.3	<0.3	36.2	682	<1	61.4	22.5	50.2	11.4	15.2	84.1	23.8	4.7	260	10	91	3.33	0.02	7.5	1.5	39	0.20	0.58	0.92
	enrich. factor			0.62	0.76		0.7	0.79	0.34		7.52	0.5	0.45	0.52	0.35	0.41	0.78	0.53		0.53	0.36	0.76	0.68	0.42	0.64
	TR 5	<0.3	<0.3	36.9	487.6	<1	57.6	19.9	83.5	5.3	11.7	112.5	24.3	15	410	22	94	3.09	0.18	10.7	2.6	41	0.24	0.66	1.20
	enrich. factor			1.37	1.16		1.41	1.51	1.21		12.44	1.45	0.99	3.58	1.18	1.93	1.74	1.07		1.62	1.36	1.71	0.84	0.51	0.83
	PA 4	<0.3	<0.3	18.2	363.2	<1	32	13	54.9	4.2	8.9	78.2	20	21.7	460	13	79	3.39	0.02	11	3.4	37	0.31	0.71	0.99
	enrich. factor			0.85	1.09		0.99	1.25	1.01		11.94	1.27	1.03	6.53	1.67	1.44	1.85	1.48		2.11	2.24	1.95	1.06	0.56	0.69
	MC 2	<0.3	<0.3	29.8	513.3	<1	51.7	21.5	66.8	5.1	10.7	89.1	20.7	12.8	130	13	83	2.87	0.04	10	3.5	30	0.35	0.63	1.07
	enrich. factor			1.15	1.27		1.32	1.70	1.01	1	11.83	1.19	0.88	3.17	0.39	1.19	1.6	1.03	S	1.58	1.9	1.3	1.20	0.47	0.7433
OAE 2	MG 2B	0.4	1.8	83	318.4	4	168.5	26.3	398.2	7.7	0.9	483.3	21.3	33.3	560	27	165	3.7	0.05	10.7	4.3	35	0.40	0.74	2.93
	enrich. factor	6.57	15.91	2.12	0.52	2.3	2.85	1.37	3.98		0.66	4.27	0.6	5.47	1.11	1.63	2.11	0.88		1.12	1.54	1.01	1.38	0.60	2.02
	MG 2G	<0.3	<0.3	104.3	330.8	<1	159.9	17.1	130.2	7.6	1.4	128.6	19.9	31	580	35	131	3.59	0.02	12.2	3.1	37	0.25	0.45	0.98
	enrich. factor			2.7	0.55		2.74	0.91	1.32		1.04	1.15	0.57	5.16	1.16	2.15	1.69	0.86		1.29	1.13	1.08	0.88	0.30	0.68
	MG 10 B	0.5	<0.3	127.6	127.6	4.6	120.3	29.2	241.7	6.2	0.3	324.8	18.3	40.8	490	18	200	3.96	0.03	11.7	5	66	0.43	0.73	1.62
	enrich. factor	10.2		4.05	0.26	3.28	2.53	1.89	3		0.27	3.57	0.64	8.32	1.21	1.35	3.17	1.17		1.52	2.23	2.36	1.47	0.59	1.13
	MG 10 G	<0.3	0.8	99.8	204	<1	86.4	13.9	140	6.3	0.2	136.5	16.4	33	410	17	133	3.14	0.01	11	2.9	64	0.26	0.61	1.03
	enrich. factor		8.64	3.12	0.41		1.78	0.89	1.71		0.18	1.48	0.56	6.62	0.99	1.26	2.08	0.91		1.4	1.27	2.25	0.91	0.45	0.71
	MG 25	0.9	5.9	154.2	291.1	3.8	105.8	16.9	611	5.9	0.9	466.6	16.8	28	530	11	173	3.41	0.14	11.3	4.2	33	0.37	0.82	2.70
	enrich. factor	19.3	68.08	5.14	0.62	2.85	2.33	1.15	7.97		0.86	5.38	0.61	5.94	1.37	0.87	2.88	1.06		1.54	1.97	1.24	1.28	0.70	1.87

Absolute contents of trace and major elements and values of enrichment factors estimated as: (trace-element content/Al content)$_{sample}$ / (trace-element content/Al content)$_{shale}$ (according to Wedepohl, 1970, 1991)
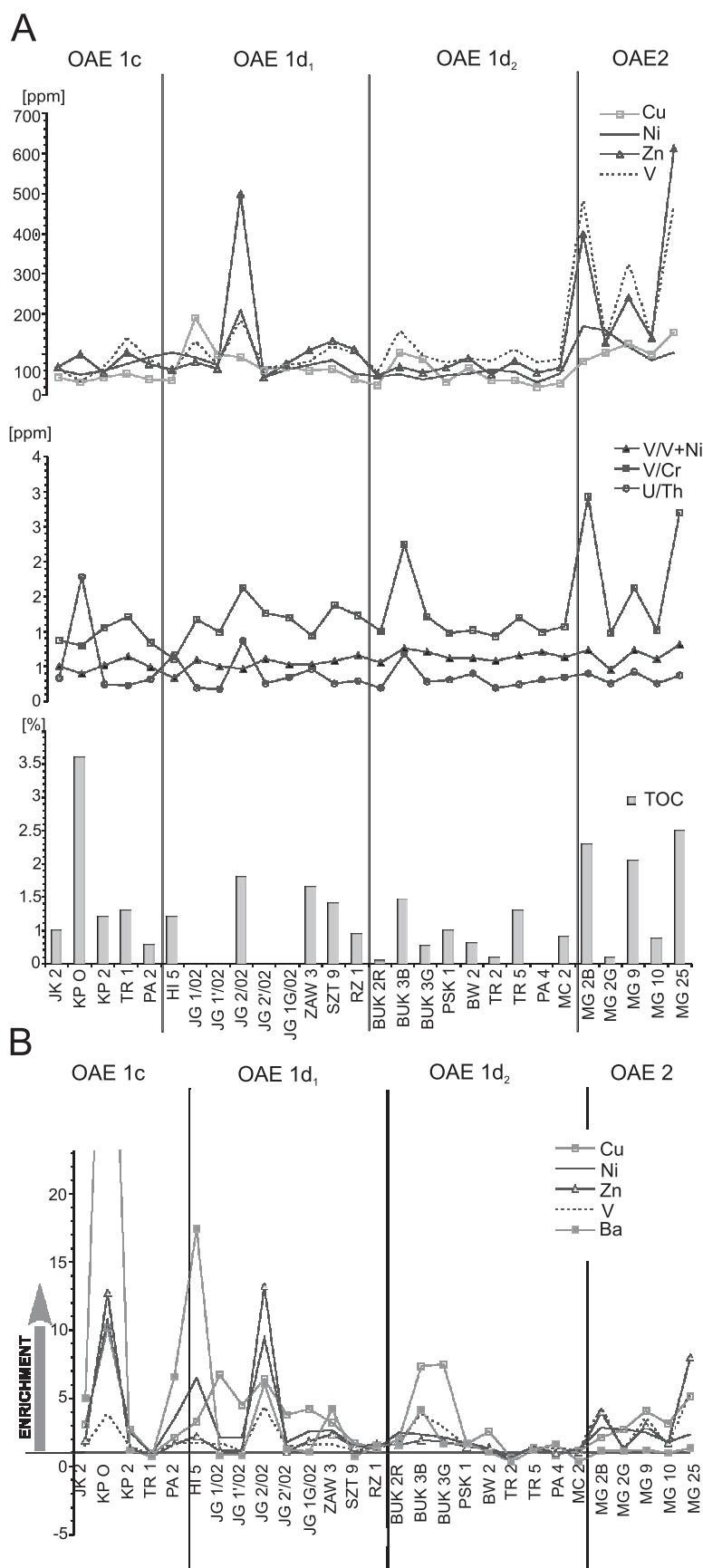
Fig. 4. A — correlation of absolute content of selected trace-elements (Cu, Ni, Zn, V) and V/V+Ni, V/Cr, U/Th, with absolute TOC content in studied samples; B — normalized concentrations of the selected trace elements (Cu, Ni, Zn, V, Ba) in the Pieniny samples

part of the Trawne Member is represented by turbiditic deposits consisting of calcareous sandstones, intercalated with ash-grey shales. A predominance of agglutinated foraminifers was observed in the turbidite samples. Representatives of *Hedbergella* and *Rotalipora* are dominant among the planktonic foraminifers (Gasiński, 1983).

ORGANIC MATTER AND INORGANIC GEOCHEMISTRY OF THE ALBIAN STRATA

The total organic carbon (TOC) content varies between 0.3% in pale grey PA samples and 3.1% recorded in the brownish-black KP 0 sample (Table 2). The organic matter is mature as shown by the HI (35–118) and T_{max} values (about 435°C). A plot of HI versus OI measured by Rock-Eval pyrolysis (Fig. 6) points to a predominantly III/IV kerogen type (vitrinite and inertinite). The highest TOC values, correlating with maximal HI in KP samples, indicates the presence of II type kerogen. Petrographic analyses of the macerals correspond with the pyrolysis data and show a dominance of macerals belonging to the vitrinite and inertinite groups: detrovitrinite, collinite and inertodetrinite; the occurrence of type II kerogen (bituminite in KP 0 and sporinite in the PA 2) was recognized.

The $\delta^{13}C$ values are –18.43 and –24.23‰ (Table 3; Fig. 8). Organic carbon significantly enriched in ^{12}C associated associated with land plants (Galimov, 1980, 1985). During coalification of organic remains, the isotopic composition of kerogen can be altered. Humus forming by combustion of higher plant remains is characterized by enrichment in ^{13}C (Galimov, 1985; Dean *et al*., 1986). The results described above indicate terrestrial derivation of organic matter (in TR 1 and PA 2 samples). However, the presence of bituminite-macerals of algal origin (in KP samples) is possible.

The upper Albian samples are usually poor in trace elements, but they contain high amounts of calcium (Table 1; Fig. 4A). The JK 2 sample collected in the Czorsztyn Succession contains notable amounts of Cd, Y and Ba. Significant concentrations of Ba characterize the PA 2 and KP 0 samples from the Branisko Succession. It is interesting that the enrichment factor estimated for most of the elements exceeds 1 (Table 1; Fig. 4B). This is the consequence of lower aluminium concentrations in the samples (3% in JK 2 and 0.6% in KP 0) than in the "average shale" standard (8.85%), with which the enrichment factor was gauged.
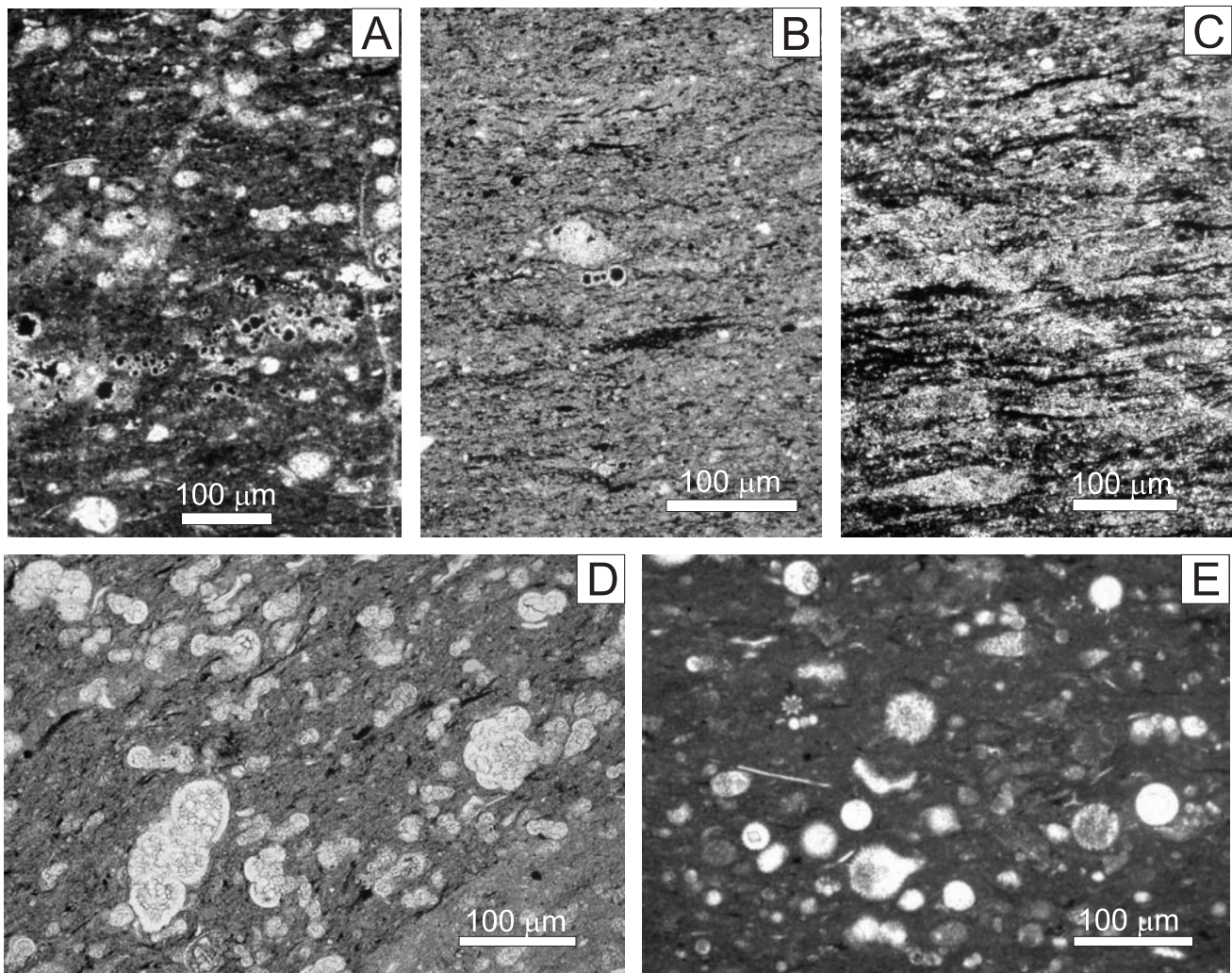
Fig. 5. Microscopic images of association of microfossils in selected samples (all photographs under normal light, one nicol)

A— radiolarians with juvenile foraminiferids (partly pyritized) in laminated marl sample KP 0; **B** — trace tests of small planktonic genera within black, laminated shales (JG); **C** — black cherty shales devoid of microfauna typical of MG samples; **D** — abundant foraminifera association including epi- and bathypelagic plankton and calcareous benthos — marly sample from JK section; **E** — radiolarian assemblage within silicified limestone (HL 5)

The TR 1 sample differs from the others from OAE 1c. It contains 11% of aluminium and a negligible amount of calcium, hence the values of the enrichment factor exceed 1 for As, Cr, Mn and Mo only (Table 1).

Barium together with cadmium are frequently referred as proxies for palaeoproductivity (Dymond *et al.*, 1992; Alberdi-Genolet and Tocco, 1999). This seems to be a reasonable explanation for the enrichment of the KP 0 sample, which includes amorphous organic matter, identified as bituminite/collinite (II/III kerogen). The higher amounts of U, As and Ag measured for KP 0 have been interpreted as a palaeoproductivity indicator as well. Silver behaves as a nutrient-like element. The high Ag concentration may result from its involvement in the biogeochemical cycle of silica (Ndung'u *et al.*, 2001). Arsenic and uranium can be bound to organic matter, especially when absorbed by algae (Mangini and Dominik, 1979). These geochemical indicators find confirmation in the microfaunal assemblage. The abundance of radiolarians could be fossil evidence of bioproductivity. But

this could also be due to a more oceanic setting. The absence of bathypelagic foraminifera and rarity of benthos, represented mainly by agglutinated species, may indicate the appearance of mid-water oxygen-minimum zone. Low values of absolute and shale-normalized V/V+Ni and V/Cr ratios and marked Mn-enrichment suggest an oxygenated environment (Table 1; Fig. 4A; Lewan and Maynard, 1982; Lewan, 1984; Quinby-Hunt and Wilde, 1994).

The JK 2 and PA 2 samples are similar to each other lithologically and geochemically. They both represent marls including abundant foraminiferal associations (Fig. 5D; plankton and benthos); they have the same proportions of Al to Ca, high absolute amounts of Cd and Ba and enrichment factors of >1 for Cu, Mn, Ni, Pb, Zn, V, Y, As, Co, Cr, U, Th, La. The samples contain more TOC than average shales, thus the content of trace elements is higher (Table 1; Fig. 4A). Sediment enhancement in trace elements due to absorption by organic matter under reducing conditions is probable, assuming that organic matter was reactive (Brumsack, 1980). The appearance of H_2S pro-

T a b l e   2

Rock-Eval analysis data

	Samples	TOC [wt.%]	T_{max} [°C]	S2	HI	OI
OAE 1c	JK 2	0.52	?	0.18	35	n.d.
	JK 2'	0.7	435	0.25	98	54
	KP 0	1.28	443	1.03	80	15
	KP 0'	3.1	434	3.67	118	n.d.
	KP 2	1.4	440	2.4	77	24
	TR 1	0.84	430	0.91	108	n.d.
	PA 2	0.37	?	0.07	18	n.d.
	RZ 2	0.4	435	0.65	130	n.d.
OAE 1d₁	HL 3	1.64	429	2.16	132	46
	HL 5	0.7	430	1.8	120	50
	HL 7	0.4	431	1.95	125	45
	JG 1	0.48	?	0.1	20	n.d.
	JG 2	3.49	437	6.3	180	n.d.
	JG 1G	1.28	438	1.66	130	n.d.
	ZAW 2	1.15	?	0.13	11	n.d.
	ZAW 3	0.98	443	0.15	20	50
	RZ 1	0.44	439	0.69	155	n.d.
	SZT 8	0.93	439	0.96	103	39
	SZT 9	0.56	439	0.43	77	n.d.
OAE 1d₂	PSK 1	0.2	?	0.26	98	143
	BUK 2R	0.04	?	0.05	n.d.	n.d.
	BUK 3B	1	433	0.35	36	79
	BUK 3G	0.25	433	0.13	50	108
	BW 1	0.26	?	0.12	46	114
	BW 2	0.3	430	0.2	n.d.	n.d.
	BW 2B	16.44	483	17.1	104	10
	BW 5	0.04	?	0.04	n.d.	n.d.
	TR 2	0.1	?	0.1	n.d.	n.d.
	TR 5	0.78	427	0.52	67	n.d.
	MC 2	0.36	?	0.13	36	105
OAE 2	MG 2G	0.1	?	0.2	n.d.	n.d.
	MG 2B	1.01	464	0.48	48	36
	MG 10G	0.13	?	0.16	n.d.	n.d.
	MG 10B	1.81	464	0.94	52	33
	MG 18	1.55	469	0.43	27	84
	MG 20	0.37	465	0.1	27	97
	MG 25	1.95	466	0.72	36	50

S2 — hydrocarbons generated by pyrolitic decomposition of the kerogen; HI (hydrogen index) — quantity of pyrolizable organic compounds from S2 relative to TOC (mg HC/g TOC); OI (oxygen index) — quantity of terrestrial organic matter (mg OC/g TOC); n.d. — not detected, ? — uncertain results

Fig. 6. Types of kerogen based on Rock-Eval data

A — diagram of hydrogen index vs. oxygen index, B — S2 vs. TOC plots for investigated samples

In sample TR 1 most trace elements occur in relatively low amounts (Table 1; Fig. 4A). Concentrations of As, Mo, Pb are higher. These metals are sulphide-forming; they may also be incorporated into organic matter (Brumsack, 1980). Concentrations of sulphur and euhedral and polyframboidal pyrite indicate that pyritization happened diagenetically (Wilkin *et al.*, 1996; Wignall and Newton, 1998). Elements such as Ba, Cr, V may have been absorbed by clay minerals. The V/V+Ni ratio about 0.64 can indicate oxygen deprivation (Table 1 and Fig. 4A; Lewan and Maynard, 1982). However, it is only 0.49 after shale normalization.

THE ALBIAN/CENOMANIAN POMIEDZNIK, KAPUŚNICA AND WRONINE FORMATIONS

The second event of deposition of C-rich deposits investigated (designated as OAE 1d₁) is dated to the early Cenomanian *Planomalina buxtorfi–Rotalipora appenninica* (Fig. 2; Gasiński, 1988).

The Pomiedznik Fm. within the Halka section consists of black and dark grey shales with intercalations of cherty limestone. The microfaunal, association includes oligotaxic planktonic and benthic foraminifers and radiolaria (Gasiński, 1988). The microfaunal assemblage from the cherty HL 5 sample comprises mainly planktonic genera (epiplanktonic foraminifera and radiolaria) without calcareous benthos (Fig. 5E).

The ZAW samples from the Branisko Succession contain mineral and organic detritus. The marly shales and mudstones include arenitic layers. Wavy and lenticular lamination is observed in these fine-grained rocks. The laminae show ductile

duced during decomposition of OM might mean precipitation of sulphides (Fe sulphides above all). Excessively low amounts of Fe (below 3.5%) low values of V/V+Ni and V/Cr ratios and high Mn amounts (absolute and shale-normalized; Table 1 and Fig. 4A) seem to be contraindications of euxinic conditions. (Lewan and Maynard, 1982; Lewan, 1984; Quinby-Hunt and Wilde, 1994; Veto *et al.*, 1997). An abundant calcareous microfauna indicates a hospitable environment within the whole water column.
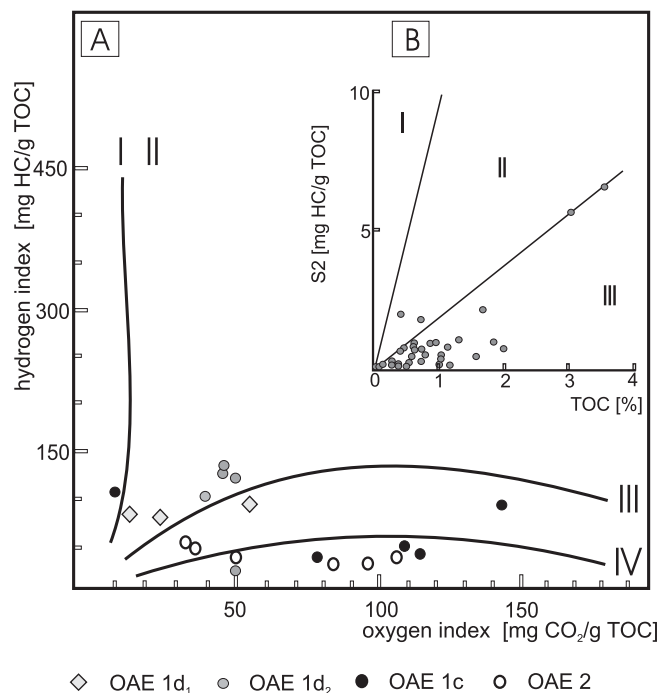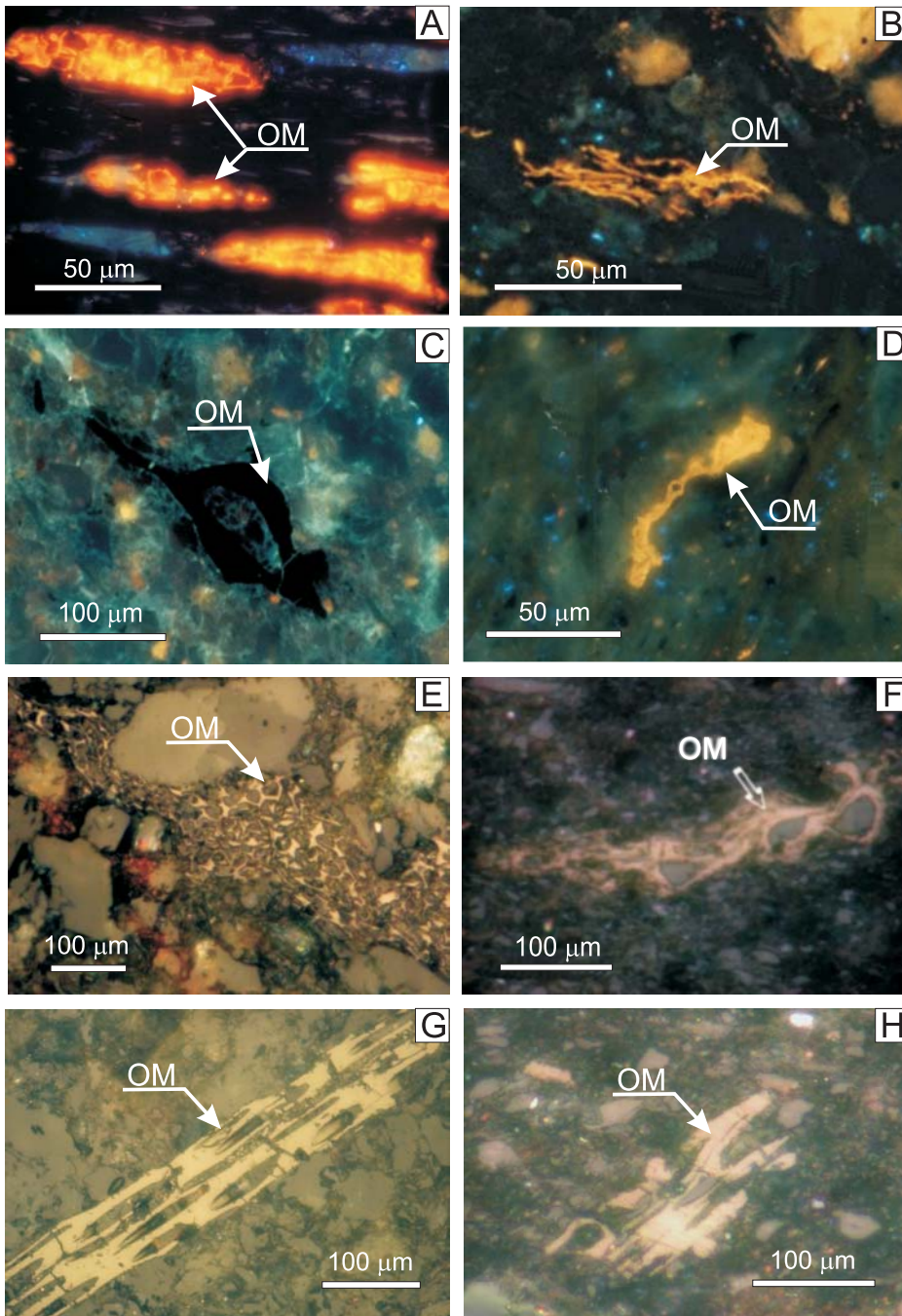
Fig. 7. Microscopic images of macerals in reflected light

A — resinite infilling pore spaces within structured inertinite maceral (BW 2 sample) (UV light); **B** — unstructured liptinite maceral-bituminite in RZ 2 sample (UV light); **C** — inertinite maceral from arenitic MC 2 sample (UV light); **D** — sporinite-granular megaspore (TR 5) (UV light); **E** — vitrinite maceral with internal cell structure (PA 4) (reflected light); **F** — sclerotinite-cellular structure (MG 25) (reflected light); **G** — tellovitrinite maceral within PA 4 sample (reflected light); **H** — semifusinite (inertinite type) maceral from MG 18 sample (reflected light); OM — organic matter

fauna. The microfaunal assemblage consists of individual benthic organisms, i.e. *Lenticulina* and ostracods, and radiolaria as an exclusive representative of the plankton.

ORGANIC MATTER AND
INORGANIC GEOCHEMISTRY
OF THE ALBIAN/CENOMANIAN
STRATA

The samples collected from the Szczawnica Rzeźnia section (RZ) are characterized by very low organic carbon contents (below 0.5%) that are close to 1% for samples HL 3, ZAW 2 and SZT 8 (Table 2). Only sample JG 2 contains more TOC, at 3.5%. The T_{max} values range from 430 to 443°C and indicate maturity at the oil window level. The hydrogen index (HI) values, at between 120 and 180, show the kerogen to be of type II/III (Fig. 6). These pyrolysis data correspond with optical identifications of macerals. They are wispy in shape and amorphous reddish-brown, black in transmitted light and bright under reflected light. Macerals were recognized as of the vitrinite group (collinite) with minor amounts of bituminite. The vitrinite was derived from land plant remains composed of cellulose and lignin. Bituminite belonging to liptynite macerals is a decomposition product of algae, zooplankton, bacteria and other lipid substances (Fig. 7B).

The isotopic composition of the organic carbon (Table 3; Fig. 8) may indicate terrestrial derivation of organic matter, because the δ^{13}C values are close to –26‰ (Deines, 1980; Galimov, 1985).

The geochemical composition of sample HL 5 shows a very high Ca concentration that diminishes the absolute amounts of Al and trace elements (Table 1; Fig. 4A). Normalization to the "average shales" explains the high values of enrichment for most elements (Fig. 4B). Relatively high values were noted for sulphide-related metals such as Fe, Ni, Pb, As and Co. Precipitation of pyrite and other sulphides may be the main reason for the enrichment in metals. The lack of benthos may be evidence of occasional bottom water anoxia. The U/Th ratio equalling 0.67 (after shale-normalization 2.31) and low absolute Mn amounts may

deformation. It is notable, that these samples contain abundant calcareous micro- and macrofaunal remnants.

The JG samples collected from the profile of the Niedzica Succession are represented by variegated shales with an intercalation of black shale. Sample JG 2 is from the C$_{org}$.-rich level. This is a laminated deposit lacking any fauna (Fig. 5B). The samples (SZT, RZ) collected from the Wronine Formation represent laminated brownish marly shales with sparse micro-

Carbon isotope composition of selected samples

Samples	Kerogen	Carbonates	TOC [wt.%]
	$^{13}C_{org.}$ [PDB, ‰]	$^{13}C_{carb.}$ [PDB, ‰]	
TR 1	−18.43	−0.56	0.8
PA 2	−24.5	1.6	0.4
HL 6	−26.06	2.07	0.7
ZAW 3	−25.8	0.7	1.15
SZT 9	−25.89	0.07	0.9
TR 5	−25.23	1.11	0.8
MG 9	−23.59	n.d.	1.8
MG 15	−23.89	n.d.	1.5
MG 20	−23.56	n.d.	0.4

indicate deposition under oxygen-free conditions (Jones and Manning, 1994; Veto *et al.*, 1997). However, absolute as well as normalized V/V+Ni and V/Cr ratios that are too low negate this thesis (Fig. 4A; Lewan, 1984).

The remarkably high amounts of As and U associated with Ba in particular may suggest high primary productivity (Dymond *et al.*, 1992; Mongenot *et al.*, 1996, Alberdi-Genolet and Tocco, 1999). This corresponds to a considerable quantity of siliceous microfauna and amorphous, possibly of algal origin, organic matter. Sample JG 2 contains relatively high amounts of TOC and of many elements (Ni, Pb, Y, Ba and Co; Table 1; Fig. 4A). Note the high values of enrichment factors of Cd and Ag (Table 1). Sample JG 2 contains a considerable amount of S. The framboidal shape of pyrite and its size (3 μm average) may suggest the presence of H$_2$S in the water column (Wilkin *et al.*, 1996; Wignall and Newton, 1998). The undisturbed lamination and, low content of microfauna (Fig. 5B) indicate anoxic condition. However, absolute and shale-normalized V/V+Ni and V/Cr ratios are lower than the level of anoxity established (Fig. 4A; Lewan, 1984). In an oxygen-free or even H$_2$S-bear-

ing environment the trace elements could have been absorbed from the water during slow accumulation and trapped into sulphides or into reactive OM.

The ZAW samples are generally poor in trace elements. Nevertheless, As, Ba, Ag, Cd, Zn, Ni and V occur in large amounts. All of the trace-elements measured display the enrichment factor >1 (Table 1 and Fig. 4B). Their presence may be related to diffusion into sediment under reducing conditions (Brumsack, 1980, 1986). They were bound to organic matter and also precipitated as sulphides. Pyrite has replaced recrystallised calcareous and silica tests, which points to diagenetical pyritization (Wilkin *et al.*, 1996; Wignall and Newton, 1998). Moreover, absolute and normalized V/V+Ni and V/Cr ratios are not high enough to indicate anoxity of the bottom water (Fig. 4A; Lewan and Maynard, 1982; Lewan, 1984). Therefore, the ZAW section was deposited below OMZ.

The SZT and RZ samples collected from the Wronine Fm. (the Grajcarek Succession) are very similar. Micropalaeontological investigations of samples suggest that they were deposited under oxygen-limited conditions. However, geochemical examinations did not confirm a wholly anoxic environment at the bottom: V/V+Ni ratios vary from 0.58 to 0.66, the V/Cr ratios are below 2 and U/Th is equal only to 0.3 (Table 1 and Fig. 4A; Lewan and Maynard, 1982; Lewan, 1984; Jones and Manning, 1994). The shale-normalization decreases the V/V+Ni and V/Cr ratios and increases the U/Th ratio (Table 1). Additionally, the Mn content is very high (Quinby-Hunt and Wilde, 1994; Veto *et al.*, 1997). The values of enrichment factor exceed 1 for most elements. Pyrite oc-
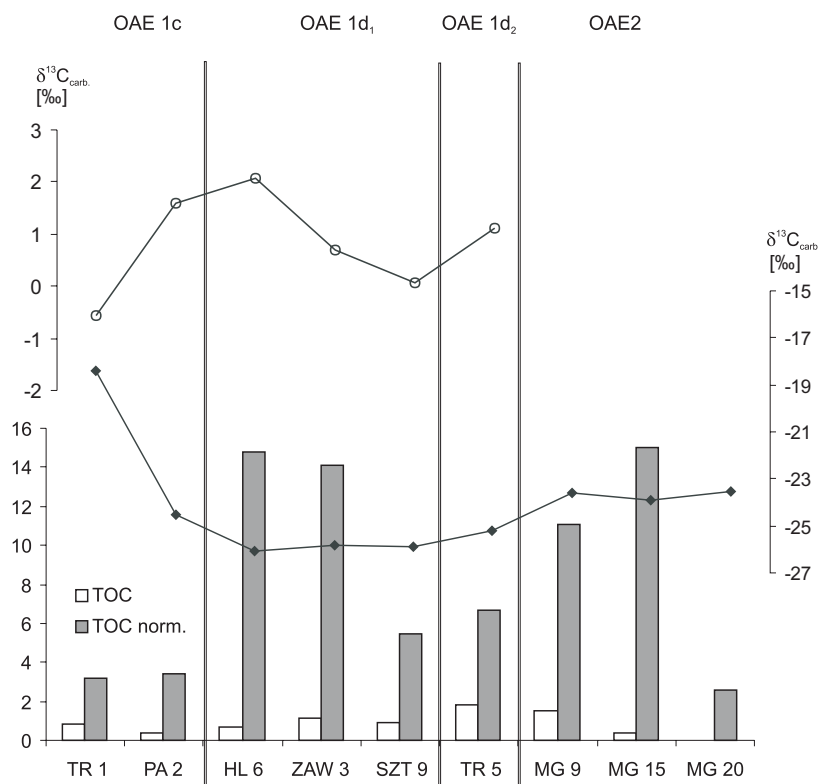

Fig. 8. Variation in TOC (wt.%), carbon isotope composition of organic carbon ($\delta^{13}C_{org.}$ per mil relative to PDB standard) and carbon isotope composition of carbonate carbon ($\delta^{13}C_{carb.}$ per mil relative to PDB standard) composition in selected samples

curs as large (> 10 μm) euhedra and framboids. These forms are typically postdepositional (Wilkin *et al.*, 1996; Wignall and Newton, 1998). Many elements, such as Cu, Zn, Pb, V, Ni, As, Co are easily bound to sulphides. Therefore, pyritization may be the main reason for metal enrichment. The same elements are often associated with organic matter (Brumsack, 1980, 1986; Breint and Wanty, 1991). Some of the metals (e.g. Mo, U, V, Cr) might have been concentrated during early diagenesis by diffusion into deposits and fixation after a reduction step due to oxidation — reduction reactions at the expense of OM (Shaw *et al.*, 1990).

THE MIDDLE CENOMANIAN
JAWORKI FORMATION

The enhanced deposition of organic matter that occurred in the mid Cenomanian (OAE $1d_2$; *R. reicheli–R. greenhornensis* Local Partial Concurrent Range Zone — LPCRZ) is recorded within the Jaworki Formation in the Branisko, Niedzica and Pieniny successions (Figs. 2 and 3).

The profiles selected both in the Branisko (the Trawne Stream section: TR 2–5) and in the Niedzica successions (the Bukowiny Hill — BUK) look similar. They contain red and variegated marls intercalated with black shales. Wavy lamination was noted inside dark layers. The rare microfauna consists of radiolarian tests and agglutinated foraminifera. Samples representing calciturbiditic lithotypes were collected in the Branisko Succession (the Pasieczny Stream — PA 4), in the Niedzica Succession (the Biała Woda Valley — BW, the Skalski Stream — PSK), and in the Pieniny Succession (the Macelowa Mount — MC profile). They contain abundant microfauna including abundant planktonic and benthic foraminifera.

ORGANIC MATTER AND INORGANIC GEOCHEMISTRY
IN THE MIDDLE CENOMANIAN STRATA

Within the middle Cenomanian samples, the maximum TOC contents were measured in the BUK 3B and TR 5 samples. Percentages of TOC are 0.8 to 1%. In the red and variegated marls (BUK 3G, BW 5, TR 2) and arenitic grey (BW 2, PSK 1, MC 2, PA 4) samples, TOC does not reach 0.5%. Kerogen is characterized by low values of HI and S2, therefore it was defined as of type III/IV (vitrinite/inertinite). The T_{max} values are between 423–433°C and indicate that kerogen is just below the oil window. In the TOC-free samples, the T_{max} values and the degree of maturation were difficult to establish. Note worthy is the elevated TOC content (16%) and T_{max} value (483°C) in sample BW 2B that for the main part is a coal fragment. The high value of T_{max} indicates an advanced maturity of kerogen that can be called as "dead carbon" (Table 2; Fig. 6).

The results of thin section investigation correspond with the pyrolysis data. The marly black shales (BUK 3B and TR 5) contain amorphous organic matter, identified as collinite (colomorphous vitrinite). The macerals occurring within detrital samples (BW 2, PSK 1 and MC 2) were recognized as detrovitrinite (Fig. 7C). Observations of the BW 2B and PA 4 samples show the presence of large pieces of maceral with internal cellular structure (tellinite/fusinite; Fig. 7E). The amor-

phous matter infilling cell lumens within sample BW 2 was identified as resinite (Fig. 7A).

All samples of the OAE $1d_2$ event are Ca-rich, regardless of organic carbon content (Table 1 and Fig. 4A). The geochemical comparison of the BUK samples shows strong correlation between TOC contents and trace element amounts. The TOC-rich sample BUK 3B is distinctive. It contains higher concentrations (absolute contents and values of enrichment factor) of Ag, Cd, Cu, Ni, Pb, Zn, V, As, Ba, Co and U (Fig. 4A, B) and has also the lowest Mn amount, a V/V+Ni ratio reaching 0.75, a V/Cr ratio exceeding 2 and a U/Th ratio of 0.7. The normalisation relative to the "average shale" led to decreasing V/V+Ni and V/Cr ratios, but values of U/Th are higher (Fig. 4A). The geochemical character of sample BUK 3B may be recognized as typical of dysoxic/anoxic conditions, but without H_2S (Lewan and Maynard, 1982; Lewan, 1984; Jones and Manning, 1994; Quinby-Hunt and Wilde, 1994; Veto *et al.*, 1997).

In contrast to the BUK samples, the TR samples are similar geochemically, in spite of the varying TOC content. The absolute amounts of many trace elements low. Values of the enrichment factor are about 1 (Fig. 4B). However, increasing TOC values correlate with increasing S amounts, and less clearly with the amounts of Zn, V, As, Ba and Co. The V/V+Ni ratio, being 0.7 for the dark TR 5 sample, may suggest dysoxic conditions of the bottom water and corresponds with the absence of benthos (Lewan and Maynard, 1982; Lewan, 1984). The euhedral and massive forms of pyrite within the TR samples indicate that the pyritization was diagenetic (Wilkin *et al.*, 1996; Wignall and Newton, 1998). Precipitation of sulphides may be an explanation for the Zn, As, Co enrichment (Brumsack, 1980, 1986). Likewise, some elements might have been fixed into sediment in the reduction stage at the expense of OM. The geochemical enhancement may be related with absorption by clay minerals in the case of the red TR samples.

The calciturbiditic samples (pelitic BW2, PSK1 and MC1) are very low in trace elements (Table 1 and Fig. 4A). Based on geochemical indicators, the presumption of oxic environment is justifiable, and is in accordance with palaeontological conclusions. Numerous assemblages of calcareous foraminifers suggest a biologically hospitable environment within the whole water column.

THE CENOMANIAN/TURONIAN
MAGIEROWA MEMBER

The latest episode of organic matter deposition (OAE 2) was dated as late Cenomanian to early Turonian. This event is recorded within the Magierowa Member. It is difficult to determine biostratigraphically. The planktonic foraminiferal assemblage in the lower part of the member corresponds to the early part of the *Rotalipora cushmani* Zone of the middle Cenomanian. The upper part of the Magierowa Mb. includes a foraminiferal association indicative of the early Turonian *Helvetoglobotruncana helvetica* Zone (Birkenmajer and Jednorowska, 1984). Therefore it is assumed that black shales occurring between them represent the Late *Rotalipora cushmani* to Early *Helvetoglobotruncana helvetica* Zone (after Gasiński,

1983, 1988; Fig. 2). The Magierowa Member samples (MG) consist of alternating beds of laminated black shales and of bioturbated green mudstones. Trace fossils within green samples are attributed to *Chondrites.* This material includes also sparse agglutinated foraminiferal and pyritized radiolarian skeletons. The black samples are of siliceous, laminated shales, completely devoid of microfauna (Fig. 5C). Pyrite occurs sporadically as individual small euhedra and/or it forms of framboids.

ORGANIC MATTER AND INORGANIC GEOCHEMISTRY IN THE CENOMANIAN/TURONIAN STRATA

The colour of samples is determined by the presence of organic matter. The TOC contents vary from 0.1% within green samples to 1.9% within black shales. The temperature of maximum pyrolysis (T_{max}) exceeds 465°C (Table 2). The high T_{max} values correlate with extremely low HI values and indicate the post-maturity level of the kerogen. The diagram of hydrogen index (HI) versus oxygen index (OI) shows a predominantly type IV kerogen, termed inertinite (Fig. 6).

Petrographic analysis of the kerogen showed angular fragments with preserved cell structures and wispy, amorphous material belonging to macerals of the inertinite group. The macerals are identified as semifusinite (Fig. 7H) sclerotinite (Fig. 7F) and inertodetrinite (Fig. 7F).

The isotopic composition of organic carbon shows ^{12}C enrichment. The δ^{13}C value of kerogen varies from –23.9 to –23.59 (n=3) (Table 3; Fig. 8) and was explained by input of terrestrial organic matter (Dean *et al.*, 1986; Hoefs, 1997), and so the organic matter accumulated within the Magierowa Mb. sediment is of land plant provenance.

The Magierowa Member samples are characterized by a negligible Ca content. In general, absolute concentrations of trace elements correlate with TOC values (Table 1; Fig. 4A). The correlation is clear between the organic carbon content and the concentration of Ag, Cd, Mo, Zn, V, and weaker for U, Cr. These elements might be bound by organic matter or by H_2S under euxinic conditions (Brumsack, 1980, 1989; Breint and Wanty, 1991). The amounts of S are difficult to determine, because of oxidation of the sulphide minerals. The TOC values increase with increased values of some indicative ratios: V/V+Ni, V/Cr and U/Th. The V/V+Ni ratios exceed 0.7 and V/Cr exceeds 2 in the black samples. The shale-normalisation induces decrease of the V/V+Ni and V/Cr ratios, but causes a higher U/Th ratio (Table 1; Fig. 4A). The concentrations of As, Ba, Co, REE, Cu, Mn, Ni and Y appear to be independent of TOC. Moreover, all of the MG samples are characterized by low amounts of Mn. The significant content of Al within the MG samples suggests relatively high amounts of clay minerals.

The sedimentation rate of the Magierowa Member was sluggish, therefore trace elements diffused into sediment where they were trapped by clay minerals and/or sulphides. The enrichment of trace elements into the $C_{org.}$-rich sediment could have occurred under reducing conditions. The significantly high values of V/V+Ni and V/Cr ratios indicate an anoxic environment (Lewan and Maynard, 1982; Lewan, 1984; Jones and Manning, 1994). The same may be deduced from the low content of Mn (Quinby-Hunt and Wilde, 1994; Veto *et al.*, 1997).

INTERPRETATION

The first episode of organic matter deposition investigated is dated as late Albian (*Rotalipora subticinensis–R. ticinensis* Zone). Enhanced runoff from land brought with it a significant amount of terrestrial material: organic particles and nutrients. Detritic macerals (inertodetrinite and detrovitrinite) accumulated on the shelf, close to the coast, in the Czorsztyn Succession (Lower Pomiedznik Fm., JK samples; Fig. 9A). Due to excessive organic flux and advanced coalification of the kerogen, it was not completely oxidized. However, the water column was oxic and the accumulation rate was sluggish. The nutrients and low-density organic remains (amorphous) were widely distributed. The organic matter was deposited on the continental slope, eg. in the Niedzica and Branisko successions (Lower Kapuśnica Fm., KP samples). Fertilization of the surface water stimulated primary productivity and the development of an oxygen-minimum zone in mid-water (Fig. 9A). This initially appeared in the Czorsztyn Succession (in the Albian) and spread across the entire Pieniny Basin (in the Vraconian). The upper part of the Pomiedznik Fm. in the Czorsztyn Succession (HL sample) was formed beneath the oxygen-minimum zone, under oxic conditions (Fig. 9B). The upper part of the Kapuśnica Fm. in the Niedzica Succession (JG), in the Branisko Succession (ZAW) and also in the Pieniny Succession (the Podskalnia Mt. section, *cf.* Bąk, 1999) was deposited in a similar environment. On the upper part of the slope (Czorsztyn and Niedzica successions) the layer of oxygen-free water occasionally reached the bottom. At the same time, a stagnant pool developed in the area of the Grajcarek Succession, where the Wronine Fm. was deposited (SZT, RZ) — Figure 9B.

The Cenomanian was a time of uniform pelagic deposition of green and red marls in every unit of the Pieniny Basin. The bottom water was generally oxic. The intercalations of black shales represent records of enhanced $C_{org.}$ storage (middle Cenomanian: *Rotalipora reicheli–R. greenhornensis* Zone). The O_2 minimum zone moved back, covering only the shelf and upper/middle slope (the Czorsztyn Succession, the Niedzica Succession and part of the Branisko Succession; Fig. 9C). In deeper parts of basin stagnant pools may have formed, where the Skalski Mb. and the upper part of the Trawne Mb. (TR 5) were deposited (Fig. 9C). Down the slope, turbidity currents flowed that resulted in calciturbiditic sequences with organic detritus (the Sneżnica Mb. in the Pieniny and Niedzica successions).

The black shales dated to the Cenomanian/Turonian boundary interval (an analogue of the Bonarelli horizon) occur across the whole Pieniny Basin: in the Czorsztyn Succession black cherty interlayers (named as the Altana Beds) are inserted within the red marl and marly shales of the Pustelnia Mb., while in the Niedzica and Branisko successions $C_{org.}$-rich shales are interbedded with by green marls; in the Pieniny Succession they form a thick sequence of cherty black and green shales (the Magierowa Mb.). The geochemistry of the Magierowa Mb. indicates that it was deposited under anoxic/euxinic conditions (Fig. 9D). It is possible that this stagnant basin was formed in a hallow of the sea bed. Isolated basins, which were anoxic or even H_2S
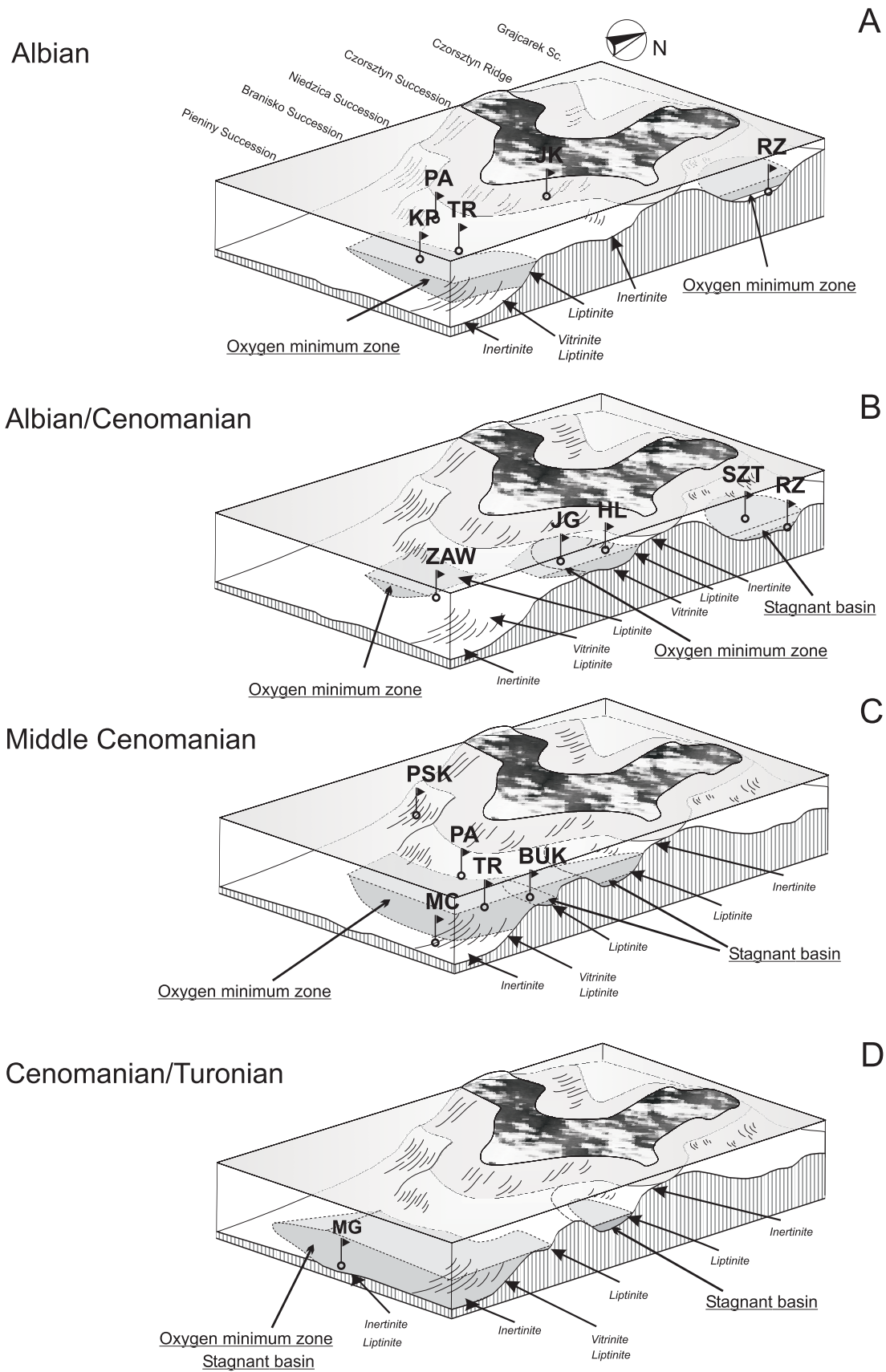
Fig. 9. Models of development of oxygen-depleted environments in the Pieniny Basin during mid-Cretaceous time

For other explanations see Figure 1

bearing, existed on the shelf (Fig. 9D). The slope was still occupied by the oxygen minimum zone (Bąk and Bąk, 1994; Bąk and Sawłowicz, 2000).

Summarizing, the episodes of $C_{org.}$ deposition may reflect a change in the nutrient supply from land, production of saline bottom waters that formed stagnant pools, or periodic changes from negative (little land runoff, high evaporation, flow of nutrient-depleted surface water into the basin) towards positive (large land runoff, low evaporation, flow of nutrient-rich surface water out to the open ocean) fresh-water balance. Large runoff brought with it a significant amount of terrigenous organic matter, which was quickly buried in a marine environment. The resulting anoxic processes correspond well with the model of a "Detrital Anoxic Event" (Erbacher and Thurow, 1995). The organic carbon content was controlled by $C_{org.}$ flux (productivity and vertical $C_{org.}$ flux) and inorganic accumulation rate (Stein, 1986*a*, *b*; Einsele, 2000). Fresh-water input decreased the water temperature and the nutrient content of the surface water (Hay, 1995). The plankton productivity and oxidation of organic particles led to consumption of O_2 at mid-water levels ("Productivity Anoxy Event" *cf.* Michalik *et al.*, 1999). The expanding oxygen-minimum zone could occupy the whole water column and form stagnant pool conditions ("Stagnant Anoxic Event" *cf.* Michalik *et al.*, 1999).

CONCLUSIONS

1. Pelagic deposition of black levels within the lower part of the Pomiedznik Fm. (sample JK 2, the Czorsztyn Succession) and the Trawne Mb. (sample PA 2, the Branisko Succession) occurred under oxic conditions. The organic matter (terrestrial detrovitrinite and angular inertinite) was preserved because of excessive supply of organic particles.

High productivity and vertical flux of organic matter have influenced deposition of the lower part of the Kapuśnica Fm. in the Branisko Succession (KP sequence). Decomposition of terrestrial (collinite) and marine (bituminite) organic remains produced a mid-water oxygen-minimum zone. Deposition of the KP sequence took place under poorly oxygenated or anoxic conditions. The lower part of the turbiditic Trawne Mb. contains terrestrial organic matter. The content of organic matter was probably sufficient to cause reduction of sediments. The redox condition could be also inherited. The measured trace element enrichment may have been the effect of fixation by reactive terrestrial organic matter and of diagenetic pyritization.

2. The environment of deposition of the upper part of the Pomiedznik Fm. (HL sequence) seems to have been dependent on primary productivity (bituminite) and the supply of terrestrial

(collinite) organic matter. Oxidation of OM occurred within the mid-water oxygen-minimum zone that occasionally reached the bottom. The enrichment in trace elements is related to the precipitation of sulphides caused by diagenetic processes of degradation of OM and euxinia during of sedimentation.

The deposition of the Upper Kapuśnica Fm. in the Niedzica Succession (JG sequence) occurred in an oxygen-free or even H_2S-bearing environment, where trace elements were absorbed from water during slow accumulation and trapped into sulphides or into reactive OM (terrestrial collinite and bituminite — algal provenance).

The ZAW section (Upper Kapuśnica Fm.; the Branisko Succession) was deposited under aerobic conditions, below an oxygen-minimum zone formed due to oxidation of terrestrial and marine organic matter. The partial redeposition of detrital material cannot be excluded.

The possible chemical regime during deposital of the RZ and SZT samples (the Wronine Fm.; the Grajcarek Succession) was similar to a stagnant basin, where massively accumulated OM induces the reduction of oxygen within bottom water. The enrichment in trace elements was the consequence of trapping by organic matter or by precipitated sulphides.

3. The deposition of the BUK section (the Jaworki Fm.; the Niedzica Succession) took place in a pelagic regime. The bulk of supplied organic matter (telinite, collinite) was sufficient for oxygen exhaustion. Trace element enrichment during diagenesis cannot be excluded.

The geochemistry of sample TR 5 (upper part of the Trawne Mb.; the Branisko Succession) may suggest dysoxic conditions of the bottom water. The enrichment in selected metals might be explained by the precipitation of sulphides; some elements were fixed into the sediment on the reduction step at the expense of OM.

The oxic environment for the calciturbiditic sediments (BW, PSK, MC) of the Jaworki Fm. in the Niedzica Succession can be explained by redeposition of the organic particles (detrovitrinite).

4. The deposition of the Magierowa Mb. (the Pieniny Succession) took place under anoxic (black shales) occasionally changing to oxic/dysoxic conditions (green layers). Degradation of organic matter and a low sedimentation rate led to exhaustion of oxygen. The whole water column was anoxic; occasionally the boundary of anoxity went up above the bottom level.

REFERENCES

ALBERDI-GENOLET M. and TOCCO R. (1999) — Trace metals and organic geochemistry of Machiques Member (Aptian-Albian) and La Luna Formation (Cenomanian-Turonian), Venezuela. Chem. Geol., **160**: 19–38

ALEXANDROWICZ S. W., BIRKENMAJER K., SCHEIBNER E. and SCHEIBNEROVA V. (1968) — Comparison of Cretaceous stratigraphy in the Pieniny Klippen Belt (Carpathians). Bull. Acad. Pol. Sc., 16 (2): 77–90.

ARTHUR M. A. and PREMOLI SILVA I. (1982) — Development of widespread organic carbon-rich strata in the Mediterranean Tethys. In: Nature and Origin of Cretaceous Carbon-rich Facies (eds. S. O. Schlanger and M. B. Cita): 7–55. Acad. Press, London.

BĄK M (1999) — Cretaceous Radiolaria from the Pieniny Succession, Pieniny Klippen Belt, Polish Carpathians. Stud. Geol. Pol., 115: 91–115.

BĄK K. and BĄK M. (1994) — Microfaunal assemblages of the Upper Cenomanian/Lower Turonian anoxic deposits in the Pieniny Klippen Belt, Carpathians, Poland. Abstract Book of Annual Assembly IGCP Project No. 362, Tethyan and Boreal Cretaceous, 3–09.10. 1994, Smolenice (Slovakia): 73–74.

BĄK M. and SAWŁOWICZ Z. (2000) — Pyiritized radiolarians from the Mid-Cretaceous deposits of the Pieniny Klippen Belt — a model of pyritization in an anoxic environment. Geol. Carpathica, 51: 91–99.

BAUDIN F., FIET N., COCCIONI R. and GALEOTTI S. (1998) — Organic matter characterisation of the Selli Level (Umbria-Marche Basin, central Italy). Cret. Res., 19 (6): 701–714.

BIRKENMAJER K. (1960) — Badania geologiczne w pienińskim pasie skałkowym. Prace Inst. Geol., 30 (1): 205–213.

BIRKENMAJER K. (1977) — Jurassic and Cretaceous lithostratigraphic units of the Pieniny Klippen Belt, Carpathians, Poland. Stud. Geol. Pol., 45: 1–159.

BIRKENMAJER K. (1979) — Przewodnik geologiczny po pienińskim pasie skałkowym. Wyd. Geol., Warszawa.

BIRKENMAJER K. and GASIŃSKI M. A. (1992) — Albian and Cenomanian palaeobathymetry in the Pieniny Klippen Belt, Polish Carpathians. Cret. Res., 13: 479–485.

BIRKENMAJER K. and JEDNOROWSKA A. (1984) — Upper Cretaceous stratigraphy in the Pieniny Nappe at Sromowce Niżne. Pieniny Klippen Belt (Carpathians Poland) (in Polish with English summary). Stud. Geol. Pol., 83: 25–50.

BIRKENMAJER K. and JEDNOROWSKA A. (1987) — Late Cretaceous foraminiferal biostratigraphy of the Pieniny Klippen Belt, Carpathians (Poland). Stud. Geol. Pol., 92: 7–28.

BIRKEMNAJER K. and MYCZYŃSKI R. (1977) — Middle Jurassic deposits and fauna of the Magura succession, near Szlachtowa, Pieniny Klippen Belt (Carpathians) (in Polish with English summary). Acta Geol. Pol., 27: 337–400.

BRASS G. W., SOUTHAM J. R. and PETERON W. H. (1982) — Warm saline bottom water in ancient ocean. Nature, 296: 620–623.

BREINT G. N. and WANTY R. B. (1991) — Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. Chem. Geol., 91: 83–97.

BRUMSACK H. J. (1980) — Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36, 41). Chem. Geol., 31: 1–25.

BRUMSACK H. J. (1986) — The inorganic geochemistry of Cretaceous black shales (DSDP 41) in comparison to modern upwelling sediments from the Gulf of California. Geol. Soc. Spec. Publ., 21: 447–462.

BRUMSACK H. J. (1989) — Geochemistry of recent Corg.-rich sediments from the Gulf of California and the Black Sea. Geol., Rundschau, 83 (3): 851–882.

BRUMSACK H. J. and THUROW J. (1986) — The geochemical facies of black shales from the Cenomanian/Turonian boundry event (CTBE). Mitt. Geol.-Palaon. Inst. Univ. Hamburg, 60: 245–265.

CARON M., DALL'AGNOLO S., ACCARIE H., BARRERA E., KAUFFMAN E. G., AMEDRO F. and ROBASZYNSKI F. (2006) — High-resolution stratigraphy of the Cenomanian–Turonian boundary interval at Puebo (USA) and wadi Bahloul (Tunisia): stable isotope and bio-events correlation. Geobios, 39: 171–200.

CHAMLEY H. and ROBERT C. (1982) — Paleoenvironmental significance of clay deposition in Atlantic black shales. In: Nature and Origin of Cretaceous Carbon-rich Facies (eds. S. O. Schlanger and M. B. Cita): 101–112. Acad. Press, London.

DEAN W. E., ARTHUR M. A. and CLAYPOOL G. (1986) — Depletion of ^{13}C in Cretaceous marine organic matter: source, diagenetic or environmental signal? Mar. Geol., 70: 119–157.

DEINES P. (1980) — Handbook of Environmental Isotope Geochemistry, 1, Amsterdam. Elsevier: 329–406.

De BOER P. (1982) — Some remarks about the stable isotope composition of cyclic pelagic sediments from the Cretaceous in the Apennines (Italy). In: Nature and Origin of Cretaceous Carbon — rich Facies (eds. S. O. Schlanger and M. B. Cita): 129–145. Acad. Press, London.

De GRACIANSKY P. C., BROSSE E., DEROO G., HERBIN J. P., MONTADERT L., MULLER C., SIGAL J. and SCHAAF A. (1987) — Organic-rich sediments and palaeoenvironmental reconstructions of the Cretaceous North Atlantic. In: Marine Petroleum Source Rocks. Geol. Soc. Spec. Publ., 26: 317–344.

DYMOND J., SUESS E. and LYLE M. (1992) — Barium in deep-sea sediment: a proxy for paleoproductivity. Paleoceanography, 7: 163–181.

EINSELE G. (2000) — Sedimentary Basin. Evolution, facies and sediment Budget. Springer-Verlag. Berlin Heidelburg, New York.

ERBACHER J. and THUROW J. (1990) — A model for a sea-level controlled evolution of mid-Cretaceous black shales and Radiolaria. Europal, 8.

ESPITALIE J. (1985) — Use of Tmax as a maturity index for different types of organic matter. Comparison with vitrinite reflectance. In: Thermal Modeling in Sedimentary Basins (ed. J. Burrus): 475–496. Edition Technip, Paris.

GALIMOV E. M. (1980) — Kerogen, insoluble organic matter from sedimentary rocks. Paris. Edition Technip: 270–297.

GALIMOV E. M. (1985) — The biological fractionation of isotopes. London, Orlando, Acad. Press.

GASIŃSKI M. A. (1983) — Albian and Cenomanian planktic foraminiferida from the Trawne beds (Pieniny Klippen Belt, Polish Carpathians). Cret. Res., 4: 221–249.

GASIŃSKI M. A. (1988) — Foraminiferal biostratigraphy of the Albian and Cenomanian sediments in Polish part of the Pieniny Klippen Belt, Carpathian Mountains. Cret. Res., 9: 217–247.

GASIŃSKI M. A. (1991) — Albian and Cenomanian palaeobathymetry of the Pieniny Klippen Belt Basin (Polish Carpathians) based on foraminifers. Bull. Acad. Polon., 39 (1): 1–10.

HAY W. H. (1995) — Cretaceous paleoceanography. Geol. Carpath., 46 (5): 257–266.

HAY W. H. (1997) — The effect of changes of the mean salinity on ocean circulation. Miner. Slov., 29 (5): 243–244.

HOEFS J. (1997) — Stable Isotope Geochemistry. Springer Verlag, Berlin.

JENKYNS H. C. (1985) — The Early Toarcian and Cenomanian-Turonian anoxic events in Europe: comparisons and contrasts. Geol. Rundschau, 74 (3): 505–518.

JONES B. and MANNING D. (1994) — Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. Chem. Geol., 93: 111–129.

KSIĄŻKIEWICZ M. (1972) — Budowa geologiczna Polski., 4 (Tektonika), 3 (Karpaty), Inst. Geol., Warszawa.

LEWAN M. (1984) — Factor controlling the proportionality of vanadium to nickel in crude oils. Geochim. Cosmochim. Acta, 48: 2231–2238.

LEWAN M. and MAYNARD J. (1982) — Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. Geochim. Cosmochim. Acta, 46: 2547–2560.

MANGINI A. and DOMINIK J. (1979) — Late Quaternary sapropel on the Mediterranean ridge: U-budget and evidence for low sedimentation rates. Sed. Geol., 23: 113–125.

MICHALIK J., REHAKOVA D., LINTNEROVA O., BOOROVA D., HALASOVA E., KOTULOVA J., SOTAK J., PETERČAKOVA M., HLADIKOVA J. and SKUPIEN P. (1999) — Sedimentary, biological and isotopic record of Early Aptian paleoclimatic event in the Pieniny Klippen Belt, Slovak Western Carpathians. Geol. Carpath., 50 (2): 169–191.

MONGENOT T., TRIBOVILLARD N. P., DESPRAIRIES A., LALIER–VERGES E. and LAGGOUN–DEFARGE F. (1996) — Trace elements as palaeoenvironmental markers in strongly mature hydrocarbon source rocks: the Cretaceous La Luna Formation of Venezuela. Sedim. Geology, 103: 23–37.

NDUNG'U K., THOMAS M. A. and FLEGAL A. R. (2001) — Silver in western equatorial and South Atlantic Ocean. Deep - Sea Res. II, 48: 2933–2945.

QUINBY-HUNT M. S. and WILDE P. (1994) — Thermodynamic zonation in the black shale facies based on iron-manganese-vanadium content. Chem. Geol., **113**: 297–317.

ROHLING E. J. and HILGEN F. J. (1991) — The eastern Mediterranean climate at times of sapropel formations: a review. Geol. Mijnb., **70**: 253–264.

SCHLANGER S. O. and CITA M. B. (1982) — Nature and Origin of Cretaceous Carbon-rich Facies. Acad. Press, London.

SCHLANGER S. O. and JENKYNS H. C. (1976) — Cretaceous oceanic anoxic events: Causes and consequences. Geol. Mijn., **55**: 179–184.

SHAW T. J., GIESKES J. M. and JAHNKE R. A. (1990) — Early diagenesis in differing depositional environments: the response of transition metals in pore water. Geochim. Cosmochim. Acta, **54**: 1233–1246.

SIKORA W. (1971) — Esquisse de la tectogenese de la zone des Klippen des Pieniny en Pologne d'apres de nouvelles donnees geologiques (in Russian with French summary). Rocz. Pol. Tow. Geol., **41** (1): 221–237.

STEIN R. (1986*a*) — Surface-water paleo-productivity as inferred from sediments deposited in oxic and anoxic deep-water, environments of the Mesozoic Atlantic Ocean. Mitt. Geol.-Palaon. Inst. Univ. Hamburg, **60**: 55–70.

STEIN R. (1986*b*) — Organic carbon and sedimentation rate-Further evidence for anoxic deep-water conditions in the Cenomanian-Turonian Atlantic Ocean. Mar. Geol., **72**: 199–209.

THIEDE J., DEAN W. E. and CLAYPOOL G. E. (1982) — Oxygen-deficient depositional palaeoenvironments in the Mid-Cretaceous tropical central Pacific Ocean. In: Nature and Origin of Cretaceous Carbon-rich Facies (eds. S. O. Schlanger and M. B. Cita): 79–101. Acad. Press. London.

VETO I., DEMENY A., HERTELENDI E. and HETENYI M. (1997) — Estimation of primary productivity in the Toarcian Tethys — a novel approach based on TOC, reduced sulphur and manganese contents. Palaeogeogr., Palaeoclimat., Palaeoecol., **132**: 355–371.

WEDEPOHL K. H. (1970) — Environmental influences on the chemical composition of shales and clays. In: Physics and Chemistry of the Earth. Pergamon Press. Oxford and New York: 303–333.

WEDEPOHL K. H. (1991) — The composition of the upper Earth's crust and the natural cycles of selected metals. Metals in natural raw materials. Natural sources. In: Metals and their Compounds in the Environment. VCH, Weinheim: 3–17.

WEISSERT H. (1990) — Siliciclastics in the Early Cretaceous Tethys and North Atlantic oceans: documents of periodic greenhouse conditions. In: Geology of the oceans (ed. M. B. Cita). Mem. Soc. Geol. Ital., **44**: 59–69.

WIGNALL P. B. and NEWTON R. (1998) — Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks. Am. J. Sc., **298**: 537–552.

WILKIN R. T., BARNES H. L. and BRANTLEY (1996) — The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. Geochim., Cosmochim., Acta, **60** (20): 3897–3912.

ŻYTKO K., GUCIK S., RYŁKO W., OSZCZYPKO N., ZAJĄC R., GARLICKA I., NEMČOK J., ELIAS M., MENCIK E., DVORAK J., STRANIK Z., RAKUS M. and MATEJOVSKA O. (1989) — Geological map of the Western Carpathians and their Foreland without Quaternary formation. In: Geological Atlas of the Western Outer Carpathians (eds. D. Poprawa and J. Nemčok). Państw. Inst. Geol., Warszawa.