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RELATIONSHIP BETWEEN THE ?CRETACEOUS "BLACK SHALES" AND CRETACEOUS OCEANIC RED BEDS OF THE GRAJCAREK SUCCESSION-A GEOCHEMICAL APPROACH (PIENINY KLIPPEN BELT, WEST CARPATHIANS, POLAND)

Wójcik-Tabol P. and Oszczypko N.

Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, PL-30-063, Kraków, Poland, p.wojcik-tabol@uj.edu.pl, nestor.oszczypko@uj.edu.pl

Abstract: In the Polish Outer Carpathians, the contact zone of the Magura Nappe and the Pieniny Klippen Belt is known as the Grajcarek Succession (Unit). This succession contains the "black flysch" deposits, with controversial age, overlain by the Cenomanian radiolarian shales (CRS), followed by the Turonian through Campanian variegated shales (CORB). All these deposits have been sampled. The major and trace elements were analyzed, as well as relation of trace metals with organic matter content (TOC) was recognized. The studies performed by authors reveal that deposition of the CRS took place under oxygen deficiency condition. The trace-element distribution characterizes the hemipelagic regime of sedimentation of both the upper portion of the "black flysch" (spotty shales) as well as the CRS, which were deposited during increasing sea-level. Enrichment in redox-sensitive elements match was probably due to scavenging by H_2S-rich pore fluids. It suggests that spotty shales and the CRS were deposited under very similar sedimentary conditions. During the Late Cretaceous, crucial change in oceanic sedimentation occurred in the Tethys. The Mid-Cretaceous "black shale" facies were passed into Upper Cretaceous oceanic red beds (CORBs).

Key words: "black flysch", CORB, Cretaceous, geochemistry, anoxic event, Magura Basin, Western Carpathians

1. Introduction

The organic matter-rich black shales in the Cretaceous intervals on a global scale resulted in the concept of „Oceanic Anoxic Events" (OAEs, Schlanger and Jenkyns, 1976.). Three OAEs were introduced for the Cretaceous: the Aptian/Albian OAE 1, the Cenomanian/Turonian OAE 2 and the Coniacian/Santonian. The OAE 1 was further divided into four distinct sub-events of oxygen deficiency separated by oxic conditions: Early Aptian OAE 1a, Early Albian OAE 1b, Late Albian OAE 1c and 1d (Arthur at al., 1990).

Records of the Mid-Cretaceous anoxic events have been found in many localities. In the Mediterranean part of the Tethys, they are related to epicontinental seas, and carbonate platforms (Kuhnt et al., 1990). In the Pieniny Klippen Belt (PKB) basin that is interpreted as the northern branch of the Tethys, OAEs records were described by many authors (Wójcik-Tabol 2006 with references therein).

The Mid-Cretaceous anoxic events developing in deep-water conditions of the trench basins are known from numerous localities, also from the Polish Outer Carpathians (Bąk, 2007; Wójcik-Tabol and Ślączka, 2009). A major change in oceanic sedimentation from mid-Cretaceous organic carbon-enriched deep-sea deposits to predominantly Upper Cretaceous oceanic red beds (CORBs) occurred during the Late Cretaceous in the Tethys. This palaeoenviron-mental reconstruction has been based on sedimentological, micropalaeontological and geochemical data (Hu et al., 2005).

The Grajcarek Succession of the PKB (Birkenmajer, 1977) contains the "black flysch" deposits (the Szlachtowa and Opaleniec forma-tions), overlain by the Cenomanian radiolarian shales (CRS) and CORB. A group of major and trace elements has been analyzed in this succession. The relation of trace metals with organic matter content (TOC) was searched. The behaviour of the redox-sensitive elements in recent sediments has potential as the proxy indicator of physicochemical conditions of deposition environment. The new data derived from inorganic geochemistry might supply additional information useful in characterizing the basin in which the studied succession was formed.

The aim of our studies is to establish geochemical relationship between these deposits, and compare studied profiles with standard profiles in the Alpine-Carpathian region, which documented transition between the Lower and Upper Cretaceous deposits (e.g. Brumsack, 1986; Bąk, 2007; Wójcik-Tabol, 2006).

2. Geological Setting

The Małe Pieniny Mts. are located in the southern part of the Polish Western Carpathians, between the Dunajec River Valley on the west and Polish/Slovak state boundary on the east and south (Fig. 1). The studied area occupies the contact position between the Magura Nappe and the PKB. The boundary between the Magura Nappe and the PKB runs along the Grajcarek Stream (Fig. 1C). The Magura Nappe, situated north of stream is composed of the Palaeogene flysch deposits belonging to the Krynica facies-tectonic zone (Birkenmajer and Oszczypko, 1989). These deposits are composed mainly of thick- to medium-bedded turbidites of the canal-lobe provenance. Along the Grajcarek Valley, the Magura Nappe is in a contact with narrow, strongly deformed the Peri-PKB Zone, known as the Grajcarek Unit (Birkenmajer, 1979).

The Grajcarek Succession comprises Jurassic, Cretaceous and Palaeocene, pelagic and flysch depos-

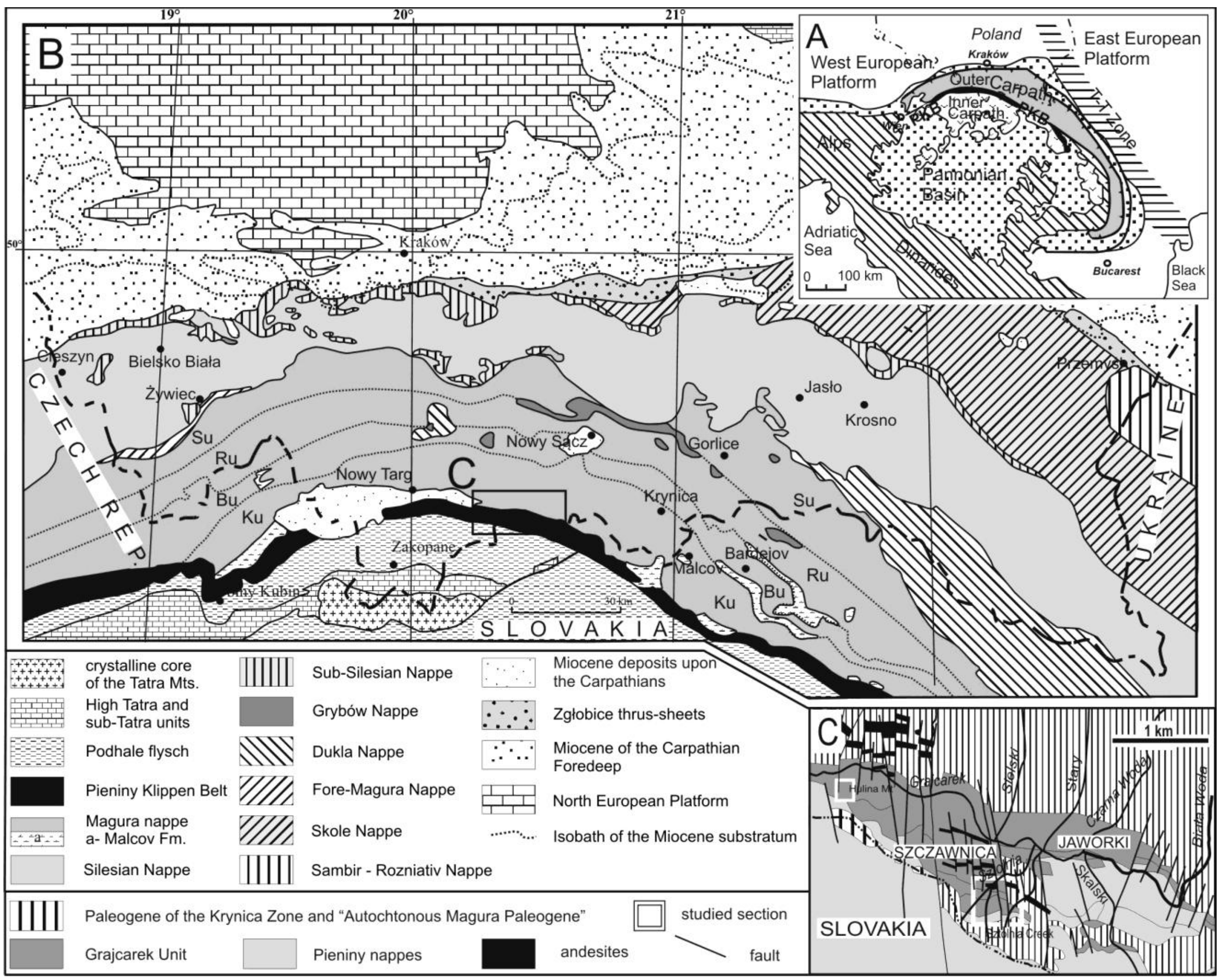

Fig. 1. Location of the studied area at the background of main geological units: A. Simplified tectonic scheme of the Alpine orogens; PKB – Pieniny Klippen Belt (after Kováč et al. 1998, modified); B. Central part of Polish Carpathians (after Oszczypko and Oszczypko-Clowes. 2009); C. Detailed division of the Małe Pieniny region (after Birkenmajer 1979, simplified).

its of the Magura Basin succession, incorporated in the structure of the PKB. The Szlachtowa and Opaleniec formations (black flysch) are up to 220 m thick. Their age, either Jurassic or Early Cretaceous, is a subject to a long-term controversy. Recently Oszczypko et al. (2004) presented new arguments to suggest the Albian-Cenomian age of these sediments, whereas Birkenmajer et al. (2008) support the idea of their Jurassic age.

This black flysch facies is followed by the 2-10 m thick Cenomanian radiolarian shales (CRS, Hulina Fm), variegated shales of the Turonian – Campanian Malinowa Fm. (20-100 m) and the coarse clastic deposits of the Jarmuta Fm (Maastrichtian – Paleocene) reaching 100-400 m (Birkenmajer, 1977). The thickness of the other pelagic formation is highly condensed and does not exceed 15m.

3. Studied Section

The studied exposures are located in the upper course of the Sztolnia Stream along a 250 m long cross-section (Oszczypko et al., 2004; Birkenmajer et al., 2008 and references therein), which comprise three sections (A, B and C; see Fig. 2). In the section Sztolnia A, the Szlachtowa Formation is represented mainly by dark-grey and black marly shales, claystones and siltstones (samples: 12/06, 13/06, 16/06, 17/06, SZT WOD-1, SZT WOD-2, 5/08, 14/08) and fine-grained, calcareous sandstones containing a lot of mica shining flakes (samples: KR 33, KR 34). This formation is overlain by the Opaleniec Fm composed of the light grey marly claystones with intercalations of spotty limestones and sideritic dolomites (samples: 1-2/06). In the Sztolnia section B, this formation is developed as a 20 m thick sequence of dark-grey, green-grey, blue-grey, sometimes fucoid spotty shales with pyrite concretions and intercalations of lenses and beds of grey spotty limestones and sideritic dolomites of a thickness not exceeding a few dozen centimeters (samples: 9-11/06, 6/08, 8/08, 9/08, 15/08, 17/08). The Opaleniec Formation is overlain by the CRS composed of manganese shales, radiolarian shales and radiolarites with pyrite framboids (samples: 3/06, 4/06, 8/06, 15/06;

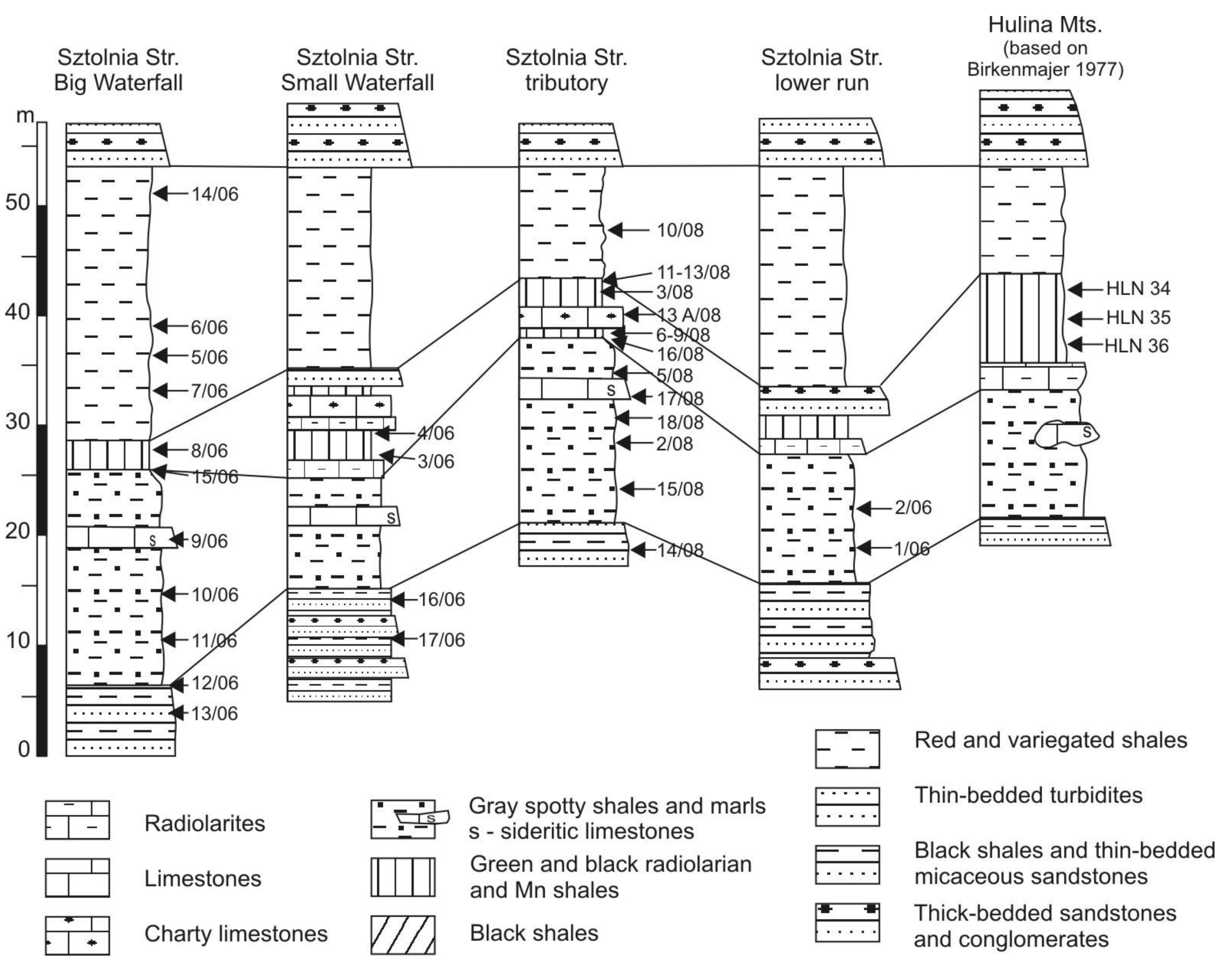

Fig. 2. Lithological log of the Sztolnia sections after Oszczypko et al. (in preparation), Hulina section after Birkenmajer and Gedl (2007), reinterpreted by Oszczypko et al. (in preparation).

3/08, 7/08, 11/08, 12/08, 13/08). These strata have been described by Birkenmajer (1977) as the Hulina Formation (Albian – Cenomanian).

In the Sztolnia Creek section A, C (see Fig. 2), the Cenomanian green shales are followed by non-calcareous, cherry-red and green argillaceous shales (14/06, 5-7/06) of the Malinowa Shale Formation (Birkenmajer, 1977; Birkenmajer and Oszczypko, 1989), whereas in the section B, the lower part of this formation is composed of massive cherry marls (sample 10/08). In the lowermost part of the Malinowa Fm. (section A), on the northern limb of a small anticline, we found a 1 m thick bed of light fine-grained sandstone conformably overlain by 10 cm of green radiolarite, whereas on the southern limb of the anticline, the red radiolarite (5 cm) occurs at top of cherty limestone (sample 22, see Oszczypko et al., 2004).

Additionally, the exposures on the S slope of the Hulina Hill (Fig. 2) have been sampled. The samples (HLN 34B, HLN 34G, HLN 35G, HLN 35A, HLN 35B, HLN 35 Mn, HLN 36G) represent the Hulina Formation.

4. Analytical methods

Microstructures, mineralogy and organic petrological features were investigated in thin-sections using optical microscopy - Nicon ECLIPSE, E 600 POL under transmitted and reflected light. The samples were studied by X- ray diffraction (XRD) both as bulk rocks and in clay fractions (<0.2 μm) separated from these rocks. The clay minerals were separated using the complete Jackson procedure, applied in order to dissolve carbonates and remove organic matter and iron oxides. They were studied as oriented preparations, sedimented on glass slides, both in air- dry and ethylene glycol saturated form. A Philips diffractometer, equipped with a Cu lamp, and a monochromator were used. The identification of clay minerals followed the method outlined by Moore and Reynolds (1989).

The amounts of major oxides were determined in 50 samples using inductively coupled plasma – optical emission spectrometry (ICP-OES). Trace-elements were determined by the inductively coupled plasma – mass spectroscopy (ICP-MS) using a Perkin Elmer Elan 6000 ICP at the ACME Analytical Laboratories, LTD, in Vancouver, Canada.

The amounts of major, minor and trace elements were normalized using Al as a detritus index.

5. Results

5.1. Microfacies and mineral composition

The samples of the Szlachtowa Fm. are represented by dark grey-black mudstones and paper shales. They are parallel laminated, barren of fossils. Rare grains of quartz and light mica occur within clayey or marly matrix. X-ray diffraction analysis defines the clay minerals as kaolinite, illite, smectite and lesser admixture of chlorite. Organic matter is represented by vitrinite.

The spotty marls of the Opaleniec Fm. contain mineral detritus (silty-sized quartz, feldspar, mica) dispersed within marly matrix. Based on XRD, composition of clay minerals appears similar to clay minerals of the Szlachtowa Fm. Calcareous tests (mainly echinoderm spines) are common. The dark spots are cross-section of ichnofossils. There is abundant amorphous organic matter associated with framboidal or massive pyrite.

The CRS from the Sztolnia A, B sections are full of radiolarian tests dispersed within a siliceous-clayey matrix. Clay minerals are represented by kaolinite, illite and traces of chlorite as well. The sulphides concretions are developed at the top of the layer. They have few mm in size. Internal core consists of radial crystals of iron sulphides encircled by euhedra of pyrite.

All of samples of the Hulina Fm., collected from the Sztolnia C section, reveal an abundance of radiolarian tests that are recrystalised by silica. Silica and clay minerals are major components of the matrix. Basing on XRD, clay minerals was identified as illite/smectite admixed with chlorite; presence of small amounts of kaolinite cannot be excluded. Scarce detritus is represented by silt-sized grains of quartz, feldspar and mica. The green shales (HLN 35G, HLN 36) contain higher amount of clay minerals and feldspar relative to black shales. Within ferrous shales (HLN 35A) a negligible amount of illite occurs, as one of clay mineral. Feldspar is absent. Black shales are enriched in organic matter that is developed as black and brownish amorphous matter.

The samples of the Malinowa Fm. are composed of calcite admixed with quartz and clay minerals, i.e. illite and chlorite.

Summing up, the clay mineral composition, lower part of the section (Szlachtowa and Opaleniec Fms) is enriched in kaolinite, the content of which diminishes upwards the section, contrary to increasing amounts of illite and chlorite. Detrital minerals are present through the whole studied interval. Their minimal amounts were recognised in the siliceous shales and radiolarites of the Hulina Fm., but within the overlying Malinowa Fm. amounts of terrigenous material increase again.

5.2. Bulk sediment geochemistry

The chemistry of the studied samples is presented in the table 1. Chemical composition of the studied samples was compared to the standard siliciclastic deposits–Post-Archean Australian Shale (PAAS, Taylor and McLennan, 1985). Determined amounts of the redox-sensitive trace elements were additionally correlated with recent organic matter-rich deposits from the Black Sea and Gulf of California (Brumsack, 1989).

The major chemistry of sediments from the Gulf of California in principle reflects a mixture of terrigenous detritus with a PAAS- like composition and organic-derived silica material (plankton remains). The slight biogenic carbonate component is apparent as well (cf. Brumsack, 1989). The similarity of the Gulf of California deposits to the studied Hulina Fm. is supposed.

The Black Sea marls represent the mixture of detrital clays and biogenic carbonate (coccoliths) with varying amounts of organic matter (Brumsack, 1989). In present paper, they will be compared to the sediments of the Szlachtowa and Opaleniec Fms.

5.3. Detritus index vs. primary productivity

Comparing to PAAS, the tmajority of studied samples are enriched in CaO at the expense of SiO_2. The contents of Al_2O_3 are similar to PAAS. Only the Hulina Formation samples are relatively enriched in SiO_2. They seem to be analogous to upwelling sediments from the Gulf of California (Brumsack, 1989).

The major element composition of the studied material is shown in the triangular plot (SiO_2 – Al_2O_3 x 5 – CaO x 2, Fig. 3). This presentation is based on the assumption that marine sediments may be regarded as mixtures of three components: 1. aluminosilicates (represented by the Al_2O_3 and SiO_2 contents), 2. biogenic silica (partly represented by the SiO_2 contents), 3. biogenic carbonate (largely represented by the CaO contents). It seems to be evident from the diagram that the studied samples represent a mixture of terrigenous detrital material and biogenic silica with various amounts of carbonate, and resemble the Black Sea sediments. Majority of samples plots in the field near the PAAS. The CRS are shifted toward the SiO_2 corner like sediments of the Gulf of California. It suggests that siliceous shales contain the biogenic silica, however presence of diagenetic minerals (carbonate and chalcedony) is supposed. Biogenic derivation of silica finds confirmation in negative correlation between SiO_2 and Al_2O_3 (Fig. 4).

In the SiO_2 vs. Al_2O_3 diagram the correlation is positive for rest of samples. Data describing the Szlachtowa and Malinowa Fms are situated along one, short line. The samples from the Opaleniec Fm. resemble the rest of samples.

The TiO_2/Al_2O_3 diagram illustrates the positive correlation between oxides for all samples (Fig. 4). The samples of the Szlachtowa and Malinowa Fms co-draw line that is shifted towards higher values of TiO_2. The Opaleniec Fm. samples are located irregularly close to other samples.

Contents of TiO_2 in the studied samples are lower than that in the PAAS. The lowest concentration were determined in the Hulina Fm. (e.g. HLN 35 B and HLN 36 Mn or 8/06, 13A/08). TiO_2 distribution trough the Hulina Fm. is parallel to Zr pattern. The TiO_2 distribution through the Szlachtowa and Opaleniec Fms differs in some extent and correlation with Zr is irregular. The brownish-green, marly shale samples (2/08 and KR 33) are enriched of TiO_2, contrary to the clayey shales (calcareous 9-11/06 and non-calcareous 16/06), that are poor. TiO_2 enrichment can be related to presence of both: layered aluminosilicates and “heavy” minerals, whereas Zr occurs in zircon – typical “heavy” mineral. Relatively high and constant amounts of TiO_2 and Zr occur within the Malinowa Fm.

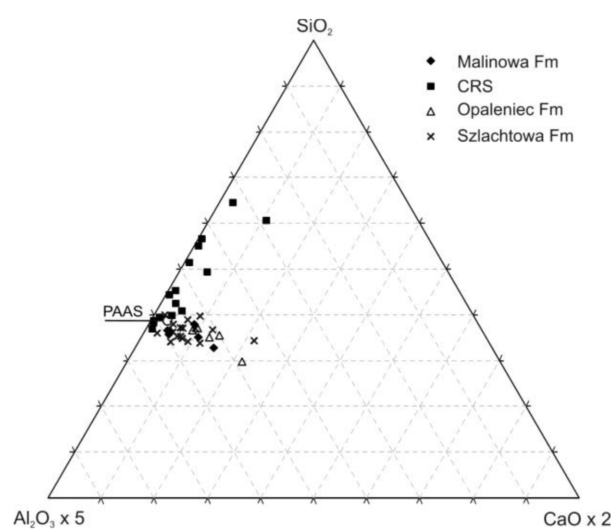

Fig. 3. Triangular plot SiO_2 – Al_2O_3 x 5 – CaO x 2.

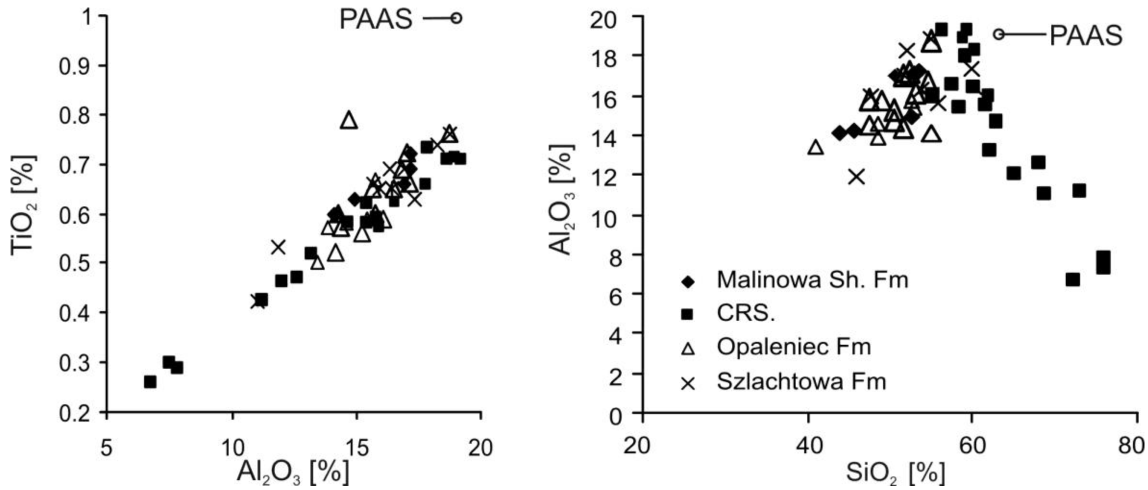

Fig. 4. Diagrams of SiO_2/Al_2O_3 and TiO_2/Al_2O_3 relations in the studied samples from the Małe Pieniny area.

Good correlations between SiO_2, Al_2O_3, K_2O and TiO_2, and correlation with the minor elements Zr, Rb and Nb in the sections depends on the detrital provenance of these elements. The bulk samples are characterised as mixtures of terrigenous-detrital matter comparable to PAAS with varying amount of calcium carbonate.

Variations in the element/Al ratios within the sections are indicative of varying inputs of quartz, heavy minerals and clay minerals. Lower part of the succession consists of abundant clay minerals associations dominated by kaolinite. The fine-grained samples of both: the Szlachtowa and Opaleniec Fms contain higher amounts of detrital quartz, mica and dense minerals. It is probable that the Opaleniec Fm. samples contain Ti-bearing layered aluminosilicates, because no correlation to other “immobile” elements is apparent. The CRS are poor of detrital components.

The studied samples display values of normalized K_2O about 0.2, like in PAAS. The K_2O contents strongly and positive correlate with Rb (r^2 equals 0.9) and K_2O/Rb ratio is constant (Fig. 5).

The investigated samples have the K_2O/Rb ratio similar to detritus derived from the upper continental crust (Plank and Langmuir, 1990).

All studied samples contain small amounts of P_2O_5. Values are rather constant (exception of micaceous sample, KR 33), slightly below that in standard PAAS and organic matter-rich sediments from Gulf of California and Black Sea.

A correlation between P_2O_5, SiO_2 and organic matter is visible in the Hulina Fm.. C, Si and P represent the major nutrient elements and their concentrations suggest an enhanced bioproductivity. Enrichment of Ba and high values of Ba/Sc ratio give evidence of productivity.

The contents of Ba in all studied samples are lower than those in the standard organic matter-rich sediments. Values of Ba are high in the siliceous samples of the Hulina Fm. (max. in HLN 34 B and HLN 35 B, 35 Mn) relative to the other samples. The Opaleniec and Szlachtowa Fms have the lowest contents of Ba. This pattern is followed by Ba/Sc. The highest values of Ba and Ba/Sc ratio were determined for the Hulina Fm. samples. They contain high amounts of Ba and low amounts of Sc. Downward the section (from the Malinowa Marl Fm. to the Szlachtowa Fm.), the Ba and Ba/Sc ratios decrease.

5.4. Redox conditions

The content of MnO and concentration of redox-sensitive elements (Mo, Cu, Ni etc.) are important

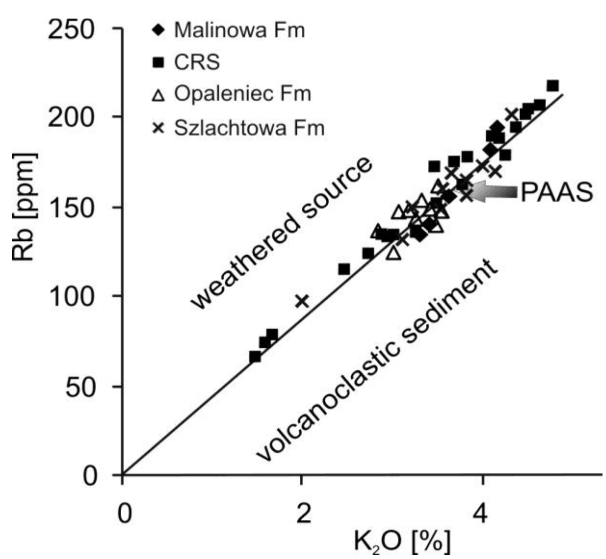

Fig. 5. K_2O vs. Rb diagram. The values of K_2O/Rb ratio in the studied samples are similar to that of the PAAS (McLennan et al., 1990).

Table 1. Major and trace element chemistry of the studied samples. <0.1 or <0.5 – below the detection limit.

Fm	Lithology	Sample	SiO_2 %	Al_2O_3 %	CaO %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	Ba ppm	Ga ppm	Nb ppm	Rb ppm	U ppm	V ppm	Zr ppm	Y ppm	La ppm	Ce ppm	TOT/S %	Mo ppm	Cu ppm	Pb ppm	Zn ppm	Ni ppm	As ppm	Se ppm	V/V+Ni	Ba/Sc	U/Th	TOC %
MALINOWA FM	red marls	SZT 10/08	50.49	15.29	6.98	3.69	0.56	0.1	0.2	257	19.9	11.9	168.5	1.9	124	99.5	33.3	34,0	67.5	0.02	0.2	21.6	13.5	80	89.4	1.6	0.5	0.58	18.35	0.15	nd
	red marly shales	SZT 14/06	52.89	17.14	3.34	4.15	0.72	0.125	0.1	304	21.1	14.6	194.4	2.7	153	136.7	28.8	36	74.4	<0.02	0.2	40.4	25.8	67	69.1	1.5	<0.5	0.69	19	0.19	nd
	red marly shales	SZT 5/06	45.57	14.23	7.19	3.41	0.6	0.123	0.14	297	18.4	13.3	147.9	3.1	107	120.8	23.8	28.5	55	<0.02	0.2	17.5	10	58	51.9	1.9	<0.5	0.67	24.75	0.29	nd
	pale calcareous sandstone	SZT 6/06	44.01	14.12	10.2	3.25	0.6	0.122	0.11	273	18.4	12.5	136.3	3.4	107	118.8	24.4	28.1	55.9	0.03	0.2	23.4	12.2	53	40	2.1	<0.5	0.73	19.5	0.29	nd
	red marly shales	SZT 7/06	53.46	17.19	2.89	4.09	0.69	0.14	0.11	302	22.8	14.5	181.3	3	124	128.6	27.4	32.9	65.9	<0.02	0.3	19.1	18.9	66	62.7	3.8	<0.5	0.66	20.13	0.23	nd
HULINA FM	olive-green radiolarian shales	HLN 34G	61.94	13.23	3.43	2.89	0.52	0.06	0.07	251	16.4	14.5	134.8	1.9	130	94.2	18.2	28.6	63.5	0.04	0.4	120.8	24.8	81	49.7	6.3	0.6	0.72	19.3	0.2	nd
	black radiolarite	HLN 34B	75.83	7.44	3.27	1.58	0.3	0.059	0.3	404	9.8	9.7	73.8	1.2	75	58.7	16.7	20.3	46.8	0.1	0.3	88.5	14.1	52	46.7	4.7	<0.5	0.61	50.5	0.21	nd
	green paper shales	HLN 35G	60.33	16.46	0.9	3.83	0.65	0.076	0.09	286	21.6	17.6	178.3	2.2	157	115	24	34	73.6	0.02	0.2	143	26.3	125	62.5	6.2	0.7	0.71	15.9	0.21	nd
	ferric paper shales	HLN 35A	68.7	11.02	0.65	2.46	0.42	0.066	0.38	291	14.6	11.5	115	1.8	106	80.8	16	23.8	74.6	0.04	0.3	139.9	21.7	111	181	10.5	0.7	0.37	24.25	0.25	nd
	black radiolarite	HLN 35B	72.07	6.7	6.7	1.47	0.26	0.06	0.37	222	9.3	7.4	65.8	1	71	50.3	16.7	17.3	40.9	0.18	0.3	107.5	16.4	44	39.3	4.4	0.6	0.64	31.7	0.22	nd
	manganiferrous radiolarite	HLN 35 Mn	76.05	7.77	1.74	1.66	0.29	0.099	1.2	317	11	7.2	78.2	1.4	67	51.3	25.8	27	68.6	0.13	0.5	104	16.8	56	104.7	6.5	<0.5	0.39	39.6	0.25	nd
	beige paper shales	HLN 36G	68	12.59	0.63	2.87	0.47	0.125	0.19	317	16.7	12	135.2	3	130	84.5	25.7	27.1	65.8	0.05	0.5	181.9	22.9	126	106.4	8.7	0.7	0.55	24.4	0.33	nd
	black siliceous mudstones	SZT 3B/08	55.44	15.91	0.07	3.72	0.59	0.09	0.02	282	22.1	11.8	174.7	6.1	202	104.6	21,0	27.2	53.5	2.04	9,0	95.4	48.8	66	89.2	210	5.3	0.69	18.8	0.59	3.26
	green siliceous shales	SZT 3/08-G	59.74	19.29	0.34	4.69	0.71	0.12	0.02	341	26.8	14.3	206.3	3.2	176	121.1	26.4	31.6	71	0.07	0.1	58.1	14.8	115	67.5	10.5	0.6	0.72	17.9	0.24	nd
	black siliceous shales	SZT 3/08-B	59.42	18.82	0.35	4.56	0.71	0.12	0.02	314	26.5	15.6	204.2	4.2	247	118.9	27.1	35.9	82.1	0.13	0.4	166,0	52.2	205	70.3	24.2	6,0	0.78	17.4	0.39	0.73
	black paper shales	SZT 7/08	56.74	19.16	0.78	4.3	0.71	0.14	0.04	338	25.1	14.5	178.4	5.9	253	119.7	25.9	28.7	62.3	0.58	1	97.7	174.1	92	82.4	36.1	8.1	0.75	18.8	0.47	0.59
	black paper shales	SZT 11/08-B	60.08	18.02	0.79	4.53	0.73	0.11	0.04	293	24,0	15.4	201.2	3	167	130.4	31,0	42.8	101.8	0.03	0.1	101.5	40.9	83	139,0	4.5	0.5	0.54	15.4	0.22	0.92
	green paper shales	SZT 11/08-G	59.75	17.97	1.1	4.84	0.66	0.08	0.04	287	25.8	13.7	217,0	2.5	158	115.9	27.8	36,0	83.8	0.02	0.2	125.3	38.1	64	96.6	3.5	0.5	0.62	15.1	0.21	nd
	green spotty cherts	SZT 12/08	62.25	15.93	1.86	4.42	0.57	0.07	0.06	225	21,0	12.7	194,0	2.2	139	106.6	22.2	30,0	68.8	0.04	0.1	117,0	40.1	31	35.4	2.1	0.5	0.79	15	0.19	0.09
	black micaous mudstones	SZT 13/08	63.4	14.73	1.15	3.55	0.58	0.05	0.06	284	19.1	13.2	159.4	3.7	172	103.9	20.1	31.7	71.3	0.54	1.4	190.9	79.7	367	72.5	34	0.5	0.7	18.9	0.39	1.24
	green radiolarite	SZT 13A/08	73.7	11.2	0.55	2.75	0.42	0.03	0.01	176	14.3	10.1	123.6	1.8	128	83.9	14.4	22.2	46.8	1.06	1.3	122.7	49.3	109	66.9	36	2.1	0.65	17.6	0.24	nd
	dark green spotty chert	SZT 8/06	65	12.02	3.61	2.93	0.46	0.058	0.1	246	14.2	11.5	132.8	1.9	100	80	16.6	23.1	49.4	1.18	1	170.8	24.1	84	92.3	111.9	0.6	0.52	20.5	0.25	nd
	green spotty shales with pyrite	SZT 3/06	57.68	16.56	2.59	4.19	0.62	0.069	0.1	225	19.6	15.2	188	2.4	126	102.5	23.4	35.3	84.1	0.39	0.4	74.8	10	62	40.8	1.4	<0.5	0.75	14	0.21	nd
	dark green spotty chert with pyrite concretions	SZT 4/06	61.72	15.45	0.57	4.1	0.62	0.072	0.03	216	19.8	16.4	189.2	2.5	150	105.7	22	33.9	71.8	1.88	5	138.5	56.5	277	79.1	16.9	2.2	0.65	14.4	0.26	nd
	dark green spotty chert	SZT 15/06	58.31	15.41	3.51	3.47	0.58	0.145	0.07	376	18.4	12.5	171.6	2.2	125	104.5	37.8	39.1	94.2	0.05	0.2	215	14	81	77.5	0.5	<0.5	0.62	22.1	0.19	nd
OPALENIEC FM	green marly shales	SZT 6/08	52.57	17.22	3.83	4.04	0.66	0.12	0.16	262	23.2	13.6	172.2	2.8	123	133.6	26.5	32.6	70.1	0.02	0.1	31.5	3.1	100	72.7	0.9	0.5	0.63	17.5	0.24	nd
	grey calcareous mudstone	SZT 8/08	53.09	16.17	4.33	3.53	0.59	0.11	0.14	298	21,0	12.4	147,0	9.2	295	104.6	25.9	31.1	68.6	0.77	0.5	61,0	163.1	85	90.1	43.8	4.7	0.76	18.6	0.83	nd
	green spotty. sideritic shales	SZT 9/08	54.55	16.62	3.65	3.87	0.65	0.09	0.14	271	21.9	13.7	164.6	2.8	135	117.9	24.9	28.2	59.2	0.02	0.2	35.6	7.5	84	71.3	1.3	0.5	0.65	16.9	0.24	nd
	brown marls	SZT 17/08	47.54	14.46	5.94	3.56	0.57	0.11	0.16	261	19.2	12.9	151.9	2.9	126	120.4	24.3	27.5	57.7	0.02	0.2	18.9	11.9	68	63.3	2.9	0.5	0.66	20	0.25	nd
	black shales	SZT 19/08	47.58	15.79	5.62	3.53	0.6	0.1	0.09	315	19.8	12.9	148.8	11.4	298	122.6	23.4	33.5	70.5	0.68	0.6	56.8	104.9	77	89.3	70.1	7.3	0.77	21	0.96	1.73
	grey-green. spotty marly shales	SZT 1/06	48.51	13.84	9.87	2.87	0.57	0.17	0.14	262	17.4	13.2	136.6	2.6	121	92.7	25.2	30.9	52	0.64	0.6	54.6	19.1	79	41	11.2	1.1	0.75	20.15	0.28	nd
	green spotty sideritic shales	SZT 2/06	52.68	15.73	6.37	3.18	0.67	0.105	0.1	222	20.5	14.9	147.4	2.8	125	101.9	18.5	28.5	50.5	0.26	0.6	56.5	19.9	69	30	6.6	0.9	0.8	14.8	0.28	nd
	grey-green. spotty marls	SZT 9/06	41.04	13.42	15.19	2.89	0.5	0.097	0.29	161	16.5	12.4	134.2	2.4	112	97.8	25.6	32	55.8	0.91	1.2	62.5	25.1	60	42.1	16.5	<0.5	0.72	13.4	0.22	nd
	blue-grey marly shales	SZT 10/06	48.61	14.57	8.77	3.02	0.58	0.08	0.13	178	18.3	14.1	134.2	4.6	127	110.6	25.5	31.3	56.6	3.6	7.5	55.3	36.2	95	61	27	1.9	0.67	13.7	0.44	0.17
	grey-green. spotty marls	SZT 11/06	52.88	15.4	6.76	3.32	0.59	0.072	0.19	184	18.3	15.4	153.6	2.5	113	112.6	22.2	33.6	64.1	0.4	0.1	37.5	12.7	66	37.6	3.4	<0.5	0.75	13.1	0.22	nd
SZLACHTOWA FM	black paper shales	SZT 12/06	53.74	16.35	5.06	3.49	0.69	0.104	0.09	273	18.9	15.4	150.9	3.2	141	134.9	22.8	33.2	60.5	0.87	7.5	56.2	34	62	47.5	21.9	1.2	0.75	17	0.29	0.66
	green marly shales	SZT 13/06	47.64	15.94	6.52	3.5	0.65	0.134	0.11	267	20.5	13.8	138.6	2.8	109	126.1	23.4	28.8	57.5	0.05	0.1	25.7	10.3	66	43.7	1.3	<0.5	0.71	19.1	0.26	nd
	green paper shales	SZT 16/06	59.8	17.37	1.41	4.33	0.63	0.104	0.06	253	22.4	13.7	201	2.2	135	107.5	25.9	35.3	81.2	0.03	0.1	105.6	41.8	55	55.1	0.6	<0.5	0.71	15.8	0.19	0.04
	black paper shales	SZT 17/06	52.1	18.24	4.61	3.77	0.74	0.109	0.08	226	22.3	15.9	161.9	2.6	155	114.6	20.4	33.2	62.5	1.08	1.7	61.5	20.5	101	57.5	39.6	0.8	0.73	13.3	0.23	nd
	brownish calcareous siltstone	KR 33	45.91	11.86	14.3	1.99	0.53	0.45	0.14	147	14.1	13.3	96.1	2.7	107	116.9	33.3	33.3	70	0.37	0.3	18.4	15.1	60	23.3	7.8	0.6	0.82	13.3	0.32	nd
	brownish calcareous mudstone with mica	KR 34	55.8	15.65	4.88	3.06	0.66	0.09	0.09	224	19.9	15.1	145.9	2.8	134	108.6	19.3	28.9	51.3	0.54	1	126.7	20.2	83	52.6	6.3	0.6	0.72	14.9	0.28	nd
	black paper shales	SZT WOD-1	55,00	18.79	2.23	4.18	0.76	0.1	0.05	238	23,0	17.5	169.4	3	163	131.6	23.2	38.3	77.2	0.73	0.5	67.3	22.9	88	57.6	30.1	0.6	0.74	14	0.23	0.71
	black paper shales	SZT WOD-2	51.63	16.94	5.6	3.44	0.69	0.19	0.06	211	20.2	16.2	139.8	2.9	137	123.1	27.2	32.9	63.9	1.18	1.1	61.8	23.8	91	75.3	47.7	1.1	0.64	13.2	0.27	nd
	grey marly shales with mica	SZT 2/08	50.7	14.71	6.33	3.21	0.79	0.1	0.07	288	18.8	14.8	137.1	2.8	122	208.9	27.4	31.7	64.1	0.02	0.4	30.5	13.1	69	58.2	1.7	0.5	0.68	19.2	0.25	nd
	black calcareous mudstones with mica	SZT 5/08	49.04	15.7	8.34	3.13	0.65	0.19	0.11	250	20.4	14.8	131.5	2.5	133	102.9	24.1	30.9	59.4	0.61	1.1	65.8	24.1	107	84.9	41.6	1.4	0.61	16.7	0.29	0.87
	black marly shales	SZT 14/08	51.76	14.31	9.19	3.03	0.6	0.12	0.14	189	17.5	13.9	123.5	2.4	115	103.6	19.6	27.9	50	0.73	1.3	55,0	21.7	95	56.9	29.8	1.1	0.67	14.5	0.26	0.66
	grey-green marly shales with mica	SZT 15/08	55.23	14.21	5.99	3.25	0.52	0.04	0.18	169	19.1	13.3	149.4	2	103	96.7	20.3	30.6	68.1	0.06	0.2	61.8	20.3	100	115.1	42.8	0.5	0.47	13	0.2	nd
	black paper shales	SZT 15/16-B	52.28	17.12	4.78	3.86	0.72	0.12	0.12	212	20.2	18.2	155.4	3.4	146	120.2	24.8	34.7	71.1	0.67	0.5	73.5	24.5	201	51.5	25.6	1	0.74	13.2	0.31	nd

indicators of redox condition during deposition. Trace metals could be incorporated into the sediment by reduction with H_2S and sulphides precipitation, or by absorption to organic particles under anoxic conditions, whereas Mn concentration requires the oxic conditions. Therefore, anoxic sediments are characterized by trace metal enrichment and Mn depletion.

The MnO contents vary in the studied sequence in a broad range. The strongest variation is visible between samples of the Hulina Fm. The MnO-poor, green shales co-occur with the manganiferrous shales. Generally, the Hulina Fm. samples are the most enriched of MnO relative to other samples. The Szlachtowa Fm. is the poorest in MnO. If the correlation between MnO and CaO occurs, presence of diagenetic Mn carbonates is supposed. In many samples contents of MnO correlates negatively with V/V+Ni ratio. Most of samples are characterised by values of V/V+Ni ratios above 0.6. The increased V/V+Ni ratio has been applied as an anoxic indicator (Lewan and Maynard 1982).

In the studied section, slight variation is evident in the U/Th profile. Values of the U/Th ratio are below one (mean values are about 0.25) and increase occasionally in the siliceous shales of the CRS and Opaleniec Fm. The U/Th ratio is positively correlated with V/V+Ni ratio and with organic matter accumulation, suggesting development of anoxic conditions during deposition of 3B/08, 13/08, 19/08 and others (Jones and Manning 1994). The samples 3/08-G, 3/08-B show high V/V+Ni ratio and low U/Th. They are also enriched of Zr, Rb, TiO_2 that suggests an increased siliciclastic input. The black shales intercalations within the Opaleniec Fm (10/06) have lower values of V/V+Ni ratio, but high U/Th associated with high S content. It might be explained by precipitation of sulphides under disoxic conditions.

Absolute contents of the redox-sensitive trace elements in the studied material are similar to PAAS. Relative to the recent, organic matter-rich sediments from the upwelling area of the Gulf of California (see Brumsack 1989), the studied samples are enriched in most of trace elements, but poor in Mo, U, Ba. Concentration of trace elements in the Black Sea sediments is very high (see Brumsack 1989). Amounts of Cu, As, Pb in some samples (mainly CRS) are extremely high, even higher than that in the Black Sea sediments.

The Szlachtowa and Opaleniec Fms are characterized by slightly enhanced amounts of S correlating with accumulation of Mo, Se, As, V. Interestingly, distribution of Cu does not depend on S. The highest concentration of Cu is often associated with accumulation of Pb.

The CRS samples are the most enriched in trace elements . Some samples are enriched in S and trace elements (Mo, Cu, Pb, Zn, Ni and Co, As), while others, in spite of a low content of S, contain high amounts of Cu and Ni. Distributions of Ni and As are parallel, partly affected by concentration of S and/or organic matter (OM) (HLN 34B, HLN 35B).

The Malinowa Fm. is depleted in trace elements and S. Only 14/06 sample displays slightly increased amounts of Cu and Pb.

Irregular distribution of the trace metals is difficult to interpret in terms of redox conditions during deposition. The chemical composition of the studied samples might be altered by diagenetic processes, i.e. pyritization .

6. Discussion

The Outer Carpathian and PKB basins were situated in the northern part of the Western (Alpine) Tethys, therefore the studied sections resemble lithologicaly other Cretaceous successions of the western Tethys. In the Outer Carpathians black shales and mudstones of the Věřovice Beds were formed during the Barremian – Early Aptian. They were followed by the turbiditic sedimentation that directly preceded the Cenomanian radiolarian shales (Barnasiówka Radiolarian Shale Formation), overlain by the Turonian Variegated Shales (CORB). In the Grajcarek Succession, the CRS belonging to the Hulina Fm. are followed by red shales of the Malinowa Fm. (CORB), while black shales of the Opaleniec and Szlachtowa Fms might be correlated with the Early Createaceous black shale facies.

The chemical character of the Szlachtowa and Opaleniec Fms is similar Relative to the CRS, they are enriched in CaO associated with P_2O_5 and MnO. The Szlachtowa and Opaleniec Fms contain also high amounts of such elements as Ga, Nb, Zr, Rb and TiO_2 indicating a rise of the terrigenous supply.In terms of content of major oxides, they are similar to the Black Sea sediments. However, the contents of TOC and trace elements are not high enough. The Black Sea exemplifies the type locality for a stagnant, anoxic basin. Geochemical indicators do not allow interpreting the environment of the Szlachtowa and Opaleniec Fms by a direct interpolation to the model of anoxic basins. The Szlachtowa and Opaleniec Fms can be related to the Early Cretaceous OAE 1. Taking into account the mineral composition and geochemical indices, they can be compared to the upper part of the Kapuśnica Fm of the Niedzica Succession of the PKB (see Wójcik-Tabol, 2006).

The clay minerals assemblage within the Szlachtowa and Opaleniec Fms resemble those of the Albian Lhoty Fm. of the Silesian Nappe of the Outer Carpathian (Wójcik-Tabol and Ślączka, 2009).

The records of the Cenomanian/ Turonian Boundary (CTB) in the Polish Outer Carpathians have been recently investigated by Bąk (2007) and Wójcik-Tabol and Ślączka (2009). This CTB interval including OAE-2 is recognized as the Barnasiówka Radiolarian Shale Formation. In the Pieniny Succession of the PKB, the Cenomanian-Turonian OAE 2 is recorded as the Magierowa Member of the Jaworki Fm (Wójcik-Tabol, 2006). The studied CRS are comparable to the Barnasiówka Fm. and Magierowa Mb. The contents of major elements in the CRS are similar to those in the Gulf of California sediments. Extraordinary enrichment of sulphide forming metals may be explained by diagenetic pyritization.

The mid-Cretaceous black shales facies are replaced by the Upper Cretaceous oceanic red beds (CORB). They are distributed in a broad belt extending from the Caribbean across the Central Atlantic, Europe to eastern Asia and record changing deposition conditions from anoxic/disoxic to oxic. The studied Malinowa Fm. samples are lithologically, geochemically and mineralogically similar to other CORBs (see Hu et al., 2005 and references therein).

7. Conclusions

Considering the lithological, mineralogical and geochemical characteristics, the Szlachtowa and Opaleniec Fms resemble the Věřovice Beds/Lhoty Fm. of the Outer Carpathians and upper part of the Kapuśnica Fm. of the PKB. Thus, they can be related to the Early Cretaceous OAE 1. It is supposed that studied sediments were formed under disoxic/anoxic environment of the stagnant basin. Trace metals were trapped into reactive organic matter and sulphides during sedimentation, and/or later due to diagenetic pyritization.

The studied Cenomanian radiolarian shales (CRS), like Barnasiówka Fm. and Magierowa Mb., record the OAE-2. The studied CRS resample recent sediments of the upwelling area (Gulf of California). The CRS are interpreted as settled through the mid-water oxygen minimum zone. The periods of anoxia were interrupted by intervals of disoxic conditions at the sea bottom, related to changes in surface productivity and fluctuations in bottom water circulation. The enrichment of trace elements may be explained by diagenetic pyritization.

Analysis of the detrital flux revealed that the material supply to hemipelagic sediments was mainly derived from a continental crust. Upward the section, detrital input decreases, reaching its minimum in the CRS and then it increases in the Malinowa Fm.

Deposition of the Malinowa Fm. might have been influenced by several processes: excess of organic carbon burial, global cooling, and/or intensification of bottom circulation. It is possible, that the Malinowa Fm. was developed under analogous conditions.

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