

Trace element geochemistry of the Early to Late Cretaceous deposits of the Grajcarek thrust-sheets – a palaeoenvironmental approach (Małe Pieniny Mts., Pieniny Klippen Belt, Poland)

Patrycja WÓJCIK-TABOL and Nestor OSZCZYPKO



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The chemical composition of the Cretaceous deposits of the Grajcarek thrust-sheets (Pieniny Klippen Belt, Poland) has been investigated to provide information on palaeoenvironment and provenance of pelagic and turbiditic particles. The material studied shows large variations in terrigenous and biogenic content. Phyllosilicates (mirrored in amounts of Al_2O_3 , average 15 wt.%) and carbonates (6 wt.% of CaO) are common mineral components of the deposits excluding the Cenomanian radiolarian shales (CRS) that are enriched in silica (mean content of SiO_2 is 64 wt.%). “Immobile” elements may be accommodated by phyllosilicates and accessory minerals (i.e. zircon, xenotime, apatite and Ti-oxides). Heavy minerals are significant within the Szlachtowa Fm. High field strength elements (HFSE) in the Malinowa Fm. are housed in secondary apatite and Fe-oxides. Lithophile trace elements (LILE) concentrations in the material studied are lower/comparable to Post-Archean Australian Shale (PAAS). Ba concentration in the CRS probably reflects enhanced bioproductivity. Interaction between major oxides, distributions of “immobile” and lithophile elements suggest that variation in trace elements through the succession was mainly controlled by the terrigenous input. The material studied was sourced from intermediate to felsic rocks of the Czorsztyn (Oravic) Ridge. The Szlachtowa Fm. and CRS are more mature than others due to low contents of clay minerals. The Szlachtowa Fm. also contains recycled material. The CRS correspond to the oceanic anoxic event 2 (OAE 2) whereas the “Black Flysch” of the Szlachtowa and Opaleniec formations may be related to the Early Cretaceous OAE 1.

Patrycja Wójcik-Tabol and Nestor Oszczytko, Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, 30-063, Kraków, Poland, e-mails: p.wojcik-tabol@uj.edu.pl, nestor.oszczytko@uj.edu.pl (received: March 24, 2011; accepted: December 22, 2011).

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INTRODUCTION

The Upper Jurassic-Lower Cretaceous black shales are world-wide sedimentary phenomena (Bernoulli, 1972; Schlanger and Cita, 1982; Bralower *et al.*, 1993; Wang *et al.*, 2011). Deposition of organic carbon-rich facies during the Cretaceous was on a scale that has not since been repeated. Formation of black shales associated with oceanic anoxic events (Schlanger and Jenkyns, 1976) was commonly succeeded by deposition of a hemipelagic, iron-rich succession, known as the Cretaceous Oceanic Red Beds (CORBs; Hu *et al.*, 2005). In the northern periphery of the Tethys, black shales were well-developed in the Outer (Flysch) Carpathians (e.g., Ksi kiewicz, 1962; 1 czka and Kami ski, 1998; Golonka *et al.*, 2009). They occur in the Skole Nappe (Spas Shales of the Barremian-Albian age) and Sub-Silesian/Silesian nappes (Ve ovice Shales dated on Barremian to early Aptian). In the Silesian Nappe, black

shales are followed by the turbiditic Lhota Fm. The Spas Shales and Lhota Fm. directly precede the Barnasiówka Radiolarian Shale Formation, which contains siliceous, green and black shales with manganiferous horizons. These black shales correspond to the Bonarelli Level that is equivalent to the Cenomanian-Turonian event of oceanic anoxia (OAE 2). The Barnasiówka Fm. is overlain by the Upper Cretaceous Variegated Shales. In the Fore-Magura and the Magura Nappe the Cretaceous black shales in general are unknown, because these nappes are tectonically detached at the base of the Late Cretaceous red shales (Oszczytko, 2004, 2006).

The chemical composition of sedimentary rocks is an important record of the geological evolution of the sedimentary basin and adjacent area through time (Taylor and McLennan, 1985).

The domain of the Outer Carpathian basins evolved during the Jurassic and Cretaceous into a rifted passive margin of the European plates. Development of the basin was controlled

during Late Jurassic-Aptian times by normal faulting and syn-rift subsidence that was accompanied in the Western Carpathians by the extrusion of alkali basalts ranging in age from Barremian to Aptian (*cf.* Oszczytko, 2006). Different magmatic, metamorphic and sedimentary rocks, derived mainly from continental crust, have been shown to be the chief or only source of turbiditic deposits of the Outer Carpathians basins. Ultrabasic rocks indicative of oceanic crust played a role in supplying material to the rocks of the southern part of the Magura Nappe only (Winkler and Iczka, 1992, 1994). “Black Flysch” of the Grajcarek Succession was supplied with detrital material derived from erosion of the Czorsztyn ridge (Krawczyk and Słomka, 1986, 1987; Golonka *et al.*, 2000), uplifted since the Valanginian to Albian/Cenomanian (Birkenmajer, 1977). The “Black Flysch” sandstones (see Łozinski, 1956, 1959, 1966) contain heavy mineral assemblages typical of continental crust.

In the latest Albian-Cenomanian, siliciclastic source areas were cut off (*cf.* Oszczytko, 2006). Concentrations of certain trace elements (e.g., REE, Sc, Th) provide information of source rocks, because they are not affected by secondary processes (McLennan *et al.*, 1993; Cullers, 2000). By contrast, mobile elements (such as Na and Ca) can be used to evaluate the degree of chemical weathering, that reflects palaeoclimate in the source area at the time of deposition (Nesbitt and Young, 1982).

The present paper concerns provenance of the detrital components of the Cretaceous deposits from the Grajcarek thrust-sheet. We pay special attention to weathering of the source area, sorting and recycling as processes that change the chemistry of deposited material. The succession studied consists of various lithotypes representing changing depositional environments in the southern part of the Magura Basin.

The Jurassic or Early Cretaceous age of the Szlachtowa and Opaleniec formations (known also as “Black Flysch”) is a subject of long-term controversy. Oszczytko *et al.* (2004) presented new arguments to suggest the Albian-Cenomanian age of these sediments, whereas Birkenmajer *et al.* (2008) proposed a Jurassic age.

In recent years we have documented (see Oszczytko *et al.*, 2004; Wójcik-Tabol and Oszczytko, 2010) that the transition between the Lower Cretaceous black shales and the Upper Cretaceous red sediments in the Grajcarek Succession is similar to that described from more northern nappes of the Outer Carpathians. In this paper we support this concept by provenance studies.

The geochemical indices of the deposits of the Grajcarek Succession are compared with published data concerning the Cretaceous sections from the Pieniny Klippen Belt (PKB), Outer Carpathians and other geological settings (Brumsack, 1980; Bellanca *et al.*, 1997; Hofmann *et al.*, 2001; Neuhuber and Wagreich, 2011).

GEOLOGICAL SETTING

The Male Pieniny Mts. are located in the southern part of the Polish Western Carpathians, between the Dunajec River

Valley in the west and the Polish/Slovak state boundary to the east and south (Fig. 1). The area studied occupies the contact zone 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 Paleogene flysch deposits belonging to the Krynica Slice (see Fig. 1B; Birkenmajer and Oszczytko, 1989; Oszczytko and Oszczytko-Clowes, 2010). These deposits are composed mainly of thick- to medium-bedded turbidites of the channel-lobe facies. Along the Grajcarek Valley the Magura Nappe contact with narrow, strongly deformed the peri-Pieniny Klippen Belt Zone, known as the Grajcarek Unit (Birkenmajer, 1979).

The Grajcarek Succession comprises Jurassic, Cretaceous and Paleocene, pelagic and flysch deposits of the Magura Succession, incorporated in the structure of the PKB. The Szlachtowa and Opaleniec formations termed “Black Flysch” are up to 220 m thick. These “Black Flysch” facies are followed by 2–10 m of Cenomanian radiolarian shales (Hulina Fm. *sensu* Birkenmajer, 1977), variegated shales of the Turonian-Campanian Malinowa Fm. (20–100 m) and coarse clastic deposits of the Jarmuta Fm. (Maastrichtian–Paleocene) reaching 100–400 m (Birkenmajer, 1977).

STUDIED SECTIONS

The exposures studied are located in the upper course of the Sztolnia Stream along a 250 m section (Oszczytko *et al.*, 2004; Birkenmajer *et al.*, 2008), which comprises three sections (A, B and C; see Fig. 2). In the Sztolnia Stream A section the Szlachtowa Formation is represented mainly by dark grey and black, marly shales, claystones and siltstones, and fine-grained, calcareous sandstones containing abundant mica flakes. This formation is overlain by the Opaleniec Fm. composed of the light grey, marly claystones with intercalations of spotty limestones and sideritic dolomites. In the Sztolnia Stream B section this formation is developed as a sequence of dark grey, greenish sometimes bioturbated shales with pyrite concretions. Lenses and beds of grey, spotty limestones and sideritic dolomites have thicknesses not exceeding a few dozen centimetres. The Opaleniec Formation is overlain by the CRS composed of manganese shales, radiolarian shales with pyrite framboids and radiolarites. These strata have been described by Birkenmajer (1977) as the Hulina Formation (Albian–Cenomanian). The green and black non-calcareous shales and radiolarites of the CRS (Hulina Fm.) have been collected from exposures on the S slope of Hulina Mt. (Fig. 2).

In the Sztolnia Stream (sections A–C; see Fig. 2) the siliceous shales of the CRS are followed by cherry-red and green, argillaceous shales of the Malinowa Formation (Birkenmajer, 1977; Birkenmajer and Oszczytko, 1989). The lowermost part of the Malinowa Fm. (section A) on the north limb of the small anticline contains a 1 m-thick bed of light, fine-grained sandstone overlain by 10 cm of green radiolarite, whereas on the S limb of the anticline, the green radiolarite (5 cm) occurs at the base of a cherty limestone (see Oszczytko *et al.*, 2004).

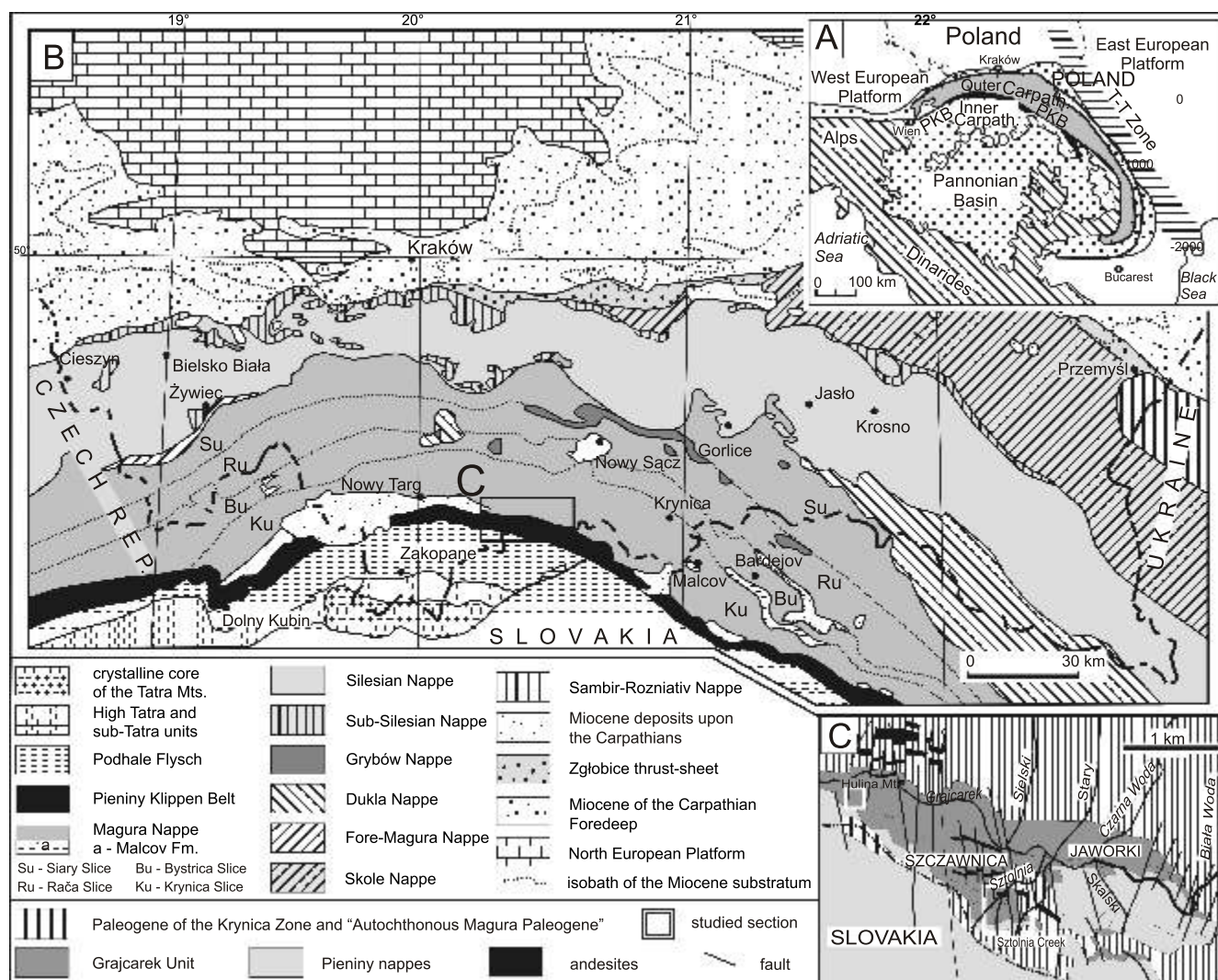


Fig. 1. Location of the area studied within the content of main geological units

A – simplified tectonic scheme of the Alpine orogens; PKB – Pieniny Klippen Belt (after Kova *et al.*, 1998, modified); B – central part of Polish Carpathians (after Oszczytko and Oszczytko-Clowes, 2009); C – detailed division of the Małe Pieniny Mts. (after Birkenmajer, 1979, simplified)

ANALYTICAL METHODS

In this study, 48 samples representing various lithotypes (e.g., fine-grained rocks, radiolarite shales, marly shales) were analysed geochemically using a *Perkin Elmer Elan 6000 ICP* at the ACME Analytical Laboratories, Ltd. in Vancouver, Canada. Total abundances of the major oxides and several minor elements (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , MnO , TiO_2 and P_2O_5) are reported on a 0.2 g sample analysed by *ICP*-emission spectrometry following Lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) is by weight difference after ignition at 1000°C . Rare earth and refractory elements (Ba, Co, Cs, Ni, Rb, Sc, Sr, Th, V, Y, Zr) are determined by *ICP* mass spectrometry following the Lithium metaborate/tetraborate fusion and nitric acid digestion of a 0.2 g sample. In addition a separate 0.5 g split is digested in Aqua Regia and analysed by *ICP mass spectrometry* to report the precious and base metals.

Concentrations of major and minor elements were compared to the Post-Archean Australian Shale (PAAS; Taylor and McLennan, 1985). For selected elements comparison to the Upper Continental Crust (UCC; Taylor and McLennan, 1985) was applied. The values of Eu anomaly were calculated using Eu/Eu^* ratio, where $\text{Eu} = \text{Eu}$ normalized to PAAS (Eu_{PAAS}) and $\text{Eu}^* = (\text{Sm}_{\text{PAAS}} \times \text{Gd}_{\text{PAAS}})^{0.5}$.

GEOCHEMISTRY

Statistics of major and trace element composition are shown in the [Tables 1–4](#). The inter-elemental relationships have been evaluated using the Pearson's correlation factor ([Tables 5 and 6](#)) and shown in bivariate and triangular diagrams ([Figs. 3–9](#)).

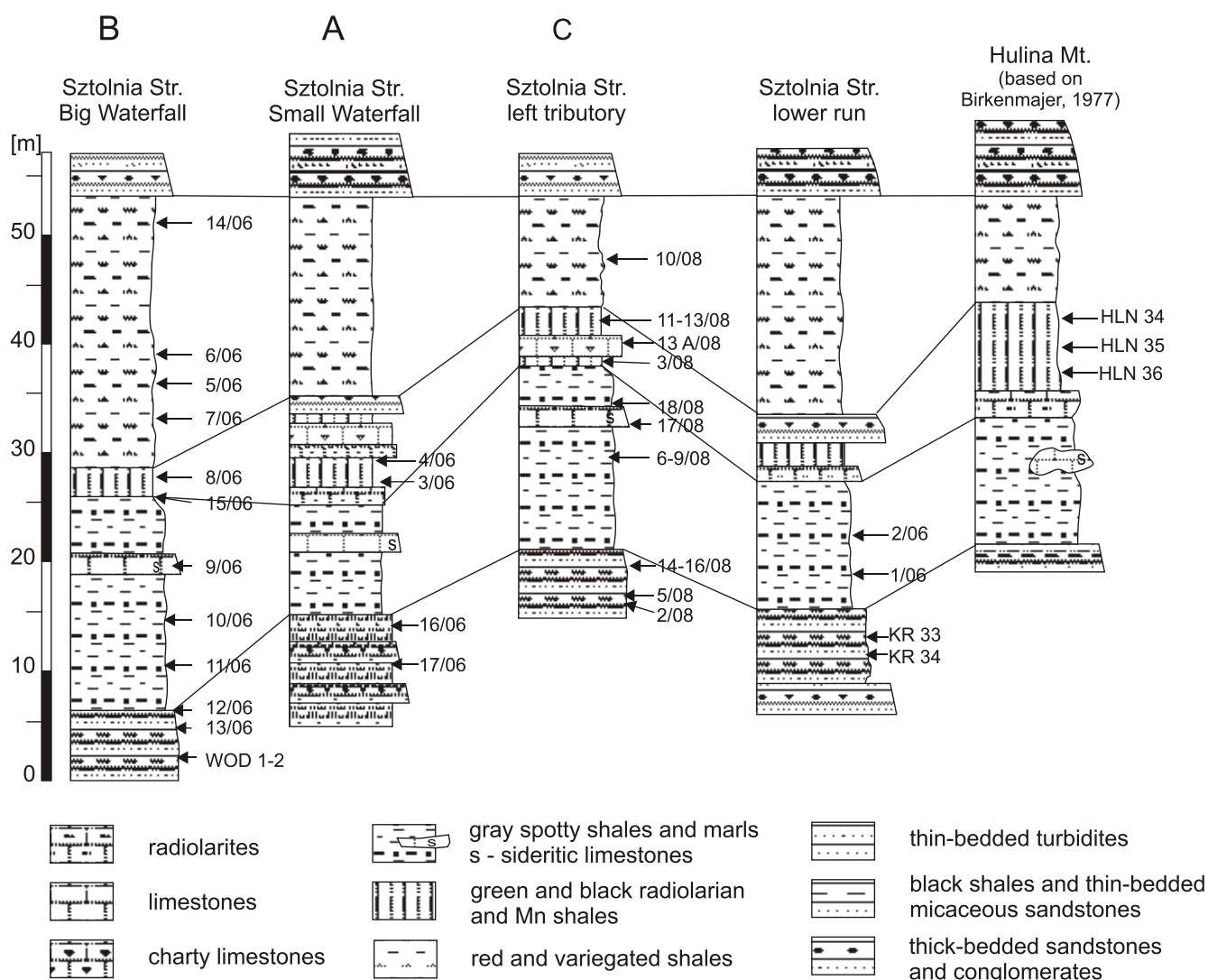


Fig. 2. Lithological log of the Sztolnia sections (based on Oszczypko *et al.*, 2012); A, B – main Sztolnia Stream (Big and Small waterfalls); section C – left tributary of the Sztolnia Stream; lower run of the Sztolnia Stream (Hulina Mt. section after Birkenmajer, 1977)

MAJOR ELEMENTS

Compared to the PAAS, most samples are enriched in CaO at the expense in SiO₂. Only siliceous samples of the Cenomanian radiolarian shales (CRS) are relatively enriched of SiO₂, especially shales from the Hulina section. They also contain the lowest amounts of Al₂O₃ relative to other samples (Table 1). A triangular diagram SiO₂ – Al₂O₃ × 5 – CaO × 2 (Fig. 3) plots the majority of the samples near the PAAS with admixture of various CaO amounts. Only CRS are shifted towards the SiO₂ corner. SiO₂ primarily represents biogenic silica in radiolarian shales and quartz within siliciclastic samples. Concentration of Al₂O₃ reflects phyllosilicate content. The bivariate diagram SiO₂ vs. Al₂O₃ (Fig. 4) shows negative correlation between concentrations of SiO₂ and increasing amounts of phyllosilicate within the CRS. Positive correlation between SiO₂ and Al₂O₃ for the rest of the formations is explained by the presence of detrital components – quartz admixed with aluminosilicates. Ratios of SiO₂/Al₂O₃ suggest the commonly occurrence of clay minerals in the material studied. The sam-

ples of CRS show a SiO₂/Al₂O₃ ratio typical of feldspars, but it could be affected by abundant biogenic silica.

The presence of feldspar is not confirmed on the Al₂O₃ vs. K₂O diagram (Fig. 4). With the exception of the Hulina samples, the material studied contains K₂O in amounts quite similar to that in PAAS (Table 1). In the diagram the samples fall parallel to an ideal muscovite line, but shifted to higher Al₂O₃ contents because of accompanying minerals (e.g., kaolinite). The correlation factors of Al₂O₃ to K₂O exceed 0.86 (Table 5).

Taking to account the Na₂O contents, only the Opaleniec Fm. is close to PAAS, whereas the rest of the formations are depleted (Table 1). The Na₂O vs. Al₂O₃ diagram (Fig. 4) shows two trends: 1) a positive correlation for the Opaleniec Fm. and CRS (mainly mudstones of the Sztolnia sections); 2) a progressive decline in Na₂O contents relative to increasing Al₂O₃ concentrations in the Szlachtowa and Malinowa formations that can be explained by an admixture of kaolinite in the Szlachtowa Fm. and other minerals in the Malinowa Fm., where kaolinite was not found.

Table 1

Major element statistical data for the samples from the Grajcarek Succession

Samples		SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		MgO		CaO		Na ₂ O		K ₂ O		TiO ₂		P ₂ O ₅		MnO		ICV		CIA		PIA	
		m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.
Malinowa Fm. (n = 5)		49.28	3.83	15.59	1.35	6.4	1.1	4.97	1.47	6.12	2.71	0.95	0.26	3.72	0.36	0.63	0.06	0.12	0.013	0.132	0.036	1.49	0.277991	76.9	0.83	93.5	1.9
CRS	Hulina Section (n = 7)	68.99	5.75	10.74	3.35	4.22	1.52	1.5	0.49	2.47	2.04	0.34	0.05	2.39	0.81	0.41	0.13	0.08	0.023	0.371	0.36	1.17	0.299041	79.7	0.35	96.8	0.75
	Sztołnia sections (n = 13)	61.02	4.46	16.19	2.44	5.2	1.24	2.35	0.49	1.33	1.15	0.83	0.58	4.00	0.64	0.61	0.09	0.09	0.034	0.047	0.028	0.9	0.134113	77.2	1.40	95	3.19
Opaleniec Fm. (n = 10)		49.9	3.85	15.32	1.16	5.59	1.09	4.02	1.28	7.03	3.32	1.04	0.33	3.38	0.38	0.6	0.05	0.1	0.025	0.154	0.053	1.44	0.275106	77.7	1.79	92.9	2.27
Szlachto-wa Fm. (n = 13)		52.36	3.54	15.94	1.79	5.39	0.54	3.06	1.16	6.09	3.11	0.61	0.41	3.40	0.57	0.66	0.08	0.14	0.096	0.1	0.036	1.24	0.32654	80	2.27	96.3	3
PAAS		62.8		18.9		6.5		2.2		1.3		1.2		3.7		1		0.16		0.11		0.85		88.23		0.92	

St.dev – standard deviation, m – mean, n – number of samples, ICV – Index of Compositional Variability, CIA – Chemical Index of Alteration, PIA – Plagioclase Index of Alteration

Table 2

High field strength trace elements (HFSE) statistical data [ppm] for the samples studied

Samples		Zr		Hf		Nb		Th		U		Th/U		Y		La		Ce		TREE		Eu/Eu*		La/Yb _(PAAS)	
		m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.	m	st.dev.
Malinowa Fm. (n = 5)		120	12.42	3.7	0.28	13.36	1.07	12.12	1.09	2.82	0.51	4.49	1.1	27.54	3.42	31.9	3.10	63.74	7.35	158	16.58	1.06	0.042	0.94	0.024
CRS	Hulina Section (n = 7)	76	22.41	2.24	0.62	11.41	3.48	7.23	1.98	1.78	0.63	4.17	0.55	20.44	4.17	25.44	5.12	61.97	12.13	133	24.22	1.025	0.04	1.04	0.055
	Sztołnia sections (n = 13)	107	13.67	3.24	0.49	13.61	1.77	10.98	1.94	3.2	1.36	3.84	1.1	24.28	5.88	32.11	5.72	72.37	16.08	162	35.77	1.03	0.082	1.02	0.11
Opaleniec Fm. (n = 10)		111	11.89	3.34	0.36	13.55	0.96	10.94	0.79	4.4	3.05	3.29	1.24	24.2	2.25	30.92	2.07	60.51	7	147	12.01	1.005	0.06	1.007	0.12
Szlachto-wa Fm. (n = 13)		122	27.23	3.64	0.80	15.07	1.49	10.45	1.18	2.71	0.37	3.90	0.6	23.97	3.75	32.28	2.80	64.37	8.8	155	18.68	1.04	0.05	1.06	0.08
PAAS		210				19		14.6		3.1		4.71		27		38		80		184.72		0.66			

For explanations see [Table 1](#)

Table 3

Large ion lithophile trace elements (LILE) and transition elements statistical data [ppm] for the samples studied

Samples	Rb		Sr		Cs		Ba		Sc		Co		Nb		V		Ni		Cr	
	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.
Malinowa Fm. (n = 5)	166	21.24	137	19.53	11.38	2.04	286	18.49	13.6	1.49	17.52	2.77	13.36	1.07	123	16.8	62.62	16.65	100.56	14.5
CRS	112	38.17	104	20.4	7.97	3.23	298	53.63	11.28	3.61	23.58	8.77	11.41	3.48	105	32.63	84.33	46.85	55.28	17.8
	180	26.85	120	32.82	12.79	2.15	277	55.26	15.77	2.69	33.56	18.18	13.6	1.77	164	44.44	77.65	24.71	99.97	28.8
Opaleniec Fm. (n = 10)	149	11.87	163	52.7	10.47	0.75	241	49.88	14.1	1.44	34.85	37.16	13.55	0.96	157	69.79	59.84	20.36	93.18	27.24
Szlachtowa Fm. (n = 13)	146	23.74	170	47.66	10.51	1.95	226	39.67	15.46	1.33	22.38	18.77	15.07	1.49	130	17.91	59.94	21.18	84.8	13.7
PAAS	160		200		15		650		16		23		19		150		55		110	

For explanations see Table 1

The diagram of Fe_2O_3 to Al_2O_3 (Fig. 4) shows positive correlation between oxides in the Szlachtowa Fm. ($r = 0.57$), and CRS from the Hulina section ($r = 0.74$) and Malinowa Fm. ($r = 0.59$) (Table 5). A $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio yields 1:4 that is typical for detrital siliciclastic sediments. Glauconite was not found, but chlorite is a common clay constituent in every formation. High concentrations of Fe_2O_3 and no linkage to Al_2O_3 in the CRS and Opaleniec Fm. can be explained by occurrence of pyrite, confirmed during thin-section examination.

Relative to PAAS, the samples are depleted in TiO_2 (mean values vary from 0.4 ± 0.13 for the Hulina samples to 0.7 ± 0.1 for the Szlachtowa Fm.). The TiO_2 – Al_2O_3 diagram (Fig. 4) shows constantly positive correlations between oxides for every formation ($r > 0.68$; Table 5). The correlation between TiO_2 and phyllosilicates (probably the clay fraction) are consistent due to weathering.

HIGH FIELD STRENGTH TRACE ELEMENTS (HFSE):
Zr, Th, U, Y, Hf, Nb, REE

The material studied contains lower amounts of Zr, Th, Nb and earth trace elements (REE) than PAAS, whereas concentrations of U and Y are comparable to those of PAAS. In general, the Malinowa and Szlachtowa formations contain the highest amounts of HFSE, while the CRS of the Hulina section show the strongest depletion in them (Table 2).

Accumulation of HFSE shows positive linkage to Al_2O_3 and K_2O (Table 5). However, in the Szlachtowa Fm., the distribution of Zr, Hf and Y is independent of or negatively related to Al_2O_3 and K_2O . In the Opaleniec Fm. concentrations of Nb have no correlation to K_2O . The Malinowa Fm. reveals negative correlation of U with K_2O and Al_2O_3 .

In the material studied HFSE are preferentially linked to minerals of the mica type having a tight association with Al_2O_3 and K_2O . Irregular accumulation of Zr, Y, Nb and U suggests that elements have affinity to accessory minerals (i.e. zircon, xenotime and Ti-oxides).

Zr and Hf are the most affected by density-related fractionation. Their amounts in sedimentary rocks are controlled by zircon and due to a combination of resistance to weathering and high density: this mineral undergoes sorting-related fractionation (Taylor and McLennan, 1985).

In the contrast, Th and Nb in clastic rocks are commonly hosted by resistate minerals such as Ti-oxides and apatite, which follow the fate of the clay-sized component. They are not seriously involved by sorting-related fractionation.

Interaction between Nb, Th, TiO_2 , P_2O_5 and Zr (Table 6) show that Th and Nb have common affinity with Ti phases and the clay fraction. Th could be also related with zircon. In the Malinowa Fm. and CRS Th and Nb are possibly also hosted by phosphates. Nb and Th reveal different behaviour in the “Black Flysch”. Amounts of Nb do not depend on Zr concentration. In the Opaleniec Fm. Th barely correlates to Ti. Thus, only Nb is related with Ti phases, whereas Th is hosted by zircon.

Distributions of U and Y are partly controlled by Al_2O_3 , K_2O and TiO_2 concentrations (Table 6). U can be hosted by zircon, as is suggested by positive correlation with Zr ($r = 0.17$ – 0.69).

Table 4

Selected average elemental ratios for the samples studied

Samples		La/Sc		La/Co		Th/Co		Th/Sc		Cr/Th	
		mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.	mean	st.dev.
Malinowa Fm. (n = 5)		2.3	0.25	1.84	0.15	0.706	0.08	0.898	0.073	8.28	0.79
CRS	Hulina Section (n = 7)	2.3	0.47	1.26	0.62	0.36	0.20	0.65	0.05	7.58	0.52
	Sztołnia sections (n = 13)	2.07	0.40	1.21	0.56	0.42	0.22	0.70	0.08	8.96	1.52
Opaleniec Fm. (n = 10)		2.2	0.25	1.61	0.75	0.567	0.25	0.783	0.08	8.45	2.12
Szlachtowa Fm. (n = 13)		2.09	0.15	1.92	0.84	0.61	0.22	0.67	0.067	8.12	0.98
PAAS		2.37		1.65		0.64		0.91		7.53	
UCC		2.21		1.76		0.63		0.79		7.76	

For explanations see Table 1

The average Th/U ratios vary from 3.29 ± 1.2 in the Opaleniec Fm. to 4.5 ± 1.1 in the Malinowa Fm. With the exception of the Opaleniec Fm., the samples have Th/U ratios higher than UCC – 3.8. Some samples of the Malinowa Fm. reveal Th/U ratios that reach that of the PAAS – 4.7 (Table 2). All this suggests that the material studied was affected by weathering. The lowest degree of weathering probably characterizes the Opaleniec Fm. Elevated U concentration within the Opaleniec Fm. is linked with the accumulation of Co, V, Ni and Cr (Table 3).

Yttrium is the major constituent of phosphate xenotime minerals, which is in agreement with positive correlation of Y with P_2O_5 concerning almost the entire succession (excluding the Malinowa Fm.; Table 6).

The total contents of rare earth elements (TREE) correlate positively with Al_2O_3 and K_2O (Table 6), thus REE have affinity to phyllosilicates. Adsorption of REE by Fe-oxides coating the mineral particles is possible due to positive correlation of TREE to Fe_2O_3 (Table 6). An involvement of REE with heavy minerals (zircon and xenotime) is considered as well. The role of Ti-oxides in concentrations of REE is limited to the Malinowa Fm. and CRS. Lack of correlation between REE and TiO_2 for the “Black Flysch” negates the importance of Ti-oxides (Table 6).

Average values of the $(La/Yb)_{PAAS}$ ratio ranging between 0.94 in the Malinowa Fm. and 1.06 in the Szlachtowa Fm. (Table 2) are comparable with those proposed by Condie (1991) for terrigenous materials. Mean values of Eu/Eu^* ratio vary in a narrow range: 1.005–1.06 (Table 2). Hence Eu anomalies are higher than those of PAAS and UCC – 0.6 (Taylor and McLennan, 1985). Eu concentrates within plagioclase (Nath *et al.*, 1992). Most of the Eu released during plagioclase dissolution could have been trapped by clay minerals by adsorption producing a positive Eu anomaly.

HFSE have the ability to be incorporated into crystalline structures and/or adsorb onto surfaces of phyllosilicates (Tay-

lor and McLennan, 1985). Certain accessory minerals accommodate the HFSE as well. The most possible is the occurrence of zircon and phosphate minerals (mainly apatite and xenotime) and Ti-oxides.

The Szlachtowa Fm. contains heavy minerals (zircon, xenotime and Ti-oxides) in amounts higher than in other formations. The Malinowa Fm. exhibits high accumulation of HFSE correlative with the clay fraction and TiO_2 as well as with apatite and Fe-oxides that probably are secondary phases.

LARGE ION LITHOPHILE TRACE ELEMENTS (LILE): Rb, Cs, Ba, Sr

Relative to the PAAS, the samples are significantly depleted in Ba, but concentrations of Cs in CRS, Sr in the “Black Flysch” and Rb in the Malinowa Fm. and CRS of the Sztołnia sections are occasionally similar to that in PAAS (Table 3). Cs and Rb contents show tight linkage to K_2O and Al_2O_3 , suggesting their affinity to phyllosilicates. Amounts of Sr correlate negatively with Al_2O_3 and K_2O . An explanation could be an association of Sr with Ca within calcareous samples (Table 5). K_2O , Cs and Rb co-occur in feldspars and are incorporated into clays during chemical weathering. In contrast, Sr and Na_2O tend to be leached (Nesbitt *et al.*, 1980). Sr behaves like Ca, which is lost significantly in initially weathered rocks and continues to be lost during later stages of weathering. Sr is trapped from sea water by settled calcite.

The barium distribution is similar that of K_2O and Al_2O_3 , though the CRS contain extraordinary high amounts of Ba concomitant with low contents of Al_2O_3 and K_2O (Table 5). The Ba concentration probably results from the organic productivity rise. This idea is supported by negative correlation of SiO_2 with Al_2O_3 (Table 5), indicating a supply of biogenic silica (Arthur and Premoli Silva, 1982) and accumulation of organic matter. Abundant radiolarian tests recognized in thin-section also suggests enhanced bioproductivity.

Table 5

Pearson correlation coefficients (r) between selected major and minor elements for the samples from the Grajcarek Succession

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Rb	Sr	Cs
Malinowa Formation	SiO ₂	1											
	Al ₂ O ₃	0.96	1										
	Fe ₂ O ₃	0.8	0.59	1									
	MgO	-0.71	-0.03	-0.8	1								
	CaO	-0.92	-0.94	-0.64	0.39	1							
	Na ₂ O	-0.17	-0.03	-0.52	0.37	0.1	1						
	K ₂ O	0.97	0.99	0.68	-0.58	-0.96	-0.16	1					
	TiO ₂	0.65	0.84	0.12	-0.08	-0.8	0.1	0.8	1				
	P ₂ O ₅	0.23	0.45	-0.32	0.43	-0.48	0.66	0.36	0.74	1			
	MnO	-0.05	-0.34	0.53	-0.44	0.28	-0.45	-0.24	-0.77	-0.85	1		
	Rb	0.96	0.95	0.75	-0.64	-0.93	-0.33	0.98	0.74	0.21	-0.14	1	
	Sr	0.28	0.01	0.74	-0.77	0.02	-0.46	0.08	-0.52	-0.79	0.91	0.18	1
	Cs	0.9	0.87	0.75	-0.72	-0.81	-0.51	0.92	0.65	0.02	-0.06	0.97	0.27
Ba	0.35	0.53	-0.07	0.39	-0.67	0.16	0.52	0.83	0.84	-0.75	0.44	-0.72	0.31
CRS (Hulina Section)	SiO ₂	1											
	Al ₂ O ₃	-0.93	1										
	Fe ₂ O ₃	-0.66	0.74	1									
	MgO	-0.94	0.82	0.76	1								
	CaO	0.27	-0.58	-0.72	-0.54	1							
	Na ₂ O	-0.63	0.82	0.73	0.79	-0.81	1						
	K ₂ O	-0.92	1.0	0.73	0.97	-0.59	0.83	1					
	TiO ₂	-0.93	0.99	0.72	0.98	-0.55	0.77	0.99	1				
	P ₂ O ₅	0.07	0.18	0.09	0.14	-0.55	0.66	0.2	0.12	1			
	MnO	0.7	-0.58	-0.35	-0.63	-0.04	-0.22	-0.58	-0.61	0.27	1		
	Rb	-0.91	0.1	0.74	0.97	-0.61	0.84	0.1	0.1	0.22	-0.57	1	
	Sr	0.33	-0.56	-0.79	-0.55	0.91	-0.82	-0.55	-0.51	-0.54	-0.16	-0.57	1
	Cs	-0.89	0.99	0.68	0.94	-0.59	0.83	0.99	0.98	0.24	-0.54	0.99	-0.54
Ba	0.48	-0.2	-0.15	-0.21	-0.39	-0.09	-0.2	-0.19	0.18	0.16	-0.18	-0.11	-0.17
CRS (Sztolnia Sections)	SiO ₂	1											
	Al ₂ O ₃	-0.75	1										
	Fe ₂ O ₃	-0.57	0.09	1									
	MgO	-0.67	0.69	0.11	1								
	CaO	0.03	-0.39	-0.09	0.11	1							
	Na ₂ O	-0.53	0.69	0.19	0.64	-0.44	1						
	K ₂ O	-0.61	0.91	-0.05	0.49	-0.38	0.42	1					
	TiO ₂	-0.72	0.97	0.09	0.66	-0.42	0.62	0.89	1				
	P ₂ O ₅	-0.71	0.73	0.33	0.63	-0.03	0.67	0.48	0.71	1			
	MnO	-0.11	-0.26	-0.13	0.28	0.89	-0.37	-0.22	-0.26	-0.14	1		
	Rb	-0.66	0.88	0.07	0.45	-0.32	0.32	0.97	0.86	0.51	-0.21	1	
	Sr	-0.16	-0.08	0.04	0.01	0.71	-0.51	-0.04	-0.02	0.22	0.57	0.09	1
	Cs	-0.73	0.8	0.3	0.49	-0.09	0.33	0.76	0.77	0.76	-0.15	0.86	0.34
Ba	-0.64	0.63	0.24	0.55	0.03	0.58	0.35	0.61	0.88	-0.07	0.39	0.26	0.68
Opaleniec Formation	SiO ₂	1											
	Al ₂ O ₃	0.8	1										
	Fe ₂ O ₃	0.1	0.04	1									
	MgO	-0.06	0.56	0.26	1								
	CaO	-0.84	-0.87	-0.33	-0.44	1							
	Na ₂ O	0.23	0.56	0.44	0.51	-0.53	1						
	K ₂ O	0.58	0.86	0.2	0.63	-0.84	0.67	1					
	TiO ₂	0.83	0.84	-0.01	0.09	-0.8	0.11	0.63	1				
	P ₂ O ₅	-0.1	-0.19	-0.15	0.06	0.1	-0.48	-0.15	-0.03	1			
	MnO	-0.56	-0.47	-0.31	-0.21	0.68	-0.11	-0.28	-0.67	-0.15	1		
	Rb	0.65	0.85	0.0002	0.47	-0.77	0.43	0.94	0.71	-0.11	-0.2	1	
	Sr	-0.45	-0.73	-0.41	-0.77	0.81	-0.81	-0.93	-0.44	0.26	0.32	-0.79	1
	Cs	0.6	0.67	-0.13	0.33	-0.63	0.46	0.69	0.49	-0.4	-0.21	0.73	-0.65
Ba	0.36	0.52	0.12	0.66	-0.68	0.41	0.58	0.39	0.42	-0.62	0.42	-0.62	0.31

Tab. 5 cont.

Samples		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Rb	Sr	Cs
Szlachtowa Formation	SiO ₂	1												
	Al ₂ O ₃	0.5	1											
	Fe ₂ O ₃	-0.07	0.57	1										
	MgO	-0.38	-0.1	-0.06	1									
	CaO	-0.8	-0.86	-0.31	0.04	1								
	Na ₂ O	-0.28	-0.09	-0.04	0.95	-0.04	1							
	K ₂ O	0.66	0.91	0.45	-0.03	-0.93	0.06	1						
	TiO ₂	0.1	0.68	0.63	0.22	-0.54	0.14	0.54	1					
	P ₂ O ₅	-0.67	-0.54	-0.1	-0.1	0.78	-0.23	-0.69	-0.37	1				
	MnO	-0.31	-0.69	-0.5	-0.05	0.6	0.002	-0.56	-0.77	0.17	1			
	Rb	0.84	0.79	0.3	-0.14	-0.94	-0.04	0.92	0.37	-0.66	-0.52	1		
	Sr	-0.36	-0.41	-0.09	-0.41	0.58	-0.58	-0.56	-0.43	0.77	0.27	-0.44	1	
	Cs	0.77	0.85	0.28	-0.38	-0.86	-0.29	0.87	0.36	-0.52	-0.55	0.88	-0.29	1
	Ba	0.16	0.49	0.41	0.52	-0.54	0.56	0.51	0.7	-0.46	-0.65	0.43	-0.64	0.34

COMPOSITIONAL ALTERATION AND PROVENANCE

MATURITY

The index of compositional variability proposed by Cox *et al.* (1995) can be applied in mudrocks as a measure of compositional maturity. It is defined as $[(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3]$. Non-clay silicates contain a lower proportion of Al₂O₃ than do clay minerals, thus ICV values for clay minerals are in the range of 0.03–0.78, and for feldspars in the range of 0.54–0.87.

The ICV values of most samples are higher than 1 (Table 1) because of the calcareous character of the samples and elevated contents of CaO and MgO. Only non-calcareous CRS display values that are within range of feldspar. These data agree with the interpretation of bivariate diagram SiO₂ vs. Al₂O₃ (Fig. 4). The CRS and certain samples of the Szlachtowa Fm. seem to be more mature among the material studied.

SUBAERIAL WATHERING PATTERNS

The most widely used chemical index to determine the degree of source-area weathering is the Chemical Index of Alteration (Nesbitt and Young, 1982). The index is calculated using the molecular proportions:

$$\text{CIA} = [\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$$

where: CaO* is the amount of CaO incorporated in the silicate fraction.

CIA values ranging from 70 to 75 in Phanerozoic shales reflect muscovite, illite and smectite composition and indicate a moderately weathered source. CIA values close to 100 charac-

terize residual clays enriched in kaolinite and Al oxy-hydroxides produced under strong weathering conditions.

The samples studied are calcareous and the CIA values were calculated without CaO. Thus, the index has only minor meaning during estimation of the degree of weathering. The Szlachtowa Fm. and the CRS of the Hulina section show the highest values of the index (average – 80), whereas the Malinowa and Opaleniec formations reveal the lowest (average – 77; Table 1). The degree of chemical weathering can be also estimated using the Plagioclase Index of Alteration (PIA; Fedo *et al.*, 1995) after the proportions:

$$\text{PIA} = [(\text{Al}_2\text{O}_3 - \text{K}_2\text{O})/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O})] \times 100$$

where: CaO* is only CaO from the silicate fraction.

Unweathered plagioclase has a PIA value of 50. The PAAS display higher PIA – 79. The samples show very high PIA values (calculated without CaO), averaging from 92 in the Opaleniec and Malinowa formations to 95 in the Szlachtowa Fm. and Hulina samples of the CRS (Table 1). The assumption that the Opaleniec Fm. shows the lowest degree of weathering was earlier shown by the low Th/U ratio.

In the triangular diagram A–CN–K (Fig. 5) estimated without CaO (to eliminate the effect of calcite admixture), the samples plot at the A–K join, between the A corner (chlorite, kaolinite) and the illite point. Very low amounts of Na₂O are crucial. Low values of Na₂O/Al₂O₃ ratio suggest the presence of clay minerals and strong weathering leading to Na leaching. Low K₂O/Al₂O₃ ratios (average 0.21–0.24) also reflect the presence of clay minerals. Material derived by intense weathering associated with recycling of older sediments generally contains a high portion of illite. The presence of recycled illite is shown by negative/absent correlation between Na₂O and K₂O

Table 6

**Pearson correlation coefficients (r) between selected major and minor elements
for the samples from the Grajcarek Succession**

Samples		Zr	Hf	Nb	Th	U	Y	Sc	TREE	Eu/Eu*
Malinowa Formation	Zr	1								
	Hf	0.93	1							
	Nb	0.92	0.87	1						
	Th	0.49	-0.22	0.58	1					
	U	0.56	0.41	0.32	-0.23	1				
	Y	-0.46	-0.22	-0.22	0.47	-0.95	1			
	Sc	0.07	0.38	-0.07	0.67	-0.15	0.37	1		
	SiO ₂	0.31	0.47	0.59	0.81	0.5	0.63	0.18		
	Al ₂ O ₃	0.55	0.7	0.77	0.89	-0.25	0.42	0.25	0.83	0.29
	K ₂ O	0.51	0.63	0.74	0.85	-0.35	0.48	0.19	0.87	0.25
	TiO ₂	0.92	0.96	0.96	0.76	0.25	-0.09	0.22	0.52	0.02
	P ₂ O ₅	0.83	0.74	0.82	0.28	0.72	-0.59	-0.19	-0.12	-0.4
CRS (Hulina Section)	Zr	1								
	Hf	0.99	1							
	Nb	0.99	0.98	1						
	Th	0.96	0.26	0.93	1					
	U	0.69	0.72	0.61	0.84	1				
	Y	0.23	0.26	0.16	0.43	0.58	1			
	Sc	0.99	0.99	0.96	0.96	0.73	0.34	1		
	SiO ₂	-0.94	-0.91	-0.92	-0.86	-0.58	-0.11	-0.9		
	Al ₂ O ₃	0.99	0.99	0.96	0.98	0.76	0.35	0.99	0.76	-0.17
	K ₂ O	0.98	0.98	0.95	0.97	0.76	0.37	0.99	0.76	-0.17
	TiO ₂	0.99	0.99	0.98	0.97	0.71	0.31	0.99	0.72	-0.25
	P ₂ O ₅	0.061	0.1	-0.04	0.31	0.69	0.86	0.16	0.57	0.77
CRS (Sztolnia sections)	Zr	1								
	Hf	0.91	1							
	Nb	0.71	0.7	1						
	Th	0.94	0.52	0.63	1					
	U	0.42	0.32	0.16	0.32	1				
	Y	0.67	0.52	0.43	0.78	0.06	1			
	Sc	0.73	0.66	0.43	0.76	0.34	0.47	1		
	SiO ₂	-0.64	-0.49	-0.53	-0.68	-0.58	-0.61	-0.58		
	Al ₂ O ₃	0.93	0.87	0.72	0.94	0.49	0.62	0.79	0.6	-0.54
	K ₂ O	0.88	0.82	0.74	0.85	0.23	0.51	0.72	0.6	-0.49
	TiO ₂	0.96	0.9	0.81	0.93	0.46	0.64	0.76	0.67	-0.51
	P ₂ O ₅	0.68	0.61	0.41	0.79	0.44	0.83	0.57	0.57	-0.08
Opaleniec Formation	Zr	1								
	Hf	0.94	1							
	Nb	0.07	0.06	1						
	Th	0.84	0.15	-0.14	1					
	U	0.16	0.37	-0.41	0.36	1				
	Y	0.18	0.15	-0.64	0.25	0.09	1			
	Sc	0.3	0.3	-0.23	0.37	0.42	0.44	1		
	SiO ₂	0.31	0.28	0.52	0.18	0.006	-0.24	0.54		
	Al ₂ O ₃	0.67	0.65	0.23	0.57	0.25	-0.05	0.58	0.48	-0.68
	K ₂ O	0.85	0.78	-0.03	0.79	0.16	0.19	0.57	0.52	-0.69
	TiO ₂	0.47	0.35	0.5	0.18	-0.01	-0.39	0.32	0.02	-0.24
	P ₂ O ₅	-0.31	-0.54	-0.39	-0.52	-0.08	0.21	0.24	-0.02	0.54

Tab. 6 cont

Samples		Zr	Hf	Nb	Th	U	Y	Sc	TREE	Eu/Eu*
Szlachtowa Formation	Zr	1								
	Hf	0.96	1							
	Nb	0.16	0.18	1						
	Th	0.42	0.31	0.57	1					
	U	0.38	0.39	0.75	0.37	1				
	Y	0.35	0.31	-0.09	-0.16	0.19	1			
	Sc	0.22	0.24	0.43	0.52	0.51	0.38	1		
	SiO ₂	-0.2	-0.19	0.14	0.52	-0.23	-0.45	-0.18		
	Al ₂ O ₃	-0.01	0.07	0.67	0.77	0.32	-0.36	0.55	0.05	-0.33
	K ₂ O	0.02	0.08	0.51	0.81	0.12	-0.35	0.4	0.12	-0.42
	TiO ₂	0.64	0.69	0.73	0.71	0.61	-0.08	0.5	-0.006	-0.29
P ₂ O ₅	-0.07	-0.13	-0.23	-0.57	0.09	0.79	0.23	0.49	0.71	

in the Malinowa Fm. ($r = -0.16$) and the Szlachtowa Fm. ($r = 0.06$; Table 5).

Intense weathering produces fractionation of the LREE/HREE. Preferential retention of HREE in solution may cause an increase in $(La/Yb)_{PAAS}$. The highest values of $(La/Yb)_{PAAS}$ appear within the Szlachtowa Fm. (1.06 ± 0.08) and CRS (1.03 ± 0.09). The Opaleniec Fm. displays values varying widely (standard deviation is 0.12). The lowest values of $(La/Yb)_{PAAS}$ characterize the Malinowa Fm. (0.94 ± 0.02) (Table 2). Values of $(La/Yb)_{PAAS}$ show positive correlation with PIA and CIA.

The high values of CIA, PIA indexes and A–CN–K diagram indicate that material of the Szlachtowa Fm. and CRS from the Hulina section is more weathered than the material of the Opaleniec and Malinowa formations. This is supported by distributions of Cs and Rb correlative to K₂O as well as REE fractionation, and Th/U ratios. The relatively high Cs and low concentrations of Zr, Hf in CRS may be attributable to the long-distance transport of aeolian dust (Nesbitt *et al.*, 1980).

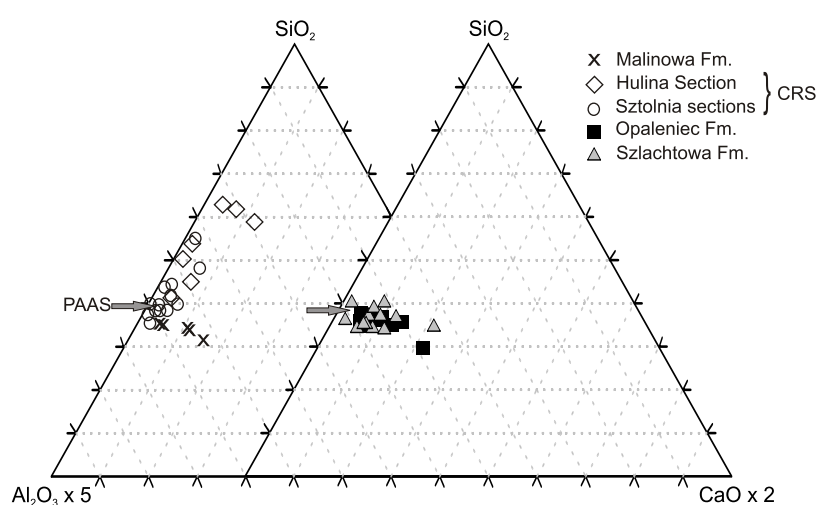


Fig. 3. Triangular plot SiO₂–Al₂O₃ × 5–CaO × 2

PAAS refers to Post-Archean Australian Shale (after Taylor and McLennan, 1985)

PROVENANCE

TECTONIC SETTING

Ternary La–Th–Sc diagram (Bhatia and Crook, 1986) has been used to constrain the provenance and tectonic settings for the deposition of the succession studied. The deposits plot within the continental islands arc (Fig. 6), which is partly in agreement with the major element tectonic discrimination shown in the K₂O/Na₂O vs. SiO₂ diagram (Fig. 7). Most of the samples plot within the fields of active continental margin and island arc. The CRS are shifted to the passive margin field due to the high silica content, which distorts the proper interpretation.

SORTING AND RECYCLING

The distribution of the chemical components is mainly determined by the mechanical properties of the host minerals. The process basically fractionates Al₂O₃ (clay minerals) from SiO₂ (quartz and feldspars). Sorting also fractionates TiO₂, mostly present in clay minerals and Ti-oxides, from Zr and Hf hosted in zircon, and sorted with quartz.

The ternary diagram 10 × Al₂O₃–200 TiO₂–Zr (Fig. 8) may illustrate the presence of sorting-related fractionation (Garcia *et al.*, 1991). The samples are near to PAAS. Most of the samples cluster without visible variation as regards amounts of Al₂O₃, TiO₂ and Zr. Only “Black Flysch”, especially the Szlachtowa Fm., shows a mixing trend. Changes in the Al₂O₃/Zr ratio may be a recycling effect. Zr enrichment during sorting can also be evaluated using the bivariate diagram Zr/Sc vs. Th/Sc (Fig. 9). The Zr/Sc ratio is an index of sediment recycling, while Th/Sc ratio is controlled by chemical differentiation (McLennan *et al.*, 1993). The samples are clustered along the primary compositional trend, near the andesite point, but the Szlachtowa Fm. falls along a trend involving minor zircon addition.

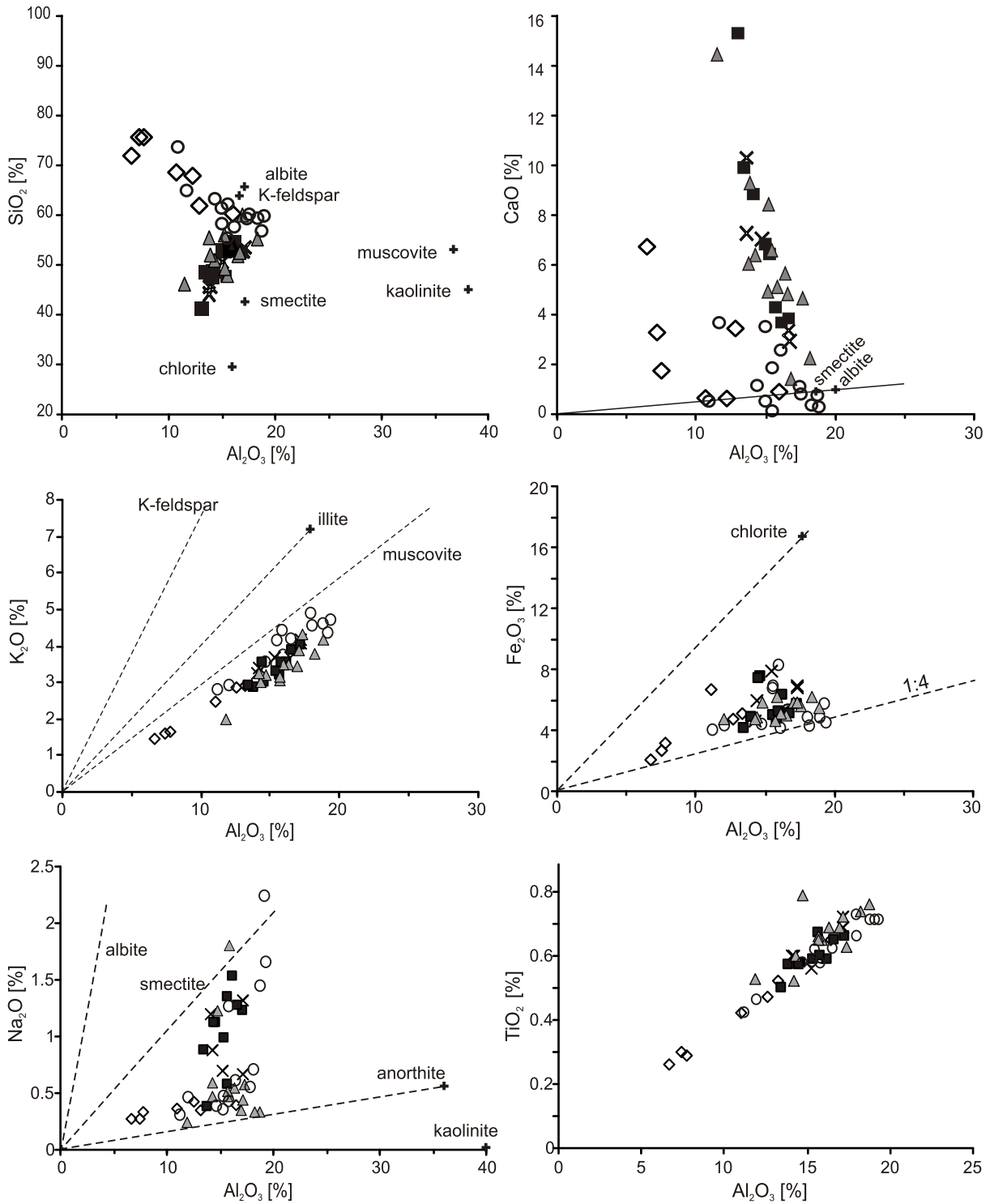


Fig. 4. Bivariate diagrams of major element composition for the Cretaceous succession of the Grajcarek thrust-sheets

$Fe_2O_3/Al_2O_3 = 1:4$ regarded as typical for detrital siliclastic sediments represents an iron content of phyllosilicates; for other explanations see Figure 3

MAFIC-FELSIC SIGNATURE

Certain trace elements or the ratios between them have been used to infer source rock composition. The concentration of Zr, La and Th is higher in the silicic igneous rocks in contrast to Cr,

Sc, Ni and Co that are housed in basic rocks (Taylor and McLennan, 1985). Relative to PAAS, the material studied is enriched in transition metals including Ni, Sc, Co and Zn. Exceptional enrichment in V and depletion in Cr distinguish the CRS of the Hulina section (Table 2).

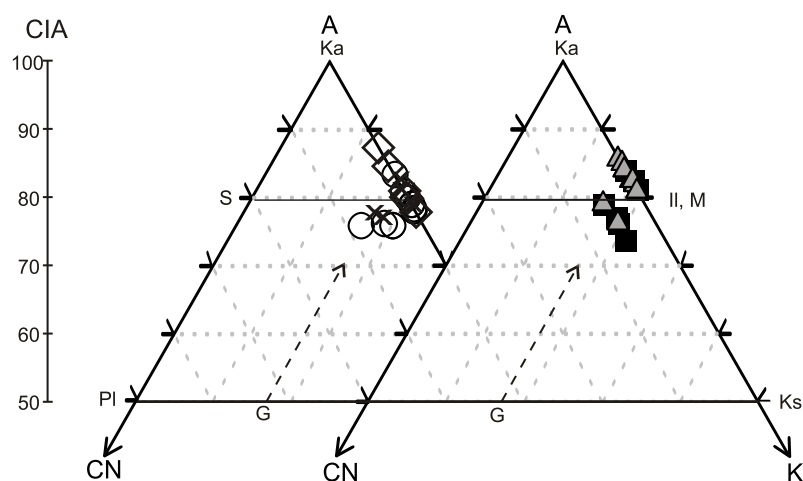


Fig. 5. Ternary A–CN–K plot and Chemical Index of Alteration

The dashed line shows the theoretical weathering trend from a typical granite source rock; G – granite, II – illite, Ka – kaolinite, Ks – K feldspar, M – muscovite, PI – plagioclase, S – smectite; for other explanations see Figure 3

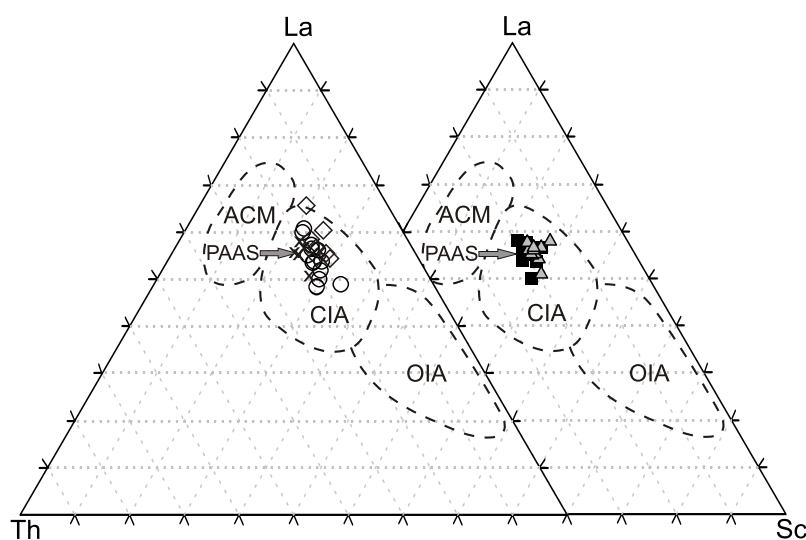


Fig. 6. Ternary diagram between light REE (La), incompatible element (Th) and compatible element (Sc) showing similarity of samples studied to PAAS

Tectonic discrimination boundaries: ACM – active continental margin, CIA – continental island arc, OIA – oceanic island arc; for other explanations see Figure 3

Cr/Th ratios are similar to these of PAAS (7.5) and UCC (7.76) for the CRS of the Hulina section. Ratios are little higher for other samples. The highest ratios are shown by the CRS of the Sztolnia sections (Table 4). With the exception of the CRS, the La/Co and Th/Co ratios reach those of UCC (La/Co – 1.76; Th/Co – 0.63) and PAAS (La/Co – 1.65, Th/Co – 0.64; Table 4). It is worth to noting that concentrations of Co were probably increased by diagenetic pyritization.

The importance of felsic supply is confirmed by the La–Th–Sc plot, and Cr/V vs. Y/Ni diagram (Bathia and Crook, 1986). In the ternary diagram La–Th–Sc, the samples fall in a field close to PAAS (Fig. 6). The La/Sc and Th/Sc ratios are quite similar to those of Upper Continental Crust

(La/Sc – 2.21; Th/Sc – 0.79) and PAAS (La/Sc – 2.37, Th/Sc – 0.9; Table 4). On the basis of the mixing curve between granite and the mafic-ultramafic end-member in the Cr/V vs. Y/Ni diagram (Fig. 9) any share of mafic-ultramafic matter in the material studied is doubtful. Considering the above, the material studied, enriched in incompatible elements, appears to be sourced from intermediate to felsic rocks. However, the CRS of the Sztolnia sections contain relatively high amounts of mafic Cr and Sc.

DISCUSSION

The transition from black shales to red/variegated deposits within the Cretaceous succession has been recorded mostly from epicontinental seas and carbonate platforms, and deep-sea environments of the Tethyan and Atlantic oceans (Jenkyns, 1980; Schlanger and Cita, 1982; Arthur and Premoli-Silva, 1982; Bralower *et al.*, 1993; Hu *et al.*, 2005; Wójcik-Tabol, 2006; Wang *et al.*, 2011).

Sikora (1962) and Ksi kiewicz (1977) have noted this pattern and postulated that the “Black Flysch” deposits almost always dip beneath the Cretaceous variegated shales (Golonka and R czkowski, 1984a, b). The Cretaceous deposits of the Grajcarek Succession display similarity to the Cretaceous sequences that are known from the Polish Outer Carpathians i.e. the Spas Shales and Ve ovice Beds (Oszczypko, 2006). Horwitz (1929) first distinguished the “Black Flysch” (or “black Cretaceous”) of the Ve ovice type section as representing the Barremian to Aptian/Albian. Oszczypko *et al.* (2004) have demonstrated the Cretaceous age of the Szlachtowa Formation, as well as of the Opaleniec Formation.

Mineral composition and geochemistry have become a basis of comparison of the “Black Flysch” deposits with the Albian equivalents from the Pieniny Klippen Belt (Upper Kapu nica Fm.) and Outer Carpathians (Lhota Fm.). The Szlachtowa and Opaleniec formations contain clay mineral assemblages including illite/smectite and kaolinite, similar to the Lhota Fm. of the Silesian Nappe (Wójcik-Tabol and 1 czka, 2009) and the Kapu nica Fm. of the PKB.

Kaolinite enrichment probably reflects widespread accumulation of material weathered under constantly warm and humid conditions (Chamley, 1989). The influence of weathering is confirmed by high values of the CIA, PIA indexes, the A–CN–K diagram, distribution of Rb and Cs, as well as REE fractionation and the Th/U ratios.

In terms of major element contents, the Szlachtowa and Opaleniec formations correlate with the Kapu nica Fm. of the PKB. The concentrations of redox-sensitive elements have

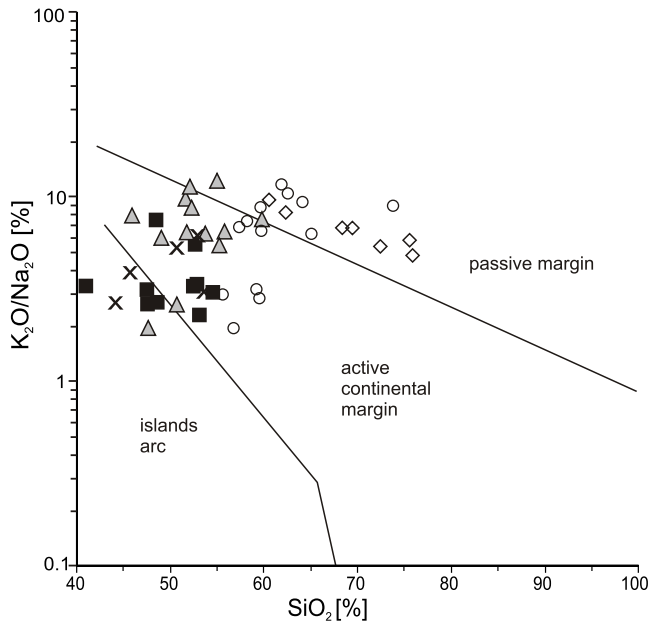


Fig. 7. Diagram of tectonic discrimination based on K_2O/Na_2O vs. SiO_2 .

For explanations see Figure 3

been discussed by Wójcik-Tabol and Oszczytko (2010). These authors have stated that the “Black Flysch” studied was deposited in dysoxic/anoxic environments of an oceanic anoxic event 1 (*sensu* Schlanger and Jenkyns, 1976). Accumulation of U, Th, Mo, As correlative to S suggests that the environment of the Grajcarek sub-basin was strongly anoxic.

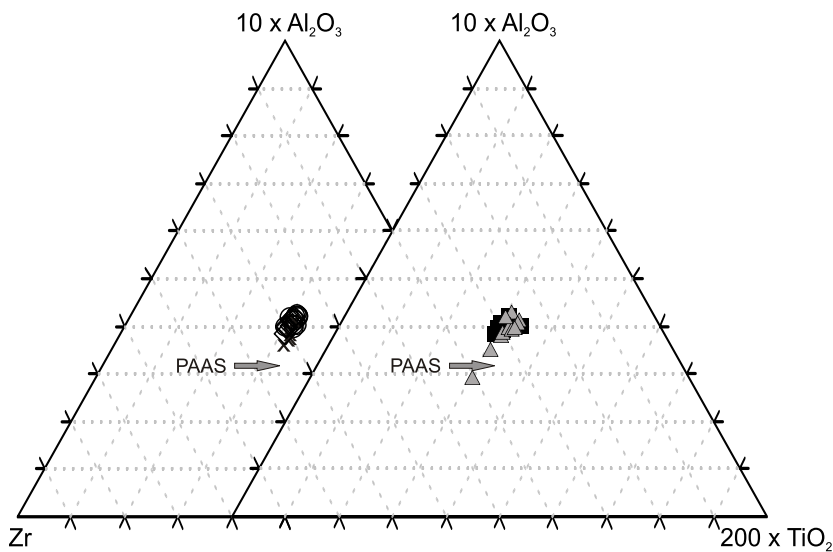


Fig. 8. Ternary $10 \times Al_2O_3$ – $200 \times TiO_2$ –Zr plot showing possible sorting trend

For explanations see Figure 3

The material studied is relatively enriched in REE positively correlated to Al_2O_3 , Zr, Y, TiO_2 that suggest affinity of REE to phyllosilicates and heavy minerals.

Concentrations of “immobile” elements (Zr, Ti, Rb, Nb) suggest contamination of black shales by terrigenous material derived from intermediate-felsic rocks, as was concluded from Y/Ni vs. Cr/V and $(V + Ni + Cr)$ vs. $(Zr + Ti)$ diagrams (Wójcik-Tabol and Oszczytko, 2010). The same was estimated for the Lhota Fm. deposited in the Silesian Basin (Wójcik-Tabol and Iczka, 2009).

As a result of the post-rift subsidence, the Early/Late Cretaceous “Black Flysch” of the Grajcarek Succession was deposited at the southern edge of the Magura Basin. This part of the basin was supplied with detrital material derived from erosion of the Czorzstyn paleo-Ridge (Krawczyk and Słomka, 1986, 1987; Golonka *et al.*, 2000), uplifted since the Valanginian to Albian/Cenomanian interval (Birkenmajer, 1977). The “Black Flysch” sandstones contain heavy mineral assemblages rich in garnet, and subsequently staurolite, kyanite and biotite (see Łoziński, 1956, 1959, 1966), that indicates erosion of continental-type crust.

Taking to account the REE patterns, the material studied has been compared to the Lower Cretaceous marlstones of the Venetian Prealps representing a section through southern continental margin of the Tethys Ocean (Bellanca *et al.*, 1997). The Szlachtowa, Opaleniec formations and CRS of the Sztolnia sections show values of Eu/Eu^* and La/Yb similar to those of dark shales within the Albian Scaglia Variegata Formation deposited in the southern Tethys.

Bellanca *et al.* (1997) proposed that sea water was the most immediate REE source in the calcareous deposits. REE scavenging may be attributed to adsorptive removal onto the surface coatings of the suspended particles and/or precipitation of Fe-sulphides. REE distribution was influenced by the chemistry of the waters of the Tethys Ocean.

The siliceous facies of the CRS are quite similar to the Cenomanian-Turonian interval (CTI) known from the Outer Carpathians (Barnasiówka Radiolarian Shales Formations; see Błk, 2007; Wójcik-Tabol and Iczka, 2009) and Pieniny Klippen Belt (Magierowa Mbr.; see Wójcik-Tabol, 2006). Deposits of the CTI consist of silica and associated clay minerals including illite/smectite and chlorite (Wójcik-Tabol and Oszczytko, 2010). Increasing amounts of illite and chlorite is typical for the CTI (compare with the Bonarelli level from the Umbria-Marche Basin; Turgeon and Brumsack, 2006) due to cooling of climate and accelerated physical weathering (Chamley, 1989).

The CRS studied are characterized by decreasing amounts of detrital elements such as Zr, Ti, Rb and Nd as well as a negative correlation between Al_2O_3 and SiO_2 that indicates diminishing input of terrigenous material (Wójcik-Tabol and Oszczytko, 2010). These geochemical features are in agreement with decreasing trends of Ti/Al

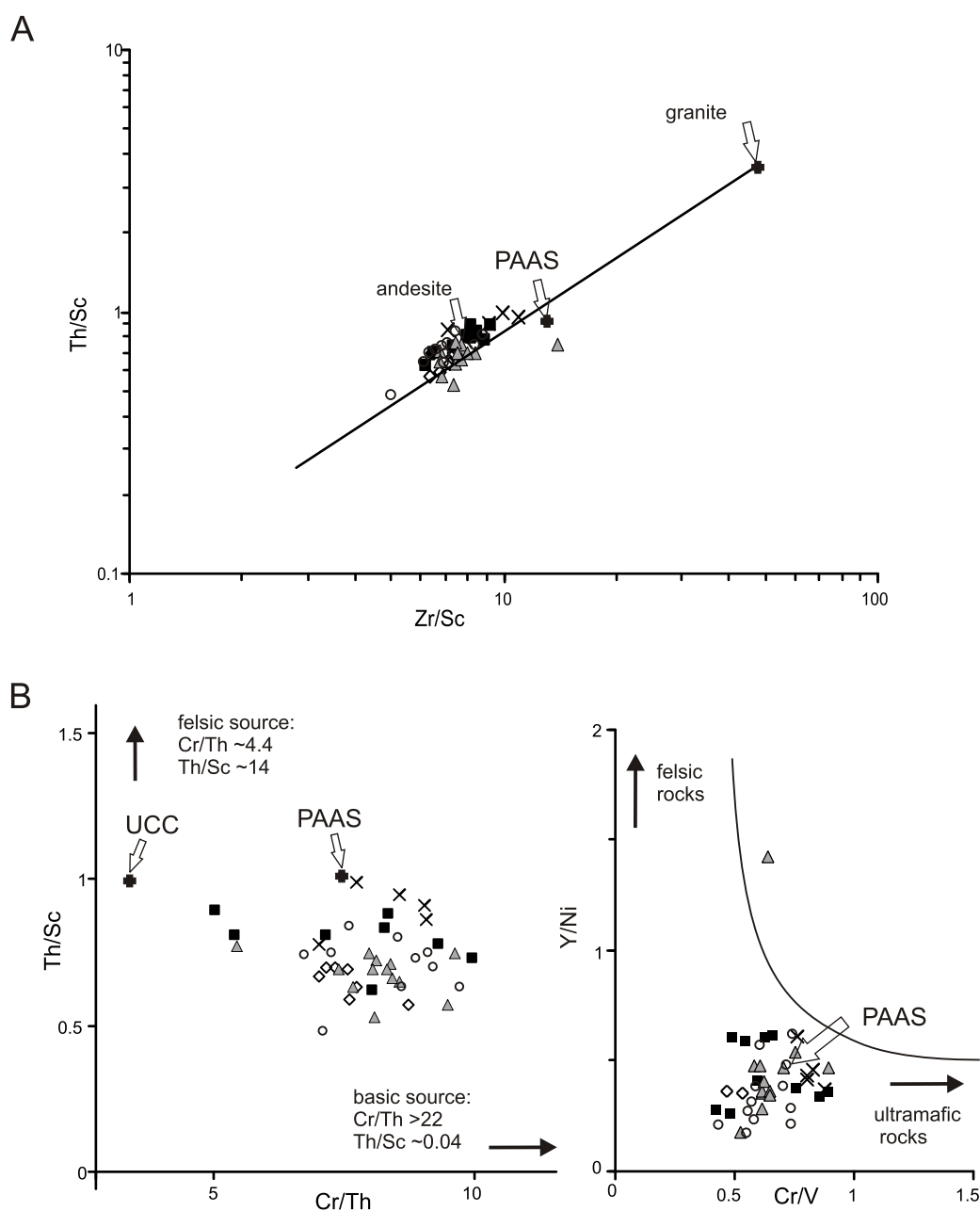


Fig. 9. Provenance and source signature diagrams of the studied Cretaceous succession of the Grajcarek Succession

A – bivariate diagram Zr/Sc vs. Th/Sc shows index of sediment recycling against indicator of chemical differentiation; the samples are mainly clustered along the primary compositional trend;
B – bivariate diagram Cr/V vs. Y/Ni

and Rb/Al ratios up to the siliceous shales of the BRSF and the lowest values of $Al/(Al + Fe + Mn)$; B k, 2007).

The concentrations of Ba, Sc, Th, REE and “immobile” elements in the CRS approximate these to the Magierowa Mbr. (Wójcik-Tabol, 2006). Radiolarites from the Hulina section are more similar to the Barnasiówka Fm. due to low amounts of “immobile” elements and Mn enrichment (B k, 2007; Wójcik-Tabol and I czka, 2009). The numerous radiolarian-rich layers probably reflect upwelling circulation and increased

productivity at the margin of the Carpathian Basin (B k, 2007) that may have been affected by eustatic sea level rise. Flooding of the source areas limited detrital input.

Contents of major and “immobile” elements (e.g., Zr, Ti, Rb) within the CRS are comparable to those of CT black shales from the Demerara Rise – Western Atlantic (see Brumsack, 2006) the Bonarelli Level from the Venetian Prealps (Bellanca *et al.*, 1997) and Umbria-Marche Basin of Central Italy (Brumsack, 2006; Turgeon and Brumsack, 2006). On the other

hand, the CRS studied are not sufficiently rich in redox-sensitive elements (Mo, Zn, Cu, As, V, Ni) relative to the Cenomanian-Turonian black shales from Tethys, the North Atlantic, and the central North Pacific (Brumsack, 1980, 2006; Arthur *et al.*, 1990; Bralower *et al.*, 1993). A possible explanation might be dilution effect caused by enhanced terrigenous input into the Grajcarek Sub-basin.

Red marls and shales of the Malinowa Fm. that represents the Upper Cretaceous oceanic red beds (CORB) follow the CRS. They occur in a broad belt extending from the Caribbean across the Central Atlantic, Europe to Eastern Asia and record changing depositional conditions from anoxic/dysoxic to oxic. The Malinowa Fm. studied resembles other CORBs (see Neuhuber and Wagneich, 2011 and references therein). The most significant similarity occurs between the Malinowa Fm. and clayey CORB of the Mazak Fm. from the Czech Republic (Jiang *et al.*, 2009) and Turonian variegated shales from the Polish Outer Carpathians (B k, 2007).

Deposition of the Malinowa Formation might have been influenced by several processes: excess of organic carbon burial, global cooling, and/or intensification of bottom circulation (Wójcik-Tabol and Oszczytko, 2010).

Recently in the Czorsztyn Succession of the Pieniny Klippen Belt, in Ukraine (Veliky Kamenets; *cf.* Krobicki *et al.*, 2004, 2008) and in the valley of the Váh in Slovakia (Vršatec; *cf.* Spišiak *et al.*, 2008, 2011), sub-marine volcanic rocks have been described (melanephelinites and alkaline basalts), that are not older than Cenomanian. This group can also include blocks of basalt from the Biała Woda, known as olistoliths in the Jarmuta Formation. These volcanic rocks correspond to oceanic island alkali basalts or within-plate alkali basalts (Krobicki *et al.*, 2004, 2008; Birkenmajer and Lorenc 2008; Spišiak *et al.*, 2008, 2011). According to Spišiak *et al.* (2011), volcanic activity was probably generated during passive asthenospheric mantle upwelling, associated with lithospheric stretching and thinning of the Czorsztyn (Oravic) Ridge. Studied material falls in the field of CIA, because it was sourced from intermediate to felsic rock. However, the CRS contain admixture of mafic elements that suggest basaltic volcanism during Cenomanian

The volcanic activity was followed by the subsidence and deepening in the Magura Basin beneath the carbonate compensation depth level (see Oszczytko and Oszczytko-Clowes, 2006). This resulted in deposition of red shales of the Malinowa Formation (Turonian–Campanian) followed by coarse-grained sandstones and conglomerates of the Jarmuta Formation (Maastrichtian to late Paleocene), that contain chromian spinels derived from oceanic crust (Oszczytko and Salata, 2005). Slight admixture of the mafic elements (Cr, Sc) occurs within the CRS of the Sztolnia sections. The Malinowa Fm. contains relatively high amounts of Cr, but this may reflect the presence of recycled phases.

CONCLUSIONS

1. The Grajcarek Succession was deposited at the southern edge of the Magura Basin. The bulk samples are characterized as mixtures of detrital matter comparable to PAAS with varying amount of biogenic components. The Cenomanian radiolarian shales are depleted in terrigenous particles. The eustatic sea level rise and flooding of the source areas caused reduction in detrital supply and produced an organic productivity rise that is recorded by increased Ba concentrations.

2. The terrigenous materials such as phyllosilicates and heavy minerals accommodate “immobile” elements. The Szlachtowa Fm. contains heavy minerals (zircon, xenotime and Ti-oxides) in amounts higher than in other formations. Amorphous Fe-hydroxide coatings on grains and/or phosphates could potentially constitute an important host for HFSE in the Malinowa Fm.

3. Due to low contents of clay minerals the CRS and Szlachtowa Fm. seem to be more mature than other formations. The CRS are probably contaminated by aeolian dust. The Szlachtowa Fm. contains small addition of recycled particles (zircon). The occurrence of recycled phases (illite) is assumed within the Malinowa Fm. The material of the Szlachtowa Fm. and CRS were affected by more advanced weathering than the material of the Opaleniec and Malinowa formations.

4. Material of the Grajcarek Succession appears to be sourced from intermediate to felsic rocks that represent continental island arcs. Detritic material was derived from erosion of the Czorsztyn Ridge, uplifted since the Valanginian to Albian/Cenomanian. The Cenomanian deposits contain an admixture of the mafic elements that correspond with sub-marine volcanism recognized in the Czorsztyn Succession of the Pieniny Klippen Belt by other authors.

5. The sections studied display a transition from relatively shallow marine, anoxic black shales to well-oxygenated deep-water red beds of the of the Malinowa Formation. This process was typical for global transition of the Lower Cretaceous black shales to Upper Cretaceous oceanic red beds. This kind of succession has been observed in all the sections studied by us in the Male Pieniny Mts., and suggests a common sedimentary history represented by these profiles.

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