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Geology of the Pieniny Klippen Belt and the Tatra Mts, Carpathians
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Part XIX

Patrycja WÓJCIK-TABOL[1]

Inorganic geochemical records of local palaeoenvironmental variability in the Jaworki Formation (Upper Cretaceous) of the Niedzica Succession, Pieniny Klippen Belt (Western Carpathians)[2]

(Figs 1–4; Tabs 1, 2)

Abstract. The Cenomanian sequence of marls and marly shales interbedded by black shales (Jaworki Formation) from the Niedzica Succession was investigated. These organic carbon-rich horizons may correspond to the event of global anoxity OAE 1d. Major and trace element profiles mirror changing environments of deposition of black shales. In black shales, the content of SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, P_2O_5 increases at the expense of CaO. All samples are characterised as mixtures of terrigenous-detrital matter with varying amount of calcium carbonate. A good correlation between SiO_2, Al_2O_3, K_2O, TiO_2, and the correlation with the minor elements Zr, Rb and Nb, point to the detrital origin of these elements. Detrital input was rather scarce. The high trace element/Al ratios in the black shales can be explained either by the adsorption onto organic matter or through the sulphides precipitation. Some black shale-samples are poorer in transitional metals. The studied sediments were deposited under oxic/suboxic conditions interrupted by irregular anoxic periods resulted from expansion of oxygen minimum zone (OMZ).

Key words: Major and trace elements, black shales facies, Cenomanian, Pieniny Klippen Belt, Carpathians.

INTRODUCTION

A number of organic-rich facies corresponding to the oceanic anoxic events (OAE *cf.* Schlanger & Jenkyns, 1976) are known worldwide in Cretaceous deposits both in oceanic and platform successions (Jenkyns, 1980; Arthur *et al.*, 1990; Erbacher *et al.*, 1996). The Cretaceous black shales ware also developed in the

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Pieniny Klippen Basin (Alexandrowicz, 1966; Birkenmajer, 1963, 1977; Gasiński, 1988; K. Bąk & M. Bąk, 1994; Wójcik-Tabol, 2006, 2008). Pelagic, hemipelagic and partly turbiditic sedimentation on the slopes of the basin and in the central furrow took place there (Birkenmajer, 1977, 1986; Mišík 1994). The organic carbon-rich facies appeared during Cenomanian in the Jaworki Formation, developed as pelagic marls with turbidite intercalations (Birkenmajer, 1977). This paper is focused on geochemical features of the Cenomanian sediments from the Niedzica Succession (see Birkenmajer, 1970). Sequence of marls and marly shales interbedded by black shales was investigated. Basing on foraminiferal biostratigraphy, the studied sequence was dated at Early-Middle Cenomanian (*Rotalipora appenninica*, *R. reicheli – greenhornensis* zones – Gasiński, 1988; Caron *et al.*, 2006). The black shales may correspond to the event of global anoxity OAE 1d (Arthur *et al.*, 1990).

GEOLOGICAL SETTING

Pieniny Klippen Belt (PKB) separates the Outer from the Inner Carpathians (Fig. 1). It is about 600 km long but only 1–20 km wide, stretching from the Vienna Basin in the West, to Romania in the East. The Pieniny Klippen Belt is composed of several tectonic units generally corresponding to stratigraphic – facies successions. The Niedzica Succession was deposited between more shallow Czorsztyn and Czertezik successions (submarine slope) and more deep Branisko and Pieniny successions (Birkenmajer, 1977, 1986).

The Cretaceous was a period of unification of the sedimentation realms in the Pieniny Klippen Basin. Thus, during Albian through Campanian, marly deposits of the Jaworki Formation formed. Its palaeobathymetry has been assessed basing on character of microfaunal assemblages (Gasiński, 1991; Birkenmajer & Gasiński, 1992). The Jaworki Formation is divided in lithostratigraphic units of member rank (Birkenmajer, 1977). The Skalski Member is developed as cherry-red and variegated marls, calcareous mudstones and marly shales. It represents the *Rotalipora appenninica, reicheli - greenhornensis* and *R. cushmani* foraminiferal zones (Early-Late Cenomanian) sometimes ranging up to *Praeglobotruncana helvetica* Zone (Early Turonian) – Birkenmajer (1963), Alexandrowicz *et al.* (1968), Birkenmajer & Jednorowska (1987). The Jaworki Fm. includes also turbidite deposits: the Snežnica Member (Birkenmajer, 1977) consists of fine-rythmical olive-green to grey and bluish calciturbidite deposits with shales predominating over thin-bedded siltstone and sandstones. It occupies biostratigraphic position between the *R. reicheli* Zone (Early Cenomanian) and the *P. helvetica* Zone (Early Turonian; Alexandrowicz *et al.*, 1968; Birkenmajer & Jednorowska, 1987).

SAMPLING AND ANALYTICAL METHODS

The studied sections are located in the Jaworki area, eastern part of the Pieniny Klippen Belt in Poland (Birkenmajer, 1970) (Fig. 1). The main section along the Grajcarek Stream, below the church (section named Jaworki below church – JKP

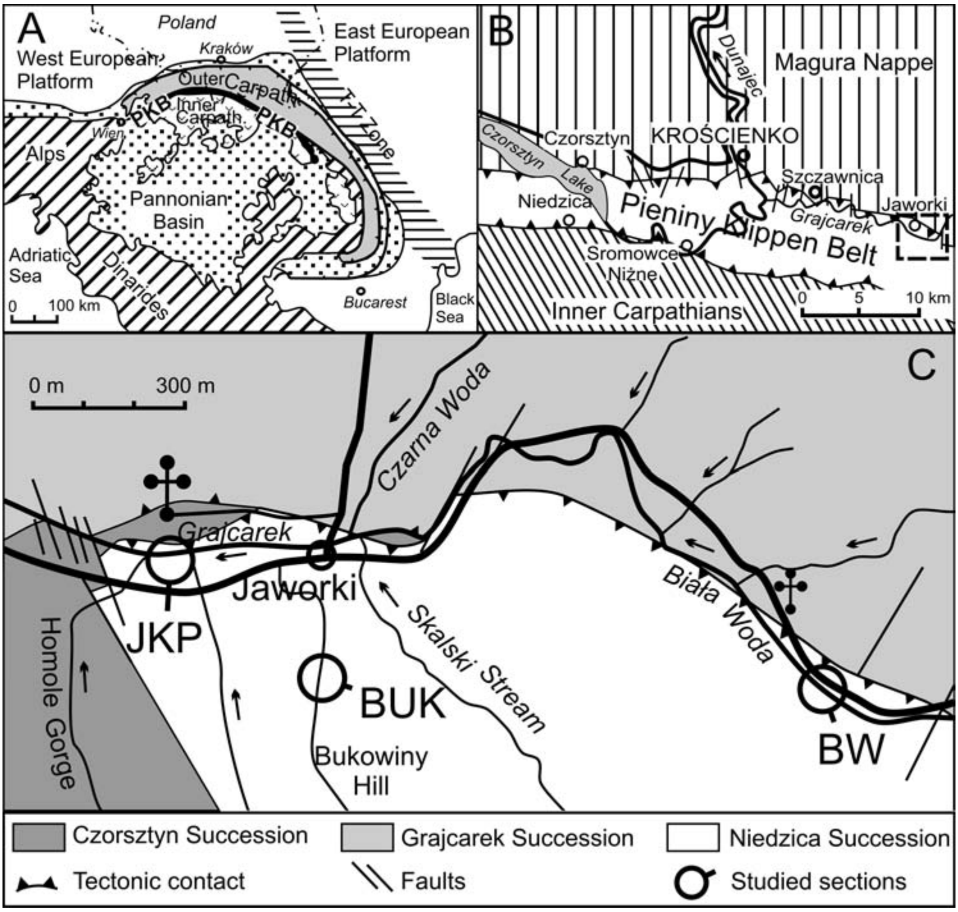

Fig. 1. Location of the studied area against the background of main geological units: **A** – simplified tectonic scheme of the Alpine orogens; PKB – Pieniny Klippen Belt (after Kovač *et al.*, 1998, modified); **B** – geological sketch of the Pieniny Klippen Belt (after Birkenmajer, 1986); **C** – detailed geological map of the Jaworki vicinity with position of the studied sections: BW – Biała Woda Valley, BUK – Bukowiny Hill, JKP – Grajcarek Stream at Jaworki below church (after Birkenmajer, 1979)

samples), exposes the Skalski Mbr. The section consists of a strongly folded sequence of variegated and grey marls, and olive green marly shales with intercalations of thin (up to 5 cm thick) black, partly siliceous shales disintegrating into small flakes. Black shales overlie the green marls (Brynczkowa Marl Member) in the lower part of this section (Fig. 2). Pink to cherry-red marls and marly limestones (Skalski Marl Member) predominate upward the succession.

From the Bukowiny Hill section (BUK samples) a sequence of red marly shales (BUK 3), black shales (BUK 1) and overlying beige sediments were sampled (Fig. 3A) from the Skalski Marl Member.

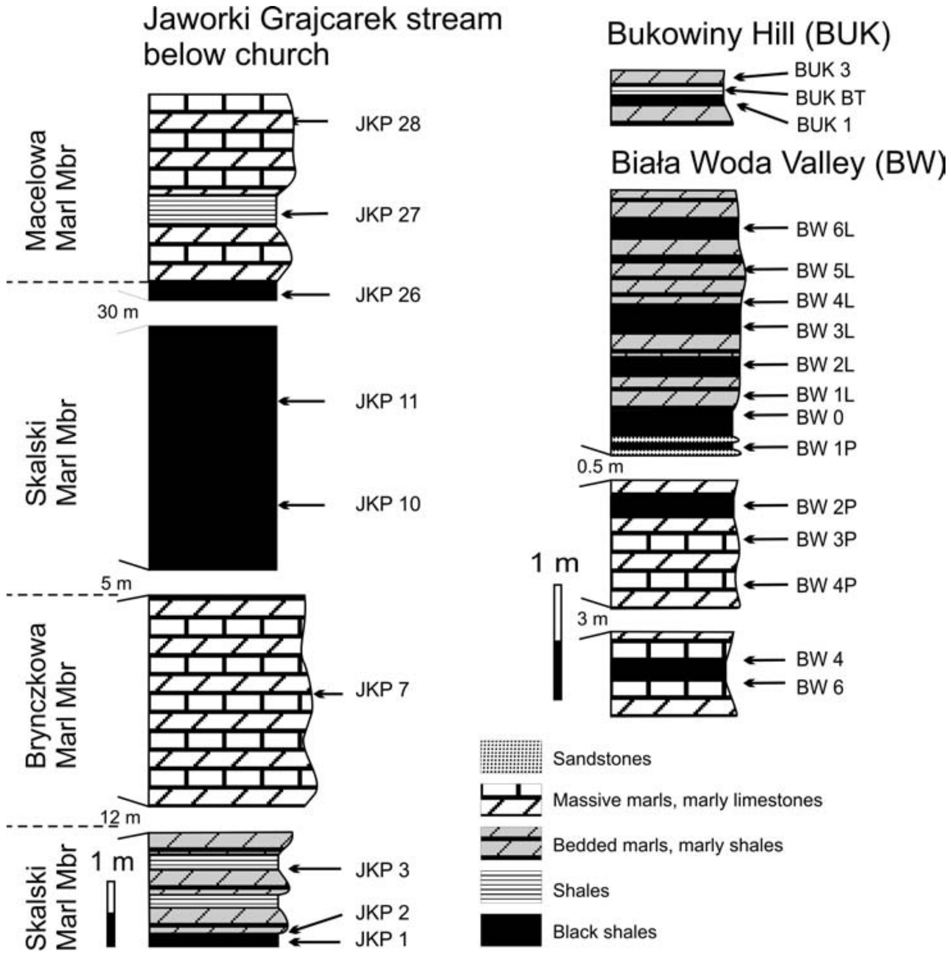

Fig. 2. Lithological logs of the studied sections (lithostratigraphic units of the Jaworki Formation after Birkenmajer, 1977)

Samples of the Skalski Mbr ware also collected at the Biała Woda stream (samples signed BW). This section exhibits a 2 m-thick sequence of variegated marls with intercalations of black shales (Skalski Marl Mbr) similar to those from the Jaworki below church section. This part of section is strongly deformed tectonically (Fig. 3B). Upward, calciturbidite deposits of the Snežnica Mbr are exposed. They include bedded, 20-cm thick greenish grey marly shales gradually alternating with dark grey marly shales (Fig. 3C). Both are bioturbated and contain fine mica.

Trace and minor elements concentrations were measured using ICP-OES spectrometry and INAA analysis. The pulverized material was analyzed after dissolution in an HCl-HNO$_3$-HClO$_4$-HF solution. Major and trace element contents were normalised relative to average shale (Wedepohl, 1971, 1991).

RESULTS AND DISCUSSION

Variations in major, minor and trace element concentration may be controlled by their behavior in the water column, redox conditions and supply of terrigenous material. The accumulation/depletion patterns are strongly influenced by diagenetic solubility of oxide or sulphide minerals, preferential adsorption of reduced or oxidized forms onto authigenic Fe-oxyhydroxides or pyrite (V, Zn and Ni), as well as selective adsorption of reduced forms with particulate Corg (V, Mo, Ni and U) (Breint & Wanty, 1991; Morford & Emerson, 1999; Shaw *et al.*, 1990).

Major elements. The investigated sections consist mainly of marly sediments: marls, marly shales and marly limestones, intercalated by weakly calcareous, easily disintegrating black paper shales (JKP 1, 10, 11, 26 and BUK 1). A clear change in major element composition is apparent in black shales. Their absolute contents of SiO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, P_2O_5 are increasing at the expense of CaO (Tab. 1). Thus, major element distributions much depend on lithology.

The bulk samples are characterised as mixtures of terrigenous-detrital matter comparable to average shale with varying amount of calcium carbonate. A good correlation between SiO_2, Al_2O_3, K_2O and TiO_2, and correlation with the minor elements Zr, Rb and Nb (Tab. 2) in the sections depend on the detrital provenance of these elements. Variations in the element/Al ratios within the sections are indicative of varying inputs of quartz, heavy minerals and clay minerals. Detrital input was, however, insignificant. High values of the element/Al ratios, compared to average shale (Wedepohl, 1971, 1991) result from lower Al content in the analysed material than normal Al-concentration in the average shale.

Trace elements. The whole sections are Bi-depleted relative to average

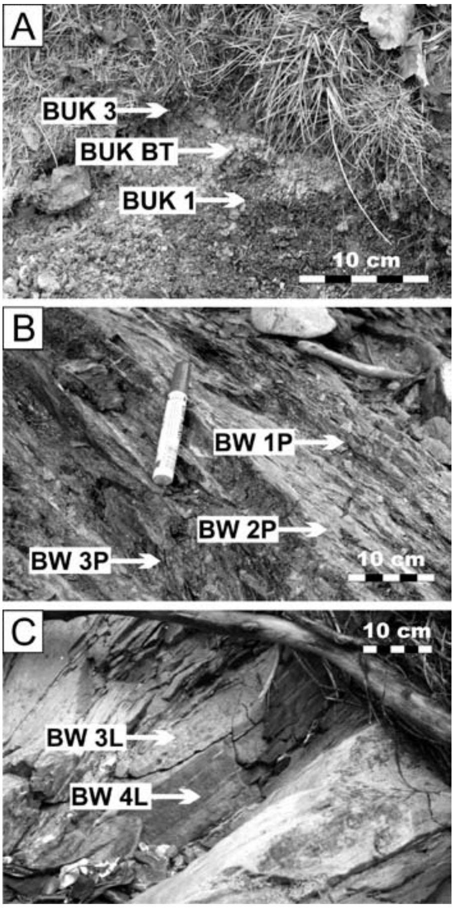

Fig. 3. A. Bukowiny Hill section: red marls with intercalation of black shales and light brown, plastic sediment; **B.** Sequence of bedded greenish-grey and dark-grey marly shales from the Biała Woda Valley section; **C.** Variegated and olive-green marly shales with intercalations of thin (up to 5 cm thick) black shales disintegrating into small flakes: Skalski Mbr in the Biała Woda Valley section

Absolute contents and element/Al ratios of investigated samples

	Mo	Cu	Pb	Zn	Ni	As	Cd	Bi	Ag	Se
SAMPLES	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
JKP1	0.1	151.5	42.9	58	89.4	3.5	0.1	0.5	0.2	1
JKP1 Al norm.	0.012	18.86	5.34	7.22	11.13	0.43	0.012	0.062	0.025	0.125
JKP3	<.1	44.6	6.3	34	34.6	<.5	0.1	0.2	<.1	<0.5
JKP3 Al norm.		16.33	2.3	12.45	12.67		0.037	0.073		
JKP7	0.1	14.2	8	29	34.4	0.8	0.1	0.1	<.1	<0.5
JKP7 Al norm.	0.031	4.36	2.46	8.92	10.58	0.24	0.031	0.031		
JKP10	0.4	33	12.6	81	47.5	6.9	0.1	0.3	<.1	<0.5
JKP10 Al norm.	0.038	3.14	1.2	7.71	4.52	0.65	0.01	0.029		
JKP11	0.7	31.2	14.3	82	45.8	12.4	<.1	0.3	<.1	0.6
JKP11 Al norm.	0.069	3.05	1.4	8.03	4.49	1.21		0.029		0.059
JKP26	1.5	90.2	36.4	276	115.9	46.6	2.1	0.5	0.4	5.4
JKP26 Al norm.	0.179	10.77	4.34	32.97	13.84	5.56	0.251	0.06	0.048	0.645
JKP27	0.1	21.7	5.7	41	31.1	4.3	0.1	0.2	<.1	<0.5
JKP27 Al norm.	0.027	5.802	1.52	10.96	8.31	1.15	0.027	0.053		
JKP28	0.2	22.6	9.8	43	53.9	3.2	0.1	0.2	<.1	<0.5
JKP28 Al norm.	0.045	5.09	2.2	9.68	12.14	0.72	0.023	0.045		
BW6	<.1	159.8	71.7	62	53.6	<.5	0.1	0.2	0.2	2.8
BW6 Al norm.		32.41	14.54	12.57	10.87		0.02	0.041	0.041	0.568
BW4	0.2	41	8.5	72	33.7	0.9	0.1	0.2	<.1	<0.5
BW4 Al norm.	0.042	8.668	1.79	15.22	7.12	0.19	0.021	0.042		
BW3P	0.1	20.1	3.4	53	43.2	0.6	0.1	0.2	<0.1	<0.5
BW3P Al norm.	0.019	3.77	0.63	9.94	8.1	0.11	0.019	0.038		
BW 2P	0.8	46.4	52.5	71	54.4	32.2	0.6	0.3	0.5	5.8
BW 2P Al norm.	0.142	8.24	9.32	12.61	9.66	5.71	0.107	0.053	0.089	1.03
BW4L	6.6	58.1	26.4	81	66.9	34.6	0.5	0.3	0.5	5.7
BW4L Al norm.	1.614	14.2	6.45	19.8	16.35	8.46	0.122	0.073	0.122	1.394
BW3L	34	49.3	81.2	148	52.8	14.8	1	0.3	0.1	3.1
BW3L Al norm.	7.039	10.2	16.81	30.64	10.93	3.06	0.207	0.062	0.021	0.642
BW0	0.1	43.2	11.8	25	15.1	0.9	0.1	0.2	<.1	<0.5
BW0 Al norm.	0.035	15.21	4.15	8.8	5.31	0.31	0.035	0.07		
BUK1	56.2	96.7	59.7	232	212.7	230.3	0.6	0.5	0.2	1.1
BUK1 Al norm.	6.004	10.33	6.37	24.78	22.72	24.6	0.064	0.053	0.021	0.118
BUK BT	14.5	196.4	20.4	116	97	31.4	1.4	0.4	0.2	0.5
BUK BT Al norm.	2.509	33.97	3.52	20.06	16.78	5.43	0.242	0.069	0.035	0.087
BUK3	0.2	63.4	7.9	34	31	2.3	0.1	0.1	<0.1	<0.5
BUK3 Al norm.	0.056	17.85	2.22	9.57	8.73	0.64	0.028	0.028		

Table 1

of the Skalski and Snežnica members (Jaworki Fm.)

Ba	Co	Nb	Rb	U	V	W	Zr	Y	Mn	Cr	TOT/S
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
305.1	32.5	11.8	172.3	2.4	160	2.2	112.5	32	380	100	0.09
37.99	4.04	1.46	21.45	0.299	19.9	0.274	14.01	3.9	47	12	0.006
1314.8	8.1	3.9	54.7	1	65	0.8	37	20.4	2400	40	0.02
481.61	2.96	1.42	20.03	0.366	23.8	0.293	13.55	7.4	879	14	0.004
138.9	9.3	4.4	59.7	0.8	47	1.3	39.7	15.5	770	40	0.01
42.73	2.86	1.35	18.36	0.246	14.4	0.4	12.21	4.769	236	12	0.002
238.2	16.6	17.3	142.9	3.6	167	1.9	131.9	26.7	300	120	0.34
22.68	1.58	1.64	13.61	0.343	15.9	0.181	12.56	2.543	28	11	0.017
339.1	17.6	16.4	126.4	2.8	170	1.9	128.2	21.8	300	100	0.55
33.24	1.72	1.6	12.39	0.275	16.6	0.186	12.56	2.137	29	9	0.029
462.8	42.8	11.2	138.3	5.4	265	2.2	102.9	21.5	230	150	1.34
55.29	5.11	1.33	16.52	0.645	31.6	0.263	12.29	2.569	27	17	0.085
141.5	7.1	5.8	68.8	1.5	72	1	55.9	20.3	697	61	0.01
37.83	1.89	1.55	18.39	0.401	19.2	0.267	14.94	5.428	186	16	0.001
168.9	9.8	6.1	84.7	1.4	64	1.4	57.6	21.2	920	82	0.01
38.04	2.2	1.37	19.07	0.315	14.4	0.315	12.97	4.775	207	18	0.001
162.5	28.3	6.4	103.4	3	192	1.1	63.2	22.1	460	130	0.01
32.96	5.74	1.29	20.97	0.609	38.9	0.223	12.81	4.483	93	26	0.001
158.6	9	8.7	92.1	2.3	103	1.6	102.9	24.2	380	75	0.01
33.53	1.9	1.83	19.47	0.486	21.7	0.338	21.75	5.116	80	15	0.001
521.7	10.4	8.7	106	1.8	87	1.3	78.3	20.2	380	75	0.02
97.88	1.95	1.63	19.88	0.338	16.3	0.244	14.69	3.79	71	14	0.002
439.9	57.4	8	96.2	7.3	185	1.3	77.4	21.1	460	95	1.01
78.13	10.19	1.42	17.08	1.297	32.8	0.231	13.74	3.748	81	16	0.095
438.8	54.1	5.3	77.6	6.8	200	0.9	47.9	20.6	540	95	0.43
107.28	13.22	1.29	18.97	1.663	48.9	0.22	11.71	5.037	132	23	0.056
174.2	20.7	7	97.3	4.3	109	1.3	60.2	20	540	75	0.28
36.06	4.28	1.44	20.14	0.89	22.5	0.269	12.46	4.141	111	15	0.031
268.1	5.1	4.6	52.3	2.2	54	0.8	49.7	17.1	610	41	0.01
94.4	1.79	1.62	18.41	0.775	19	0.282	17.5	6.021	214	14	0.002
661	131.8	12.4	184.5	38.5	263	2.1	109	24.6	230	150	0.12
70.62	14.08	1.32	19.71	4.113	28	0.224	11.6	2.628	24	16	0.007
408.7	68.3	8.3	106.6	9	125	1.7	76.5	21.5	920	82	0.02
70.7	11.81	1.43	18.44	1.557	21.6	0.294	13.2	3.72	159	14	0.002
162.3	8.7	5.3	76.8	1.1	68	1.1	52.3	19.5	610	57	<.01
45.71	2.45	1.49	21.63	0.31	19.1	0.31	14.7	5.493	171	16	

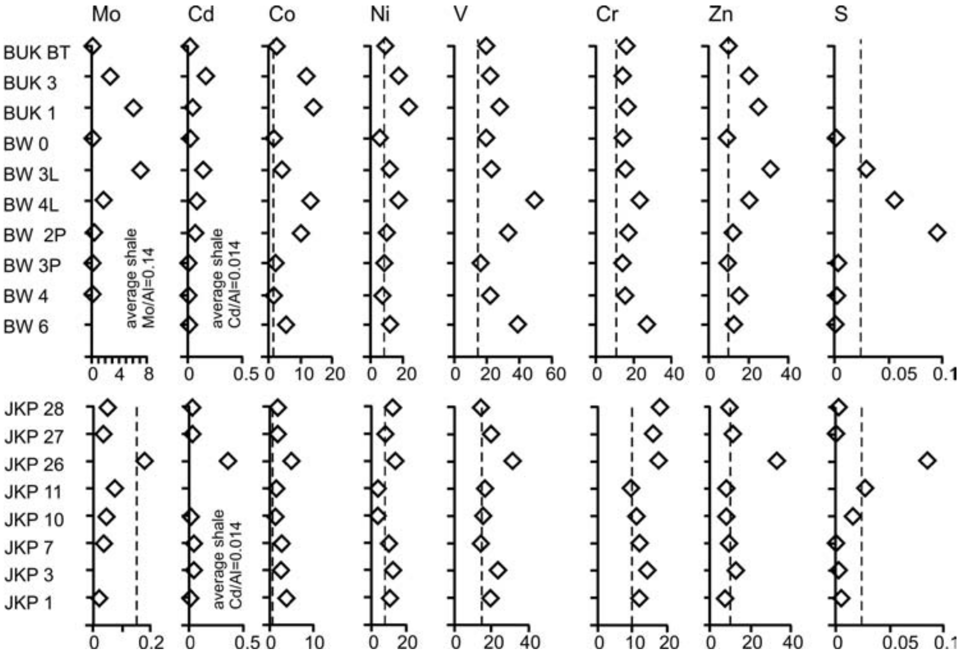

Fig. 4. Distribution of trace elements/Al and S/Al in the Skalski and Snežnica members (Jaworki Fm.) in studied sections of the Niedzica Succession; dashed line – average shale element/Al ratio

shale standard. In contrary to Bi, the measured concentrations of Co and Ni are higher than those in average shale standard (Wedepohl, 1971, 1991). Co and Ni patterns are well correlated and independent on lithology. Some of black shale samples (e.g. JKP 10, JKP 11) appear to be poor in Ni and Co, whereas the others (e.g., light coloured BUK BT) are significantly enriched (Fig. 4).

Within black shales, the Al-normalised concentrations of redox-sensitive metals elements are mostly increased relative to the greenish and red sediments, and relative to the average shale standard (Wedepohl, 1971, 1991). Trace elements are enriched in organic-rich shales due to direct or indirect interactions with organic matter (Mo, V, Ni) or due to precipitation as sulphide minerals (Zn, Pb; Lewan & Maynard, 1982; Morford & Emerson, 1999).

The black shale sample-JKP 26 is enriched in Mo, Cd, Ag, Se, V and Ni associated with high contents of S that suggests a presence of H_2S-containing pore water or even bottom water during deposition and/or during diagenesis of these sediments. Other black shale-samples (JKP 10, JKP 11) contain small amounts of V, Co, Ni and Cd despite of elevated S concentration. The BUK 1 sample shows enrichment in Mo and Ni only, however it contains a small amount of S (Fig. 4, Tab. 1).

The studied samples are generally enriched in Cr and V (Fig. 4; Tab. 1). Their distribution is well-correlated, but without strong relation to distribution of organic matter and/or S. As a redox-sensitive element, Cr can be fixed under reducing conditions because its reduced state is more insoluble than the oxic one (Calvert & Pedersen, 1993). Maximal concentration of Cr and V was noted in the dark grey marls (BW 6 and BW 4L). This indicates another fixation mechanism. Cr resembling behavior of Zr, Nb and Rb correlates to Al_2O_3. This can be explained by the detrital inputs.

Mo is easily reduced under anoxic conditions and precipitates as sulphide, but it can be also adsorbed by organic matter. The Mo/Al ratios are usually coupled to high amount of C org. (JKP 26 and BUK 1 samples). This correlation indicates that organic matter plays a key role in enrichment process by enhancing HS^- production via bacterial sulphate reduction, by providing a substrate for the scavenging of molybdenum as a thiomolybdate species (Adelson *et al.*, 2001; Helz *et al.*, 1996; Lyons *et al.*, 2003). However, poor correlation between Mo/Al ratio and organic matter exists in the JKP 10, JKP 11 samples. The lower Mo enrichments may be related to either type and amount of organic matter present (humic acids typical of terrestrial organic matter, have been shown to be efficient scavengers of Mo) or efficient scavenging of dissolved sulphide by Fe, which limited Mo concentration mechanism (Sageman & Lyons, 2003).

Table 2

Correlation-coefficients (r) of samples for selected major and minor elements

	Values of (r)
Al_2O_3-K_2O	0.829
Al_2O_3-TiO_2	0.971
Al_2O_3-Nb	0.949
Al_2O_3-Rb	0.79
Al_2O_3-Zr	0.876
K_2O-TiO_2	0.747
TiO_2-Nb	0.991
TiO_2-Rb	0.695
TiO_2-Zr	0.932
K_2O-Nb	0.698
K_2O-Rb	0.967
K_2O-Zr	0.739
Nb-Rb	0.659
Nb-Zr	0.930

Differences in the type and/or amount of organic matter may also be a key control in the enrichment of the other transitional metals. The normalized concentrations of transitional metals are generally highly linked with organic matter (V, Ni, Zn, U in JKP 26; U, Ni, V in BW 4L; U, Ni, Zn in BUK 1; Fig. 4, Tab. 1). This pattern is not visible in the case of JKP 10 and JKP 11. It is possible, that the samples JKP 10 and JKP 11 contain lower amount of terrestrial organic matter or more reactive iron (Fe^{3+} has one of the strongest affinities for humic acids among the transitional metals; Sholkovitz & Copland, 1981). The extent of adsorption of humic acids to iron oxyhydroxides increasing with decreasing of pH and Fe will outcompete other metals (Zn, Cu) with organic matter (Tipping *et al.*, 2002).

Cd, Ag and Se correlate with nutrient elements in sea-water and can accumulate in the sediment primarily bound to organic carbon (Ndung'u *et al.*, 2001; Bruland, 1980). Good correlation of Se/Al with Mo/Al and S/Al likewise shows the fixation of Se in sediments under reducing conditions as metal-selenides (Masscheleyn *et al.*, 1991). Cd and Ag can form the stable sulphides (Jacobs *et al.*, 1985).

Mo, Cd, Ni, U, Zn, Co coenrichment present in BUK BT sample may be related to diagenetic effects or palaeoenvironmental changes from anoxic to suboxic/oxic conditions. The transition from the black shale horizon to the red marls is marked by pronounced concentration peaks of trace elements also in JKP 3 (Zn, Ni, V, Ba, Y) and BW 2P (Cd, Se, Ag, S; Fig. 4, Tab. 1). However, JKP 3 sample consists of enhanced amount of CaO. It may indicate a higher bio-productivity. The BW 2P sample is S-enriched, therefore presence of sulphide-forming metals is understandable.

CONCLUSIONS

On the basis of geochemical features, the lithological variation in the Jaworki Fm may be related to depositional environments. The studied sections are predominated by pelagic/hemipelagic facies. This finds confirmation in chemical composition of the studied material. The bulk of samples contain terrigenous-detrital matter, but in negligible amounts only.

The black shale deposition on submarine slope of the Pieniny Klippen Basin in the Niedzica Succession corresponds to productivity-related oceanic anoxic event (p-OAE, cf. Erbacher *et al.*, 1996). Organic carbon-rich sediments were formed due to abundant organic supply. The p-OAEs were triggered by the leaching of nutrients from coastal areas that resulted in productivity increase.

The studied sediments was probably deposited under oxic/suboxic condition beneath the OMZ; however sporadic, short-time anoxic conditions cannot be excluded. Bacterial decomposition of OM producing H_2S allowed to enhance the OM preservation and accumulation of sulphide-forming metals. Alterations in redox sensitive elements observed between black shales and other lithotypes of the studied sections are consistent with key role hypothesized for H_2S in element fixation by organic matter. Enrichments in this matter were probably due to scavenging within sulphide-rich pore fluids. Trace elements enrichment may also be related to diagenetic effects.

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