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PELAGIC SEDIMENTS OF THE CARPATHIAN FLYSCH AND OCEANIC DEPOSITS: A COMPARATIVE STUDY

(5 Figs.)

Badania porównawcze osadów pelagicznych z fliszu karpackiego i obszarów oceanicznych

(5 fig.)

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A b s t r a c t: The present study is an attempt to compare synchronous calcareous sediments of the Flysch Carpathians with oceanic deposits ranging from Cretaceous to Miocene in age. The comparison was carried out on the basis of mineral and chemical composition of sediments, as well as concentrations and mutual correlations of trace elements, accumulated mainly due to biochemical processes – by means of phytoplankton. Participation of the latter organisms in enriching the sediments in microelements was evidenced by their high concentrations in bitumen ashes and by correlation analysis. Geochemical and mineralogical analogies were observed between some synchroneous sediments (Aptian–Albian, Campanian–Maastrichtian) whereas Palaeocene oceanic deposits could be correlated only with Carpathian biogenic calcareous intercalations in Upper Eocene and Oligocene deposits. Moreover, a good correlation was found between geochemical characteristics of Miocene deposits and coeval diatomites of the Carpathian Flysch.

K e y w o r d s: geochemistry, pelagic sediments, flysch, oceanic deposits, Carpathians.

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T r e ś ć: Przeprowadzone badania miały na celu porównanie równowiekowych osadów (kreda – miocen) z fliszu karpackiego i obszarów oceanicznych. Badania porównawcze zostały oparte przede wszystkim na występowaniu pierwiastków śladowych związanych z procesami biochemicznymi planktonu, a także na składzie mineralnym i chemicznym. Pewne podobieństwa zostały zaobserwowane pomiędzy równowiekowymi osadami aptu i albu oraz kampanu i mastrychtu. Badane paleogeńskie osady oceaniczne mogą być porównywane jedynie z biogenicznymi, wapiennymi wkładkami w osadach górnoeoceńskich i oligoceńskich Karpat, natomiast dobra korelacja występuje pomiędzy równowiekowymi diatomitami obu regionów.

INTRODUCTION

Recent geochemical studies of sedimentary rocks of the Carpathian Flysch have shown vertical differentiation of chemical and mineralogic composition of these sediments ranging from Jurassic to Oligocene in age (Gucwa, 1977; Gucwa, Wieser, 1980). This differentiation consists in abrupt changes of the content of trace elements (V, Mo, Zn, Cu, Cr), as well as in age-dependent variation of their mutual relationships (Gucwa, Ślączka, 1972).

The Carpathian Flysch sediments are compared with oceanic deposits, to find similarities in their chemical and mineralogic composition. Moreover, geochemical variability of oceanic deposits with time was compared with that of the Carpathian sediments.

All the availeble oceanic deposits were calcareous in character. Therefore, for comparison purposes only sediments rich in calcium carbonate were chosen from respective horizons of the Carpathian Flysch. It is important to compare material of similar chemical composition, since the interpretation of enrichment process in trace elements permits to concentrate on one group of enriching factors. Such factors are: 1) selective accumulation of microelements by absorption on different argillaceous minerals (Hirst, 1962) and 2) their selective concentration by various kinds of phytoplankton (Harvey, 1939; Black, Mitchel, 1952; Aron, Wessels, 1953; Aron *et al.*, 1955; Wort, 1955; Martin, Knauer, 1973; Epstein, 1972; Fortescue, 1979; Lokin, 1979 and others), especially by the rock-forming one (Gucwa, 1975). This causes accumulation of similar metals in sediments of the same mineral composition. On the other hand the differentiation observed in trace elements contents may result from the presence of various kinds of phytoplankton which selectively use different elements and thus change their proportions (Gucwa, Ślączka, 1980). Consequently biogenic deposits which have originated by phytoplankton accumulation contain metals in the form of organometallic compounds characteristic for the Chlorophyta.

THE STUDIED MATERIAL

The samples under study come from the Carpathian Flysch sediments[1] representing deposits ranging from Albian to Miocene in age. Clayey deposits rich in calcium carbonate and calcareous deposits, considered to be autochthonous, on the ground of their structural characteristics, and comparable with oceanic ones, have been selected for the present study (Table 1). Altogether, 137 samples were analyzed, on the basis of which the average chemical composition was computed for respective stratigraphic horizons.

Sixteen oceanic samples used for comparison were collected from boreholes in the Atlantic, Indian and Pacific Oceans (Fig. 1), and supplied through the assistance of the National Science Foundation, the Curators of Deep Sea Drilling

[1] The samples come from the Polish Carpathians exclusively, except of a part of Tylawa Limestones from the Slovakian Flysch Carpathians.

Table 1

Sample location
Lokalizacja próbek

Carpathian Flysch samples			Oceanic samples						
	Sample no.	Age	Leg	Hole	Core	Section	Sampled at m	Sample no.	Age
Middle Lgota Beds	I	Aptian – Albian	14	144	7	1	141 – 143	1	Upper Aptian – Albian
			14	144	5	1	97 – 99	2	Upper Aptian – Lower Cenomanian
Siliceous Marls	II	Turonian – – Senonian	14	144	4	2	127 – 129	3	Upper Cenomanian – Lower Turonian
			14	144	3	2	126	4	Upper Cenomanian – Lower Maastrichtian
			14	144	2	3	121 – 123	5	Upper Palaeocene
Hieroglyphic Beds	III	Middle Eocene	21	206C	18	3	120 – 122	6	Middle Eocene
			21	206C	16	1	104 – 106	7	Middle Eocene
			21	206C	18	1	13 – 15	8	Middle Eocene
Globigerina Marls	IV	Upper Eocene	23	223	31	4	100 – 102	9	Upper Eocene
			21	206C	15	2	86 – 89	10	Upper Eocene
Menilitic Beds	V	Eo-Oligocene	14	144A	1	2	70 – 72	11	Lower Oligocene
Siliceous Marls (from Menilitic Beds)	VI	Oligocene	23	223	31	1	62 – 64	12	Lower Oligocene
Tylawa Limestones (from Menilitic Beds)	VII	Oligocene							
Tylawa Limestones (from Menilitic Beds of Slowakia)	VIII	Oligocene							
Krosno Beds	IX	Oligocene	21	206C	10	6	51 – 53	13	Middle Oligocene
Jasło Limestones (from Krosno Beds)	X	Oligocene	21	206C	8	1	13 – 45	14	Upper Oligocene
			21	206C	2	1	111 – 113	15	Lower Miocene
Diatomites (from Krosno Beds)	XI	Oligocene – – Miocene	23	223	19	4	132 – 134	16	Middle Miocene

Each sample I, II, III ... etc consist of several individual samples – see Table 2

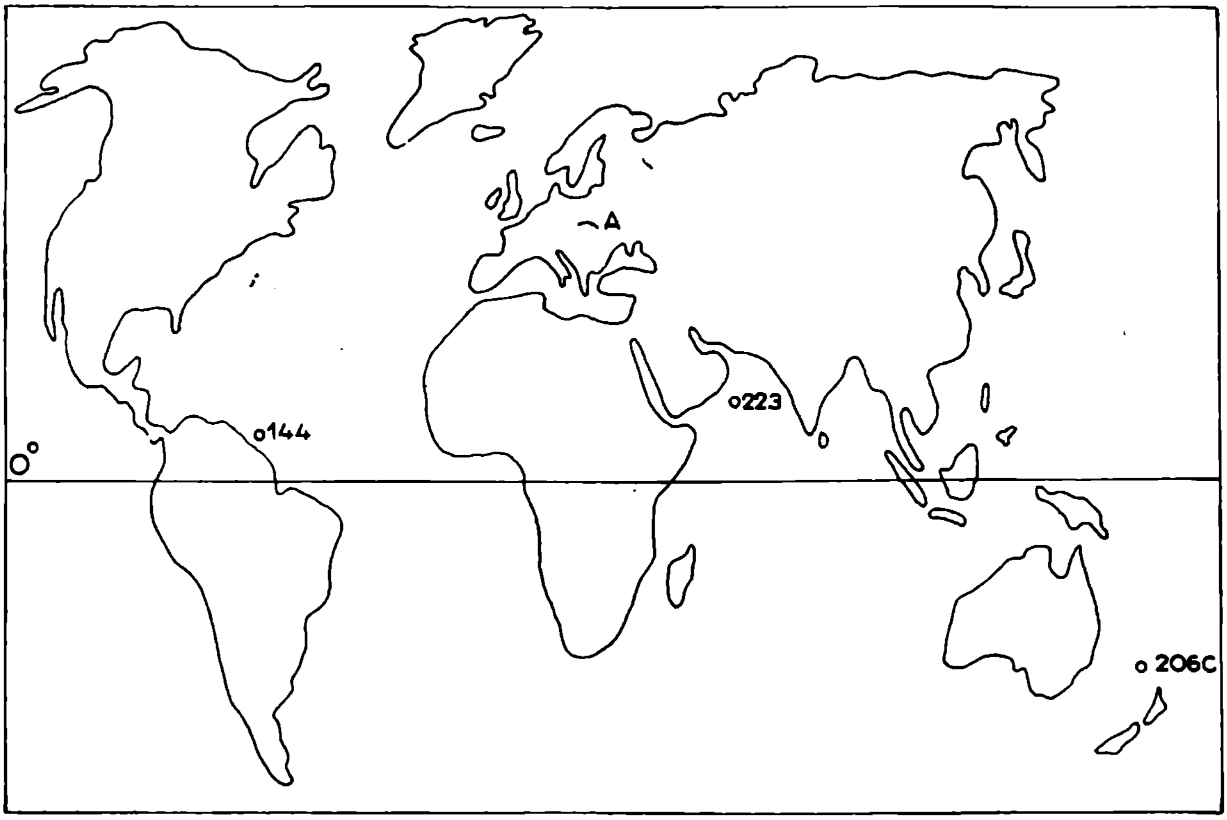

Fig. 1. Location map of oceanic sampling sites
Fig. 1. Lokalizacja prób z obszarów oceanicznych

Table 2

Chemical analyses of the Carpathian Flysch sediments (in weight percent)
Analizy chemiczne osadów fliszu karpackiego (w procentach wagowych)

Sample no.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	S	bitu-mèn A	C_{org}	Number of samples
I	64.33	0.40	6.04	7.43	6.02	0.31	4.74	0.28	0.07	1.39	4
Ia	65.22	0.49	11.49	7.30	3.01	0.42	1.95	0.64	0.07	1.32	12
II	51.90	0.09	3.26	2.10	21.62	0.53	16.95	0.17	0.08	0.59	16
III	55.68	0.45	16.11	5.60	6.71	1.46	5.19	0.37	0.11	1.19	10
IIIa	58.26	0.50	17.44	8.28	3.94	1.23	2.53	0.38	0.10	1.56	22
IV	40.38	0.39	8.73	10.02	18.47	n.d.	15.96	0.08	0.05	2.19	17
V	51.93	0.43	12.19	5.06	9.66	1.30	7.75	1.43	0.18	1.79	20
IVa	46.83	0.48	10.90	10.01	10.71	–	8.20	0.09	0.03	1.70	22
Va	54.02	0.50	14.00	6.62	5.46	1.24	3.57	1.57	0.19	2.57	47
VI	51.33	0.29	5.75	2.42	19.00	0.67	16.41	0.54	0.17	1.91	2
VII	16.56	0.09	0.92	3.17	42.32	0.12	33.23	0.55	0.19	0.87	3
VIII	27.61	0.21	3.50	2.82	34.21	1.00	27.25	0.25	0.13	0.52	5
IX	49.05	0.55	13.33	8.86	8.57	2.17	6.58	0.83	0.09	1.28	35
X	10.91	0.06	1.21	3.70	39.84	1.13	31.27	0.23	0.09	0.47	12
IXa	49.32	0.55	13.50	8.90	8.25	2.21	6.31	0.86	0.09	1.28	44
XI	76.75	0.11	5.62	7.23	0.70	n.d.	–	0.59	0.22	n.d.	13

I, II, III ... average data for calcareous sediments
Ia, IIIa ... average data for calcareous and non-calcareous sediments
Symbols of samples as in the Table 1

Table 3

Chemical analyses of oceanic sediments (in weight percent)
Analizy chemiczne osadów oceanicznych (w procentach wagowych)

Sample no.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	S	bitument A	C_{org}
1	41.04	0.61	4.86	7.20	21.75	2.12	17.07	0.40	0.16	1.62
2	32.59	0.45	8.14	9.62	21.68	1.49	17.07	0.83	0.10	2.06
3	19.91	0.18	–	4.72	33.86	1.83	26.58	1.30	1.14	5.75
4	32.25	0.30	–	5.80	27.53	1.07	21.61	0.25	0.36	3.74
5	33.48	0.33	2.90	5.79	25.70	1.34	20.17	0.31	0.33	3.70
6	27.18	0.18	1.37	2.53	26.39	0.28	20.71	0.15	0.20	1.70
7	19.36	0.14	1.16	2.86	39.64	0.47	31.11	0.13	0.41	1.21
8	19.01	0.15	1.80	2.23	37.19	0.60	29.19	0.11	n.d.	2.17
9	28.10	0.70	5.73	12.01	22.76	2.15	17.86	0.86	0.59	2.00
10	27.80	0.17	2.35	2.86	31.44	0.94	24.68	0.16	n.d.	1.86
11	19.53	0.31	3.44	5.20	35.70	0.99	28.02	0.52	0.59	0.85
12	19.70	0.55	3.70	7.00	33.57	1.40	26.39	0.41	0.14	2.04
13	17.80	0.29	–	5.84	38.50	0.77	30.22	0.15	n.d.	1.55
14	25.34	0.25	2.25	4.66	31.70	0.86	24.93	0.21	n.d.	1.21
15	14.25	0.28	1.45	3.17	39.50	0.77	31.00	0.14	0.22	1.41
16	42.55	0.44	8.18	6.97	18.99	2.57	14.90	0.51	n.d.	3.18

Symbols of samples as in the Table 1

Table 4

Trace elements contents in the Carpathian Flysch sediments (in ppm)
Zawartości pierwiastków śladowych w osadach oceanicznych (w ppm)

Sample no.	V	Mo	Cu	Zn	Cr	Ni	Mn
I	62	10	114	13	10	12	176
Ia	50	3	436	10	108	24	260
II	–	3	102	16	14	8	580
III	58	28	1200	123	310	52	990
IIIa	80	18	1020	133	253	77	1027
IV	15	2	29	40	127	34	690
IVa	16	1	35	40	157	59	434
V	112	24	566	202	155	69	438
Va	186	35	404	126	175	72	493
VI	–	19	97	10	82	32	400
VII	–	103	260	16	28	23	1315
VIII	–	37	440	5	47	39	960
IX	48	5	310	48	326	67	684
IXa	51	5	300	48	317	67	656
X	–	28	62	8	31	17	1013
XI	92	–	32	12	42	23	105

Symbols of samples as in the Table 1 – below detection limit

Projects from Scripps Institution of Oceanography, La Jolla, California, and the Lamont Doherty Geological Observatory of the Columbia University, Palisades, New York. The locations of sampling sites are as follows: site 206 – New Caledonia Basin, site 223 – SEE of Muscat and Oman, site 144 – Demara Rise (Table 1).

The samples were analysed for both major and trace elements. The major elements (Table 2 and 3) were determined gravimetrically, according to classical silicate analytical methods. The trace elements (Table 4 and 5) were determined by colorimetric methods (Sandell, 1959), the limit of errors is reported by Gucwa (1973). C_{org} and A-bitumen determinations were performed after 40 hrs extraction of the sample with chloroform in Soxhlet apparatus. Bitumen determination was carried out according to Wrighton's (1949) method.

Table 5

Trace elements' contents in oceanic sediments (in ppm)
Zawartości pierwiastków śladowych w osadach oceanicznych (w ppm)

Sample no.	V	Mo	Cu	Zn	Cr	Ni	Mn
1	40	16	167	6	609	34	273
2	133	12	211	17	456	17	206
3	1005	467	226	17	198	92	tr.
4	tr.	7	190	13	54	23	222
5	tr.	71	94	8	73	28	907
6	tr.	tr.	130	4	tr.	19	1405
7	tr.	150	198	7	tr.	16	154
8	tr.	86	160	7	tr.	26	175
9	tr.	17	223	8	173	47	380
10	tr.	45	140	4	12	10	910
11	–	36	110	39	52	13	222
12	tr.	32	273	21	115	11	356
13	tr.	91	96	15	21	19	93
14	tr.	94	138	5	25	12	136
15	tr.	27	146	8	24	21	356
16	119	tr.	398	44	323	50	1247

Symbols of samples as in Table 1; – below detection limit, tr. - traces

PETROGRAPHIC CHARACTERISTICS OF THE SEDIMENTS

CARPATHIAN FLYSCH SEDIMENTS

Clayey-calcareous intercalations in Albian sediments (central part of the Lgota Beds – for lithostratigraphy of the Carpathian Flysch see Książkiewicz 1956) are represented by calcilutites showing micrite and fossiliferous-micrite texture, rich in argillaceous minerals and occasionally quartz (up to 20%). Among organic remains there were found foraminifera (up to 10%), sponge spicules (1 – 10%) and diatoms. In the argillaceous minerals assemblage (Gucwa, Wieser, 1980) prevailed illite being accompanied by mixed-layer illite-montmorillonite.

Turonian siliceous marls are fine-grained siliceous calcarenites displaying biomicrite texture – containing foraminifera (ca. 30%), sponge spicules (up to 20%) and radiolarians (0 – 10%) – and calcilutites of fossiliferous-micrite texture, containing foraminifera (up to 10%) and sponge spicule (3 – 5%). Microscopic examination revealed some cryptocrystalline silica which might be almost entirely derived from calcitization of siliceous sponge spicules (Gucwa, Wieser, 1980). Among argillaceous minerals constituting negligible percent of the sediments (Fig. 2), there occurs montmorillonite, accompanied by mixed-layer illite-montmorillonite mineral.

Middle Eocene calcareous sediments (the Hieroglyphic Beds) are represented by laminated calcareous mudstones containing considerable admixture of terrigen-

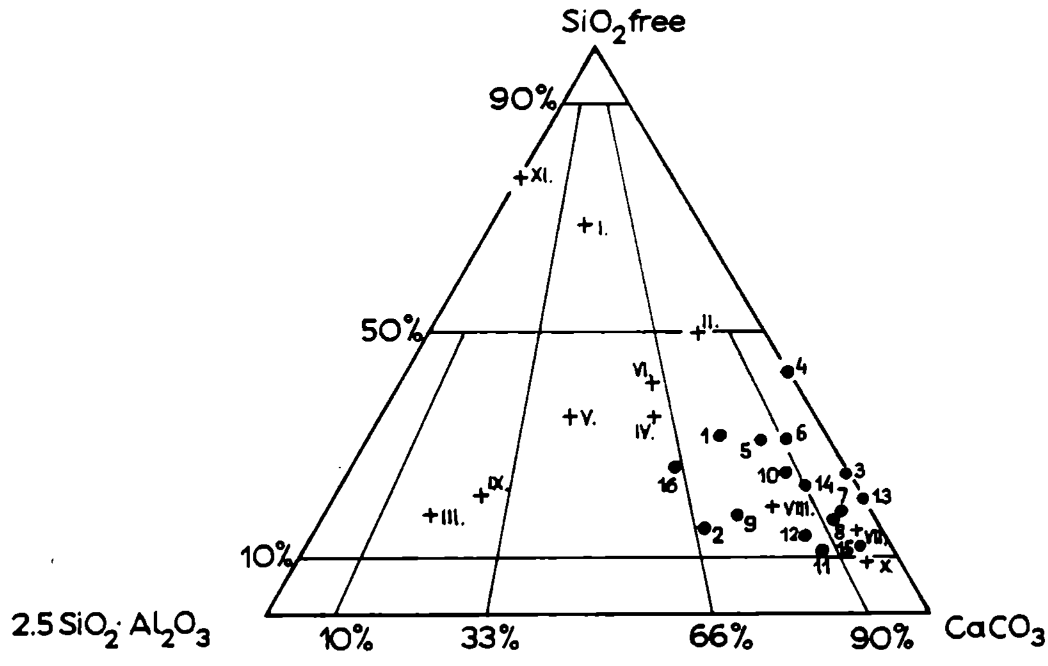

Fig. 2. Chemical composition of the examined sediments
I – XI samples of sedimentary rocks from the Carpathian Flysch, 1 – 16 samples of oceanic pelagic deposits

Fig. 2. Skład chemiczny badanych osadów
I – XI próbki z fliszu karpackiego, 1 – 16 próbki z pelagicznych osadów oceanicznych

ous material, in which foraminifera content does not exceed 1%. Montmorillonite has not been found in the argillaceous minerals assemblage (Gucwa, Wieser, 1980), whereas kaolinite is a constant component of these sediments.

Upper Eocene calcareous sediments (Globigerina Marls) are represented by calcilutites showing fossiliferous micrite and occasionally biomicrite texture, among which foraminifera (up to 15%) and quartz (up to 10%) have been observed. These sediments are bioturbated. Illite and kaolinite represent argillaceous minerals.

Calcareous intercalations in Lower Oligocene sediments (siliceous marls and Tylawa Limestones) are represented by thin calcilutite layers showing micrite texture and distinct fine lamination with small content of foraminifera (up to 3%) as well as by similar calcilutites entirely free of foraminifera. A constant admixture of pyroclastic material transformed into montmorillonite and cristoballite has been found in these sediments (Gucwa, Wieser, 1980).

Upper Oligocene sediments (shales from the Krosno Beds) are represented by calcareous mudstones containing up to 40% quartz, 5 – 10% mica and clay minerals, and 40 – 50% calcite and limestone fragments. In these sediments there occur intercalations of laminated and non-laminated calcilutites displaying biomicritic texture (Jasło Limestones). Moreover, these sediments contain diatomaceous shales and diatomites with numerous well-preserved diatoms. As regards argillaceous minerals, only illite is a constant and prevailing component of these sediments.

OCEANIC DEPOSITS[2]

Late Aptian – Albian sediment is represented by carbonaceous clays containing 20% quartz, whilst late Albian – early Cenomanian one by marls with small content of nannofossils (5%). Late Cenomanian – early Turonian deposits are zeolitic calcareous clays containing foraminifera (20%) and nannofossils (10%) whereas late Cenomanian – early Maastrichtian one – are slightly zeolitic calcareous mudstones with foraminifera (5%) and nannofossils (5%). Paleocene sediment is represented by nannofossil chalk ooze rich in foraminifera (20%) and radiolarians (10%) with clays (ca. 10%). Eocene sediments in site 206C are nannofossil ooze rich in radiolarians (up to 35%) and also containing foraminifera (up to 10%) and diatoms (up to 10%). In the site 144 there occurs nannofossil chalk ooze rich in foraminifera (25 – 40%) with clays minerals, whilst in the 223 one there are detrital silty clays rich in nannofossils (70%). Oligocene sediments in site 206C are represented by clays rich in nannofossil ooze with foraminifera (up to 5%) and sponge spicules (up to 3%) moderately mottled and burrowed; in site 223 – by white nannofossil chalk with silty clays and micarb particles (carbonate content ca. 80%). Miocene sediments in site 223 are represented by bioturbated detrital silty clays rich in diatoms (up to 60%) with nannofossils (13%) and radiolarians (5%), while in site 206 – by moderately mottled clays rich in nannofossils (up to 60%) but poor in foraminifera (up to 5%).

GEOCHEMICAL CHARACTERISTICS

CARPATHIAN FLYSCH SEDIMENTS

On the ground of trace elements concentrations and chemical composition (Tables 2 – 5) the Albian sediments (central part of the Lgota Beds) can be regarded as siliceous marls (Fig. 2) with the average SiO_2 content 64.33% and that of $CaCO_3$ – 10.73%. They are rich in molybdenum but poor in chromium (Table 3) when compared with other sediments, including non-calcareous ones of the Lgota Beds. The enrichment in molybdenum of central part of the Lgota Beds distinguishes it from the underlying sediments and the overlying part of these beds. Enrichment of calcareous varietes of the Lgota Beds in molybdenum, similarly to the remaining calcareous sediments in the Flysch Carpathians may be due to the presence of calcareous algae which use this metal as a catalyzer in their metabolic processes (Aron *et al.*, 1955). Another evidence supporting such an explanation is the high correlation coefficient Ca:Mo (r = 0.80). On the other hand, the fact that calcareous varieties of the Lgota Beds are poor in chromium is connected with lower content of argillaceous minerals in them (*cf.* Al content in Table 2). Direct relationship between argillaceous minerals and chromium is shown by high correlation coefficient Al:Cr (r = 0.86) in these sediments.

[2] Description based on Initial Reports of the Deep Sea Drilling Project, vol. XIV, XXI, XXIII.

Turonian siliceous marls are very typical as regards their chemical composition (Fig. 2). They are relatively rich in molybdenum but very poor in vanadium. Very low content of the latter metal in these sediments differs them from underlying Lower Cretaceous members (the Lgota Beds, Verovice Shales). Relatively low molybdenum content in distinctly calcareous sediments may be explained by the fact that only a part of $CaCO_3$ can be derived from calcareous phytoplankton (*cf.* low bitumen content in the rock, Table 2), whereas the remaining part was formed by calcitization of locally preserved sponge spicules. The chromium content is as low as in the Lgota Beds and correlates with small admixture of argillaceous minerals (Fig. 2).

The carbonate variety of the Middle Eocen Hieroglyphic Beds represents a siliceous-marly sediment with the average SiO_2 content 55.68% and $CaCO_3$ – 11.90%. These sediments differ from those of the underlying stratigraphic horizons by high mean contents of Mo (28 ppm) and Cu (1200 ppm). Moreover, these sediments are rather rich in Mn (Table 4). The enrichment both in Cu and in Mn can be related to submarine exhalations. High Cr concentration is connected with significant admixture of argillaceous minerals. Besides, there is observed considerable amount of Zn which, together with kaolinitic character of argillaceous minerals, may indicate rather large admixture of organic terrestial material. Apart from that, calcareous algae also contributed largely to the organic material of the sediments, this fact being supported by high positive correlation coefficient both of Mo: A-bitumen ($r = 0.59$) and Mo: Ca ($r = 0.48$). This rich in trace element assemblage is a distinguishing feature of the Middle Eocene sediments of the Flysch Carpathians geosyncline.

Upper Eocene sediments, represented by Globigerina Marls differ from the Middle Eocene ones in lower SiO_2 content amounting, on the average, to 40.38%, and in the increased $CaCO_3$ content, qualifying them as marls and siliceous marls (Fig. 2). Similarly to Turonian siliceous marls, these sediments contain – on the average – minute amounts of A-bitumens and molybdenum. On the other hand, despite similar chemical composition, the above mentioned stratigraphic horizons are distinguished by higher concentrations of vanadium in the Globigerina Marls. This is most probably connected with the occurrence of siliceous phytoplankton (siliceous Flagellata). However, minute average amounts of molybdenum and – at the same time – high $CaCO_3$ content point rather to zoogenic than phytogenic concentration of the latter. This is supported by high positive Ca: C_{org} correlation ($r = 0.66$), and lack of Ca: Mo correlation. The only exceptions in the Globigerina Marls horizon are intercalations of calcareous sediments, strongly bituminous and, at the same time, rich in Mo (up to 27 ppm), which originated by accumulation of calcareous algae (Gucwa, Ślączka, 1972).

On the basis of their mean chemical composition calcareous sediments found in the Oligocene Menilitic Beds be classified as siliceous marls with the average SiO_2 content 51.33% and $CaCO_3$ – 35.41%. Apart from increased molybdenum content (24 ppm), they are enriched in other trace metals as V, Zn, Cu connected with presence of siliceous phytoplankton, brown algae and blue-green algae, as well as siliceous Flagellata (Table 4). Such enrichment of the above mentioned trace metals is the distinctive feature of these sediments (Gucwa, Wieser, 1980). The presence, both of diatoms and brown algae (Jerzmańska, Kotlarczyk, 1975), as well as of calcareous phytoplankton in these sediments has been confirmed by microscopic observations.

The examined deposits of the Krosno Beds are almost entirely marly. They are rich both in molybdenum and in the remaining biofile metals such as vanadium, copper and zinc, though to smaller degree than the underlying Menilitic Beds. This is connected with a decreased bitumen content in the Krosno Beds (Table 2). In the Menilitic Beds, intercalations of siliceous limestones are observed, known as Tylawa Limestones. They are biogenic sediments containing a characteristic microelement assemblage rich in molybdenum and very low in vanadium (Table 4). The Jasło Limestones, structurally similar to the previous one, (mean content of $CaCO_3$ – 71.11%) but developed within the Krosno Beds, contain microelement assemblage similar to that of the Tylawa Limestones. Molybdenum was found to be positively correlated with A-bitumen (r = 0.50). High positive correlation of Mo and Cu with A-bitumen (r = 0.90) suggests biogenic character of these sediments. It was confirmed by microscopic analysis which show that Jasło Limestones originated by accumulation of calcareous algae (Nowak, 1965).

Apart from sporadic intercalations of calcareous algae deposits in the upper part of the Krosno Beds (Miocene) are observed diatomites impoverished in molybdenum but enriched in vanadium. Positive good correlation with A-bitumen (r = 0.89) is stated.

OCEANIC DEPOSITS

As regards their chemical composition, the oceanic deposits (samples 1 – 16, Table 1) can be regarded as siliceous limestones, siliceous-marly limestones and siliceous marls (Fig. 2). Unlike as in the Carpathian geosyncline, no visible differences in the macroelements content dependent on stratigraphic position were found in them; among these oceanic deposits Lower Cretaceous and Miocene sediments with increased SiO_2 content, when compared with Paleogene ones can be distinguished. Siliceous limestones are prevailing there; they contain 14.15 – 35.25% SiO_2 and 57.10 – 70.50% $CaCO_3$ and none or little admixture of argillaceous minerals (Table 2). The Paleogene sediments are chemically analogous to Jasło or Tylawa Limestones. The other quantitatively important group is represented by siliceous marly limestones containing 19.53 – 41.04% SiO_2, 38.69 – 63.72% $CaCO_3$ and 2.35 – 8.14% Al_2O_3. One of Miocene deposits is represented by siliceous marls containing 42.55% SiO_2, 33.89% $CaCO_3$ and 8.18% Al_2O_3.

Trace element assemblage is characterized by high vanadium content in Albian to Turonian and Middle Miocene samples (samples no. 1, 2, 3, 16 in Table 5). The vanadium concentration was most probably effected by diatoms which occasionally constitute 60% of the deposit. Apart from the sediments mentioned above, vanadium has been found to occur in trace amounts only. The increased

Cr content is related to sediments richer in Al and is found predominantly in stratigraphic horizons of Albian to Turonian and Miocene ages (Table 5). On the other hand, molybdenum is the constant component of almost all the examined deposits, what can be explained by the fact that they represent biogenic carbonate deposits, rich in bitumens whose prevailing organogenic component is calcareous phytoplankton. However, unlike in some stratigraphic horizons of the Carpathian Flysch, higher concentration of Cu and Zn are not characteristic for them (*cf.* Eocene – Oligocene sediments in Tables 4 and 5).

Organic accumulation of vanadium and molybdenum is shown by high concentrations of these microelements in the ashes of bitumens extracted from the samples. The content of Mo in bitumen ash is up to 27% and that of V up to 3.33% (*cf.* Table 6).

CONCLUSIONS

Although based on a relatively small number of samples, the present study has demonstrated some geochemical similarity of synchronous sediments of the Carpathian Flysch and of oceanic areas. If we consider both the absolute contents of the determined microelements and their correlations (*cf.* Fig. 3 and 4) some analogies can be drawn between Albian sediments (middle part of Lgota Beds) and coeval oceanic deposits (samples 1 and I in Fig. 3 and 4). The above mentioned sediments are characterized by quantitative prevealence of vanadium over molybdenum and presence of zinc. After Lower Cretaceous, paleogeographic changes both in the Carpathian geosyncline and in the investigated oceanic areas took place. Both the Upper Cretaceous sediments (siliceous marls) of the Carpathian Flysch and the Campanian – Maastrichtian oceanic deposits (samples II and 4 in Fig. 3 and 4) are very poor in vanadium and poor in molybdenum, copper, zinc and chromium. Examined Carpathian sediments of Middle Eocene – Oligocene age show similarities, with few exceptions, to oceanic deposits. In the Carpathian Upper Eocene sediments increased amount of molybdenum is observed and the Oligocene sediments contain higher concentration of vanadium, molybdenum, copper and zinc. The above differences can be explained by the fact that Carpathian sediments are predominantly terrigenic-biogenic in character, whereas oceanic deposits – only biogenic. Consequently, accumulation of the microelements in the latter was due to biochemical processes only, while in the Carpathian sediments it was more complex in character. There is, however, a distinct similarity between Palaeogene oceanic deposits and synchronous but entirely calcareous intercalations within the Carpathian Flysch deposits (Jasło Limestones, Tylawa Limestones, siliceous marls of the Menilitic Beds and marly-calcareous Globigerina Marls, Fig. 3 and 4, samples VI, VII, VIII, X and 9 – 14). These sediments, as well as the ashes of bitumens extracted from them, are rich in molybdenum but very poor in vanadium (Table 6).

Regarding the composition of trace element assemblage, the Middle Miocene oceanic deposits can be correlated with the Miocene flysch diatomites (Fig. 3 and

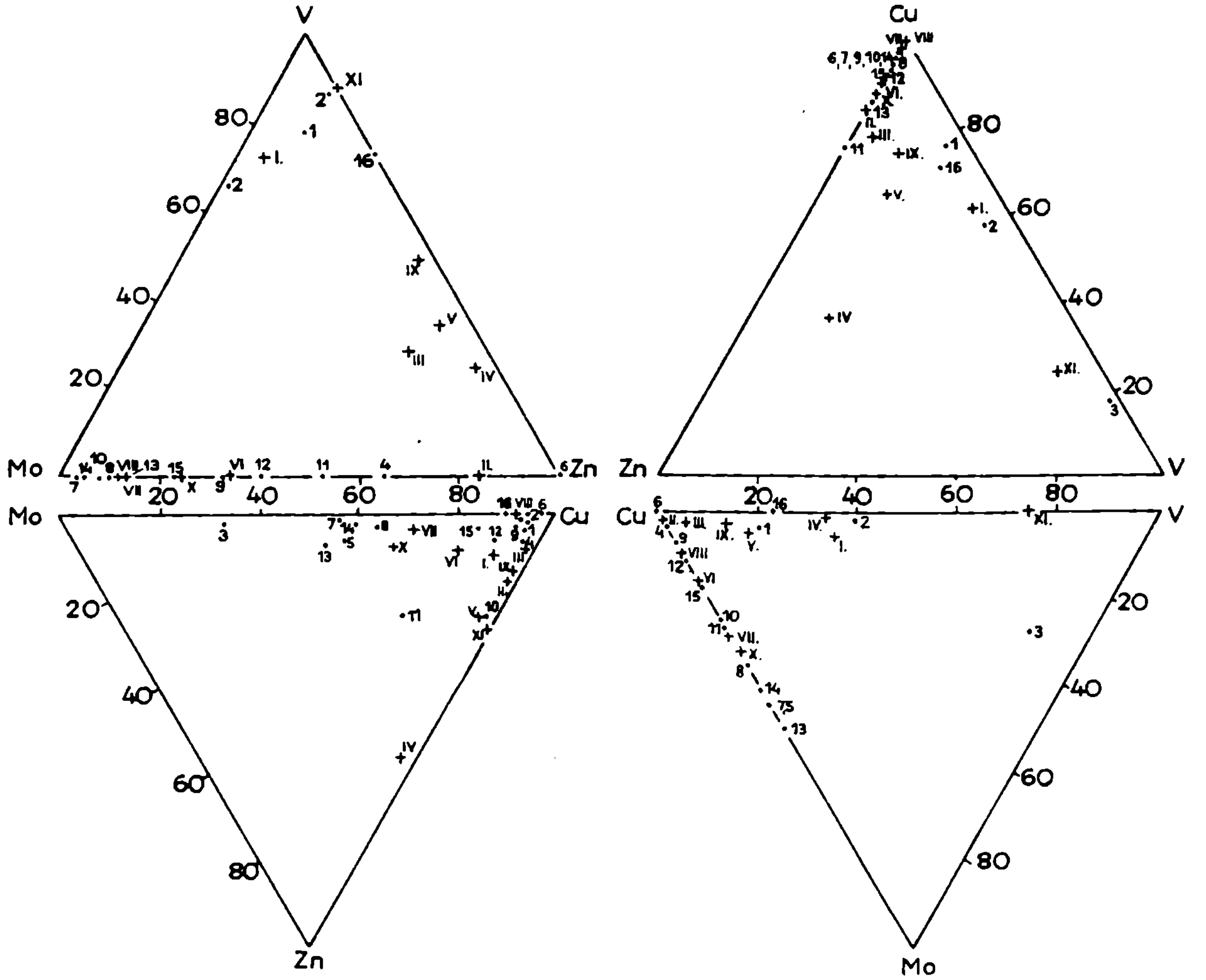

Fig. 3. Triangular presentation of quantitative relations between different trace elements in sedimentary rocks of the Carpathian Flysch (I – XI) and in oceanic deposits (1 – 16)

Fig. 3. Trójkąt przedstawiający ilościowe zależności między badanymi pierwiastkami śladowymi w osadach fliszu karpackiego (I – XI) oraz w osadach oceanicznych (1 – 16)

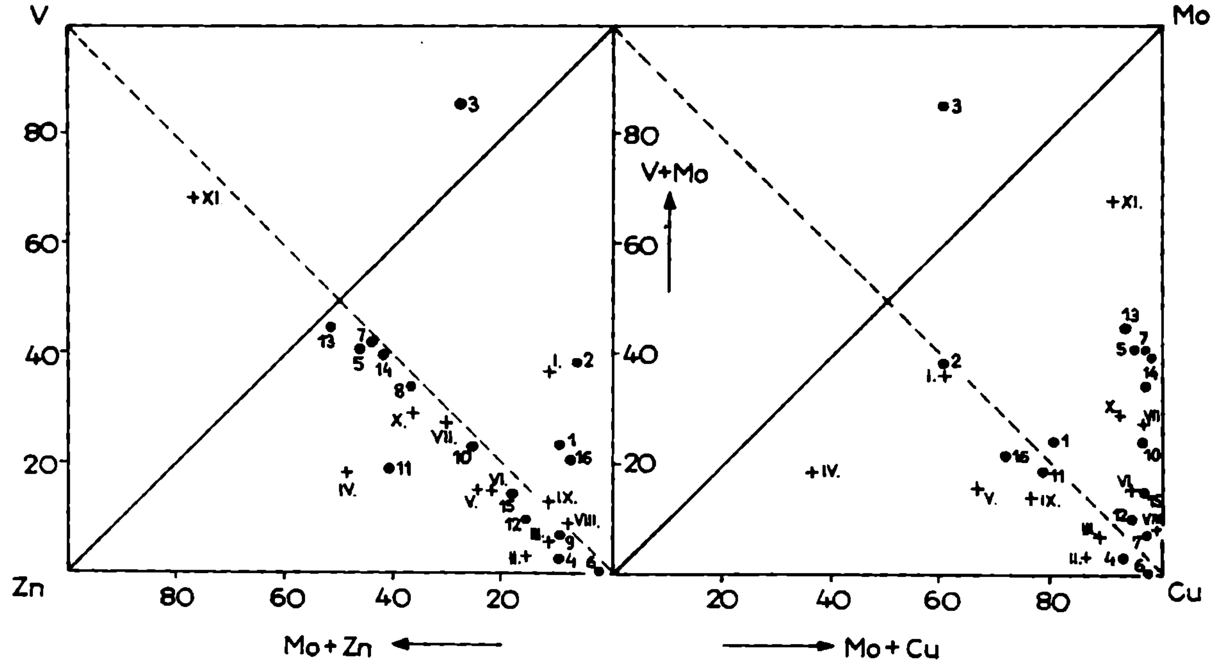

Fig. 4. Relation between the contents of V, Mo, Cu and Zn in sedimentary rocks of the Carpathian Flysch (I – XI) and in oceanic deposits (1 – 16)

Fig. 4. Zależności między udziałem V, Mo, Cu i Zn w osadach fliszu karpackiego (I – XI) oraz w osadach oceanicznych (1 – 16)

Table 6

Concentrations of trace elements in bitumen ashes
Koncentracja pierwiastków śladowych w popiołach bitumicznych

Sample no.	Content of					
	bitumen in sediments (wt %)	ash in bitumen (wt %)	Mo in bitumen (wt %)	Mo in ash of bitumen (wt %)	V in bitumen (wt %)	V in ash of bitumen (wt %)
4, 5, 6, 7, 9, 11, 12, 15	0.21	1.33	0.36	27.0	–	–
1, 2	0.12	4.95	0.81	16.0	990	2.0
3	1.05	3.84	0.91	23.6	1280	3.3
VI	0.22	0.15	0.26	20.0	–	–
VIII	0.24	2.14	0.87	40.6	–	–
X	0.07	2.40	0.72	30.0	–	–

Symbols of samples as in the Table 1

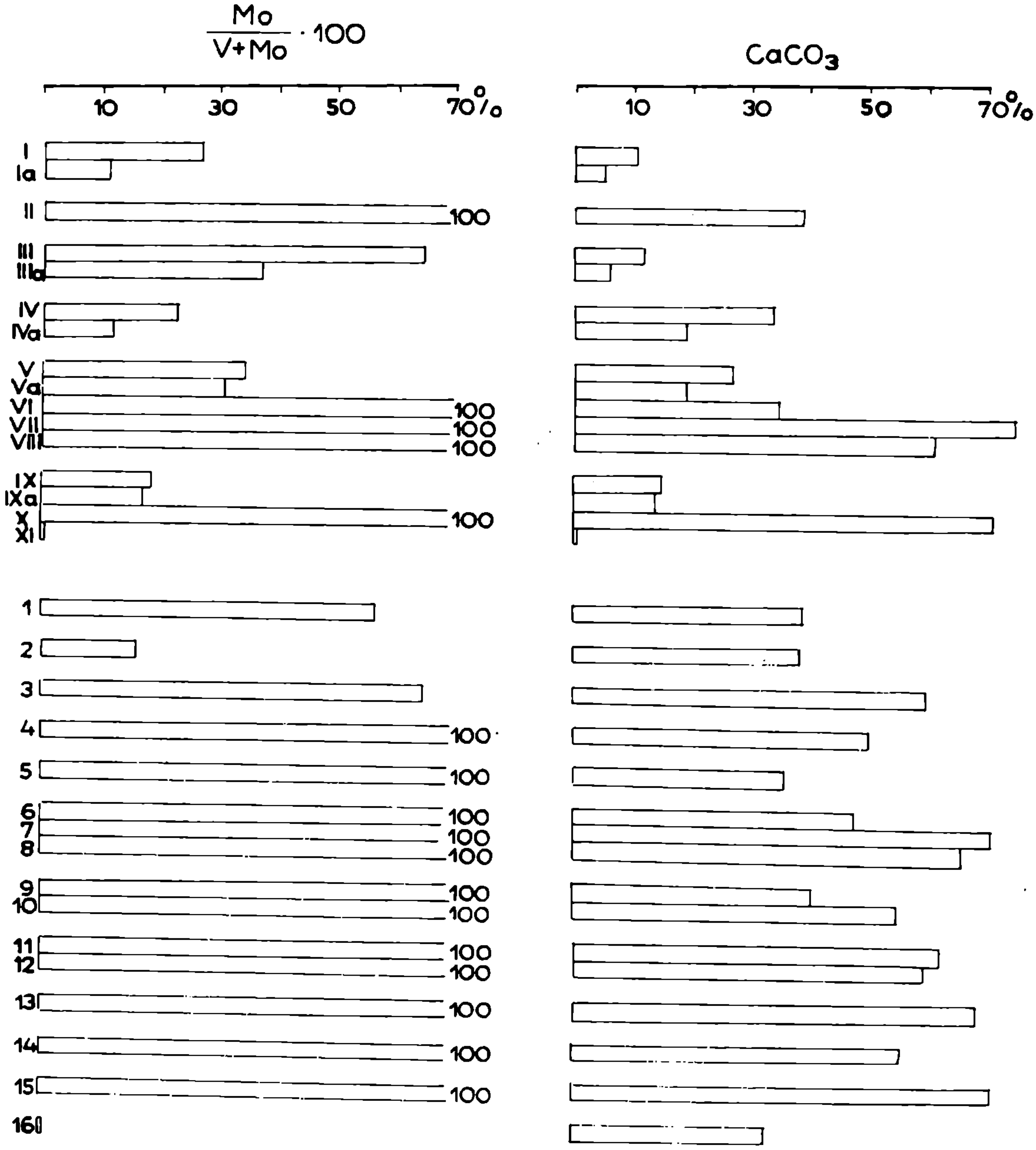

Fig. 5. Mutual relation between $CaCO_3$ content and $\frac{Mo}{V+Mo}$ ratio in sedimentary rocks of the Carpathian Flysch (I – XI) and in oceanic deposits (1 – 16)

Fig. 5. Wzajemna zależność między zawartością $CaCO_3$ a $\frac{Mo}{V+Mo}$ w osadach fliszu karpackiego (I – XI) oraz w osadach oceanicznych (1 – 16)

4, samples XI and 16). These deposits are characterized by very low content of molybdenum and enrichment in vanadium.

Estimated positive correlation of C_{org}:Mo; A-bitumens:Mo and Mo:Ca in the flysch sediments provided evidence for a biogenic origin of molybdenum concentration. An additional support for the above assumption was the detection of high molybdenum concentrations in bitumen ashes, and very low content of vanadium in the Oligocene sediments originated from calcareous phytoplankton, as well as distinct impoverishment in molybdenum and vanadium of the former deposits derived both from calcareous and siliceous phytoplankton.

Mainly biogenic character of $CaCO_3$ concentration, both in the oceanic and in the Carpathian Flysch deposits, is supported by the data presented in Fig. 5, where decrease in $\frac{Mo}{V+Mo} \cdot 100$ ratio is proportional to decrease in $CaCO_3$ content. The highest $CaCO_3$ contents were found in the deposits enriched in molybdenum.

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STRESZCZENIE

Ostatnie badania geochemiczne ilastych skał osadowych polskich Karpat fliszowych wykazały, że ich skład chemiczny i mineralogiczny, a przede wszystkim zawartość biofilnych pierwiastków śladowych wyraźnie zmienia się w czasie. W związku z tym podjęto badania porównawcze z osadami oceanicznymi w celu stwierdzenia, czy podobna zmienność występuje również w tych ostatnich oraz określenia ewentualnego podobieństwa chemicznego osadów z obu badanych obszarów. Próby osadów oceanicznych pochodzą z wierceń wykonanych w ramach Deep Sea Drilling Project (fig. 1, tab. 1). Ponieważ badane osady oceaniczne były reprezentowane przez osady wapienne, więc dla celów porównawczych z fliszu karpackiego zostały wybrane utwory podobnego charakteru (tab. 1).

Przeprowadzone badania, chociaż obejmujące stosunkowo małą liczbę próbek, wykazały, że istnieje pewne podobieństwo geochemiczne równowiekowych osadów fliszu karpackiego i osadów z obszarów oceanicznych. Biorąc pod uwagę bezwzględną zawartość badanych pierwiastków śladowych oraz ich współzależność (fig. 3 i 4), można stwierdzić istnienie pewnych analogii między osadami albu obu regionów. Osady te cechuje ilościowa przewaga wanadu nad molibdenem oraz obecność cynku. Z początkiem górnej kredy nastąpiła wyraźna zmiana na obu obszarach i badane osady kredy górnej, zarówno Karpat fliszowych jak i obszarów oceanicznych, wykazują bardzo małą (poniżej granicy oznaczalności) zawartość wanadu oraz małą molibdenu, miedzi, cynku i chromu. Istnieje również podobieństwo badanych osadów paleogenu, z niewielkimi wyjątkami spowodowanymi przypuszczalnie tym, że osady karpackie są pochodzenia terygeniczno-biogenicznego. W rezultacie akumulacja pierwiastków śladowych w tych ostatnich jest spowodowana przede wszystkim procesami biochemicznymi. Podobieństwo to jest szczególnie wyraźne w przypadku karpackich osadów biogenicznych (fig. 3 i 4, tab. 2–5). Osady oceaniczne środkowego miocenu mogą być korelowane z diatomitami z warstw krośnieńskich pod względem składu badanych pierwiastków śladowych (fig. 3 i 4, tab. 2–5).

Przeprowadzone badania wykazały biogeniczne pochodzenie koncentracji molibdenu oraz głównie biogeniczny charakter węglanu wapnia (fig. 5).