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## Geochemistry of the carboniferous coal-bearing series and the miocene cover within the Upper Silesian Coal Basin – a case study

### Introduction

The geochemistry of major and trace elements in the sedimentary record provides valuable information about the depositional history, the palaeosedimentary environment and the provenance of terrigenous material. Geochemical record variations are applicable to determine the stratigraphy and to correlate drill holes, which is particularly helpful when applied to sequences with poor biostratigraphic control. Even apparently homogeneous sequences exhibit some differences in chemical composition, which make chemocorrelation a commonly usable tool, especially in mining and exploration geology. It is also commonly used as a supplementary tool in palaeontological, palynological, mineralogical and sedimentological research (Pearce et al. 1999; Wei et al. 2003; Pearce et al. 2005; Kombrink et al. 2008; Weis-

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sert et al. 2008; Pearce et al. 2010; Ramkumar et al. 2015; Ratcliffe et al. 2016; Playter et al. 2018; Bayon et al. 2020; Ramkumar et al. 2021). Chemostratigraphy or the study of stratigraphic variations of selected elemental concentrations were initially utilized to document the changes across major chrono, litho and biostratigraphic boundaries or major catastrophic events (Ramkumar et al. 2015, 2021).

Chemostratigraphic studies have been successfully performed for most of the European coal basins (Pearce et al. 1999, 2005, 2010; Kombrik et al. 2008) but so far, chemostratigraphic tools have not been used in the study of the Silesian Coal Basin. The determination of the chemical composition of rocks accompanying coal seams is also important in terms of the storage or potential management of mining waste.

Geochemical research concerning the presence of trace and minor elements in the sedimentary rocks of the Carboniferous coal-bearing series from the USCB has primarily been concerned with rocks from interlayers or from the roof and floor of the coal seams (e.g. Hanak and Kokowska-Pawłowska 2006; Hanak et al. 2011; Kokowska-Pawłowska 2015; Parzentny and Róg 2020). In recent years, geochemical research related to the USCB has mainly focused on the possibility of obtaining critical, especially for rare earth elements from coal, coal ashes, and coal mining waste (e.g. Morga 2007; Strzałkowska 2021, 2022, 2023). Some data about the chemical composition of the Carboniferous coal-bearing series in the SW Part of the Upper Silesian Coal Basin concerning disappearing coal seams in the Upper Silesian Sandstone Series (Ciesielczuk et al. 2021) are presented in the paper. In recent years, geochemical research related to the Carboniferous coal-bearing series of the USCB geochemistry has also focused on the distribution of critical and toxic elements in sedimentary rocks (Krzeszowska et al. 2022; Kokowska-Pawłowska and Krzeszowska 2023).

The Miocene of the USCB, which is the main part of the coal-bearing Carboniferous series overburden, seems to be very well recognized, but there is almost no data available on the geochemistry of this series. Many studies have been conducted on the lithology, sedimentology, structural evolution, and paleoecology of the Miocene sediments within the USCB (e.g. Heliasz and Manowska 1991; Aleksandrowicz 1997; Oszczytko et al. 2006; Oszczytko and Oszczytko-Clowes 2012; Peryt 2013; Majer-Durman 2014; Bukowski et al. 2018; Gonera 2018; Krzeszowska and Gonera 2022). Miocene lithology and geochemistry are very important in terms of methane concentrations in the Carboniferous coal-bearing series, its emissions into mining excavations, and the possibility for safe CO<sub>2</sub> geological storage (Solik-Heliasz 2011; Kędzior and Dreger 2019; Koterias et al. 2020; Sechman et al. 2020).

Impermeable Miocene cover can block the gas emissions into mining excavations and into the atmosphere, and lead to natural gas accumulation (Kędzior and Dreger 2019; Sechman et al. 2020). Therefore, there were three main goals of this study: (1) to investigate the concentrations of the main and trace elements in the sedimentary rocks of the coal-bearing series and the Miocene cover of the USCB; (2) to demonstrate the distribution and stratigraphical variability of the selected elements; (3) to determine whether chemostratigraphy tools could be effectively applied to analyze Carboniferous and Miocene deposits of the USCB.

## 1. Materials and methods

The studied material comes from core samples from the borehole WSx, located in Kryry (near Żory) within the central part of the Upper Silesian Coal Basin. The study is based on geochemical data from 171 samples of the Carboniferous and Miocene sedimentary rocks.

A total of 120 samples from depths of 485–1298 mbs collected from the Carboniferous coal-bearing represent Mudstone Series, Westphalian A, B. It should be mentioned here that the stratigraphy of the WSx borehole has not yet been finally determined. The Mudstone Series includes two lithostratigraphic units, the Załęże Beds and the Orzesze Beds. The Mudstone Series is homogeneous and highlighted primarily by the dominance of fine clastic rocks with economical coal seams (Jureczka and Kotas 1995). In the borehole WSx Carboniferous coal-bearing series is developed as an assemblage of siltstone-claystone sequences with thin sandstone interlayers and siderite concretions.

A total of 51 samples, from depths of 78–484 mbs, represent Miocene (Kłodnica Formation – twelve samples; Skawina Formation – thirty-nine samples). The Miocene succession of the WSx borehole is characterized by high thickness and highly variable lithology. The lowermost part of the Miocene profile, at depths of 484 to 430 m, representing the Kłodnica Formation, consists of light gray clays and claystones, sandy clays, as well as marly clays with marine and brackish fauna remains. On the bottom of this unit, an 8-m-thick brown coal layer has been recognized. The upper part of the Miocene profile, from a depth of 430 m, represents the Skawina Formation. It begins with package gray to dark gray clays and claystones with intercalations of gypsum and carbonate rocks. Above, a package of brown or rusty-red clastic sedimentary rock has been found (Krzeszowska and Gonera 2022). The classification of this part of the profile as the Skawina Formation was determined through preliminary micropaleontological research. However, the exact stratigraphic position of the units described above remains unclear at this stage of the study. The paleontological research, which is in progress, will enable the unambiguous determination of the stratigraphic position of these units.

The highest part of the Skawina Formation (depths of 350 to 28 m) is made up of light gray marly and sandy clays and claystones. An abundant marine fauna of mollusks, foraminifera, and echinoid spines with a variable level of preservation was found in this unit. The Miocene succession is overlaid with Quaternary deposits with a thickness of 28 m composed mainly of sands and gravels (Krzeszowska and Gonera 2022).

Sample preparation and the analytical procedures were performed at the AcmeLab Analytical Laboratory (currently, Bureau Veritas Commodities Canada Ltd.), Vancouver, Canada. The samples were crushed, split and pulverized, with 250 g rock being reduced to a 200 mesh size (0.074 mm). The oxides of major element concentrations ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ , and  $\text{Cr}_2\text{O}_3$ ) were obtained using X-ray fluorescence (XRF) spectrometry and  $\text{Li}_2\text{B}^4\text{O}_7/\text{LiBO}_2$  fusion. The trace elements (Mo, Cu, Pb, Zn, Ni, Co, U, Cr, V, Mn, As, Th, Sr, Cd, Sb, Bi, Ba, Ti, W, Zr, Ce, Nb, Ta, Be

Sc) were analyzed using inductively-coupled plasma mass spectrometry (ICP/MS) following four-acid digestion (HF+HClO<sub>4</sub>+HCl+HNO<sub>3</sub>).

## 2. Results and discussion

### 2.1. Major oxides and chemical classification

The chemical composition of samples from the Carboniferous coal-bearing series and the Miocene cover is slightly different. The major oxides SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the predominant constituents, with contents ranging from 23.50 to 90.18% and 4.68 to 27.28%, respectively, in the Carboniferous, and from 32.55 to 95.79% and 0.62 to 25.32%, respectively, in the Miocene (Table 1, Fig. 1). The concentration of Fe<sub>2</sub>O<sub>3</sub> is diverse, ranging from 1.09 to 32.85% in the Carboniferous and from 0.73% to 15.64% in the Miocene.

Table 1. Content of major oxides in the samples of the Carboniferous and the Miocene deposits from the WSx borehole (USCB, Poland)

Tabela 1. Udział głównych tlenków w próbkach osadów karbonu i miocenu z otworu wiertniczego WSx (GZW, Polska)

Major oxides	Detection level	Carboniferous (Kokowska-Pawłowska and Krzeszowska 2023)			Miocene		
		average value (n = 120)	range of results		average value (n = 51)	range of results	
			min.	max.		min.	max.
Al <sub>2</sub> O <sub>3</sub> (%)	0.01	18.70	4.68	27.28	13.87	0.62	25.32
SiO <sub>2</sub> (%)	0.01	60.60	23.50	90.18	55.45	32.55	95.79
Fe <sub>2</sub> O <sub>3</sub> (%)	0.04	5.00	1.09	32.85	4.87	0.73	15.64
CaO (%)	0.01	0.22	0.06	1.78	6.02	0.04	27.92
MgO (%)	0.01	1.38	0.17	6.79	1.97	0.04	6.94
Na <sub>2</sub> O (%)	0.01	0.57	0.25	1.11	0.76	0.17	1.11
K <sub>2</sub> O (%)	0.01	3.07	0.94	5.69	2.40	0.06	3.43
P <sub>2</sub> O <sub>5</sub> (%)	0.01	0.11	0.02	0.72	0.18	0.03	2.84
MnO (%)	0.01	0.07	0.01	0.35	0.08	0.01	0.31
Cr <sub>2</sub> O <sub>3</sub> (%)	0.002	0.02	0.00	0.03	0.01	0.00	0.02
TiO <sub>2</sub> (%)	0.01	0.91	0.13	1.26	0.71	0.13	1.27
LOI (%)	–	9.1	1.9	24.7	13.3	1.1	24.3

High Fe<sub>2</sub>O<sub>3</sub> concentrations in the Carboniferous samples are usually accompanied by an increase in MgO and CaO contents (Fig. 2), which are related to the presence of siderite and

dolomite. In the Miocene samples, increased concentrations of  $Fe_2O_3$  are usually associated with the presence of iron oxides and iron hydroxides. The highest concentrations of Fe occur in the Miocene sediments at a depth of 350 to 370 m, within a pack of clastic sedimentary rocks of brown or rusty red color, indicating changes related to weathering processes.

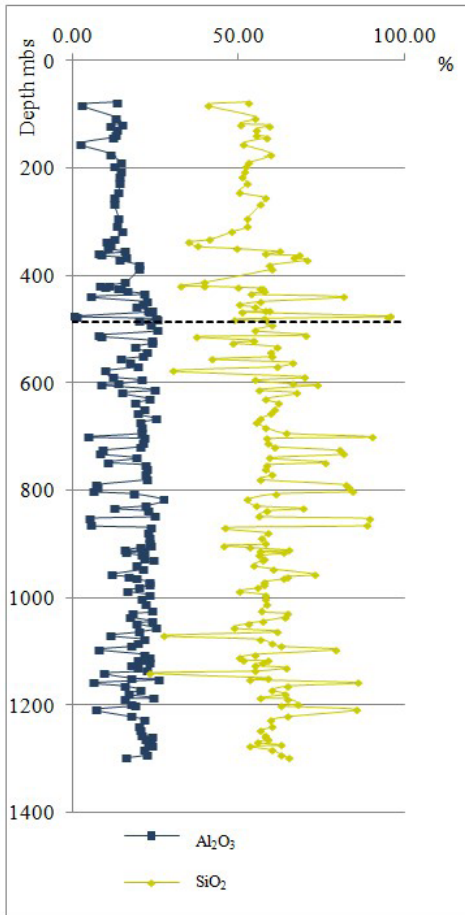


Fig. 1. Stratigraphical variability of  $SiO_2$  and  $Al_2O_3$  content

Rys. 1. Zmienność stratygraficzna udziału  $SiO_2$  i  $Al_2O_3$

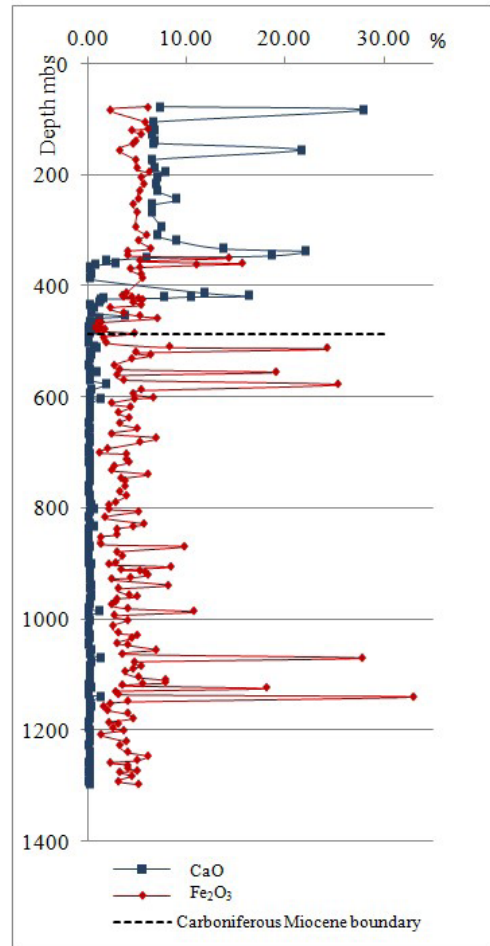


Fig. 2. Stratigraphical variability of  $CaO$  and  $Fe_2O_3$  content

Rys. 2. Zmienność stratygraficzna udziału  $CaO$  i  $Fe_2O_3$

The  $CaO$  contents in the Carboniferous series are very low (average 0.22%), while in the Miocene succession, the concentration of  $CaO$  is much higher, and varies from 0.04

to 27.92 (average 6.02%). Stratigraphical variability of the CaO content is presented on Figure 2. The high CaO contents are related to the presence of carbonate rock inserts in the Miocene deposits. The high CaO contents are related to the presence of carbonate rock inserts in the Miocene deposits. Abundant marine fauna with varying levels of preservation was discovered within the Miocene sediments containing a significant amount of CaO, suggesting their marine origin.

Other major oxides, such as MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, MnO, and Cr<sub>2</sub>O<sub>3</sub>, are present in low concentrations.

The chemical classification of lithological types proposed by Sprague et al. (2009) can be applied based on the chemical compositions of siliciclastic rocks. This classification is based on the share of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and Fe<sub>2</sub>O<sub>3</sub> in a sample (Table 2). The variability in the lithological types in the analyzed profile is presented in Figure 3. The entire profile, in both Carboniferous and Miocene deposits, is dominated by claystones (101 and 36, respectively), including 7 Fe-rich claystones in the Carboniferous series. Fe enrichment in claystones from the Carboniferous series is related to the presence of siderites, while in the samples from the Miocene, it is connected with dispersed hematite. The remaining samples were classed as siltstones and Fe-rich siltstones (11 samples), argillaceous sandstones and Fe-rich (9 samples), and sandstones (14 samples).

Table 2. Chemical classification of the siliciclastic rocks (Sprague et al. 2009)

Tabela 2. Klasyfikacja chemiczna skał klastycznych

SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	<4	Fe <sub>2</sub> O <sub>3</sub> <10%	Claystones
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	= 4–6		Siltstones
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	= 6–10		Argillaceous sandstone
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	>10		Sandstones
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	<4	Fe <sub>2</sub> O <sub>3</sub> >10%	Fe-rich Claystone
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	= 4–6		Fe-rich Siltstone
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	= 6–10		Fe-rich Argillaceous sandstone
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	>10		Fe-rich Sandstone
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	>10	MgO >5%	Dolomitic sandstone

Upon analyzing the chemical composition of samples from the Carboniferous and Miocene deposits, it was found that the primary differentiator between the two series is the significantly higher presence of CaO in the Miocene samples. The high CaO concentrations in the Miocene sediments are related to their predominant marine origin. In addition, both in the Carboniferous and in the Miocene, levels of different chemical compositions, which might be chemostratigraphic levels have been found.

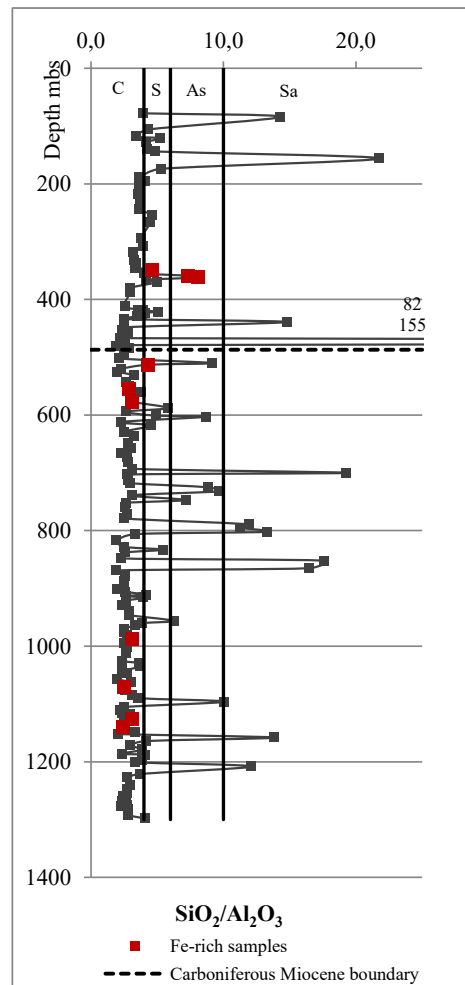


Fig. 3. Stratigraphical variability of the lithological types (Sprague et al. 2009)  
 Explanations: C – claystones, S – siltstones, As – argillaceous sandstones, Sa – sandstones

Rys. 3. Zmienność stratygraficzna typów litologicznych  
 Objasnienia: C – ilowce, S – mułowce, As – piaskowce ilaste, Sa – piaskowce

## 2.2. Elemental geochemistry and chemostratigraphic proxies

The average concentration of elements such as, Cu, Pb, Ni, U, V, Mn, As, Th, Cd, Sb, Bi, W, Ce, Ta, are similar for the samples from the Carboniferous coal-bearing series and the Miocene cover (Table 3). It was also found that for most elements, the ranges of results differ for the Carboniferous and Miocene series. Despite this, the vertical variability of the concentration of these elements does not show significant differences for Carboniferous and Miocene formations.

Table 3. Concentrations of the selected trace elements in the samples from of the Carboniferous and the Miocene deposits from WSx borehole (USCB, Poland)

Tabela 3. Koncentracja wybranych pierwiastków śladowych w próbkach osadów karbonu i miocenu z otworu wiertniczego WSx (GZW, Polska)

Elements	Detection level	Carboniferous (Kokowska-Pawłowska and Krzyszowska 2023)			Miocene		
		average value (n = 120)	range of results		average value (n = 51)	range of results	
			min.	max.		min.	max.
Mo	0.1	<b>0.5</b>	0.1	1.8	<b>4.5</b>	0.4	49.5
Cu	0.1	<b>29.4</b>	3.4	50.4	<b>30.0</b>	4.7	80.3
Pb	0.1	<b>28.4</b>	12.8	65.8	<b>25.3</b>	6.6	49.6
Zn	1	<b>110</b>	20	295	<b>81</b>	1	190
Ni	0.1	<b>46.5</b>	8.0	187.3	<b>43.4</b>	1.9	105.7
Co	0.2	<b>16.6</b>	3.0	74.5	<b>13.5</b>	0.3	32.9
U	0.1	<b>4.8</b>	1.1	7.3	<b>4.7</b>	0.9	18.4
Cr	1	<b>111</b>	11	162	<b>84</b>	14	135
V	1	<b>114</b>	14	184	<b>109</b>	17	176
Mn	1	<b>575</b>	73	2,929	<b>616</b>	27	2,457
As	1	<b>7</b>	1	39	<b>9</b>	1	59
Th	0.1	<b>13.1</b>	3.5	21.7	<b>11.1</b>	2.7	24.3
Sr	1	<b>108</b>	39	270	<b>280</b>	30	1,425
Cd	0.1	<b>0.2</b>	0.1	1.1	<b>0.3</b>	0.1	1.6
Sb	0.1	<b>0.9</b>	0.3	4.8	<b>1.1</b>	0.2	4.0
Bi	0.1	<b>0.4</b>	0.1	1.2	<b>0.4</b>	0.1	1.1
Ba	1	<b>509</b>	197	761	<b>352</b>	9	1,034
Ti	0.001	<b>0.47</b>	0.06	0.64	<b>0.36</b>	0.07	0.64
W	0.1	<b>2.5</b>	0.4	3.9	<b>1.8</b>	0.3	3.6
Zr	0.1	<b>112.8</b>	29.6	169.5	<b>76.2</b>	16.3	131.7
Ce	1	<b>63</b>	16	99	<b>57</b>	17	94
Nb	0.1	<b>14.3</b>	2.0	20.2	<b>11.8</b>	2.1	23.2
Ta	0.1	<b>1.1</b>	0.1	1.5	<b>0.8</b>	0.1	1.6
Be	1	<b>3</b>	1	7	<b>2</b>	1	4
Sc	1	<b>17</b>	2	26	<b>12</b>	2	21

Elements such as Zn, Cr, Co, Ba, Ti, Zr, Nb, and Sc show slightly higher concentrations in Carboniferous sediments. The analysis of the vertical variability of the concentration of these elements does not allow a clear division of the Carboniferous and Miocene deposits. However, in both the Carboniferous and the Miocene, units with principal geochemical features could be identified. The vertical distributions of selected elements are shown in Figure 4. It is worth mentioning the vertical distribution of elements such as Ti, Zr, Nb, Th, Cr, Sc, and Co. These elements are delivered to the sediment within the detrital fraction and



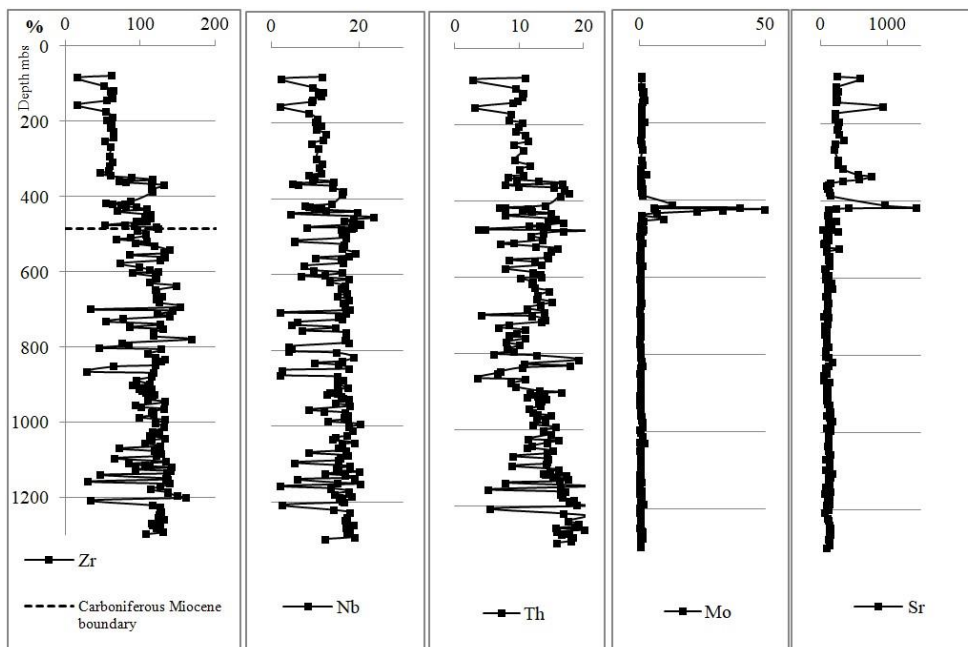


Fig. 4. Stratigraphical variability of the selected trace elements: Zr, Nb, Th, Mo, Sr

Rys. 4. Zmienność stratygraficzna wybranych pierwiastków śladowych Zr, Nb, Th, Mo, Sr

derived from terrigenous sources. Relatively high Ti, Nb and Ta concentrations are related to the presence of heavy minerals (foremost rutile, but also anatase, ilmenite and leucoxene) (Pearce et al. 2005, 2010; Ratcliffe et al. 2016). The stratigraphic profiles of these elements may show the changes in the source rock composition on a temporal scale (Ramkumar et al. 2021). By examining the abundance of Ti, Zr, and Nb, as well as Th, Cr, and Co to a lesser degree, we can identify units with either low or high concentrations of these elements. Based on the high presence of Ti, Zr, and Nb, in both Carboniferous and Miocene deposits, units with a higher detrital input can be identified.

Of the elements presented above, Zr is indicated as the most diagnostic in terms of detrital input. Zr is commonly used as a proxy for the heavy mineral zircon in both siliciclastic and carbonate studies. It is also mechanically and chemically stable. The only source of zircon is terrigenous and it cannot be derived by interactions with seawater. Therefore, it is an effective proxy for terrigenous input. The concentration of Zr in carbonate sediments can indicate the amount of zircon deposited, which in turn will relate to the amount of terrigenous material in the carbonate (Pearce et al. 2005, 2010; Craigie 2015; Ratcliffe et al. 2016; Ramkumar et al. 2015, 2021).

Elements such as Mo and Sr show significantly higher average concentrations in the Miocene cover than in the Carboniferous coal-bearing series (Table 3). Mo concentrations in the Carboniferous samples ranged from 0.1 to 1.8 ppm (average 0.5 ppm) while in the Miocene

samples, Mo concentrations ranged from 0.4 to 49.5 ppm (average 4.5 ppm). The high average concentration of Mo in the Miocene sediments results from the presence of a horizon with significantly high concentrations of this element in the bottom part of the Miocene. The remaining samples, both from the Miocene and the Carboniferous, show similar concentrations of Mo. A high content of Mo may suggest deposition under anoxic conditions. This statement would require confirmation with other redox-sensitive indicators, which are not the subject of this study.

In the Carboniferous and Miocene samples, the Sr concentrations showed a wide range, with averages of 108 ppm and 280 ppm, respectively, with values ranging from 39 to 270 ppm and from 30 to 1,425 ppm. High Sr content in Miocene sediments is also accompanied by an increase in Ca content. Therefore, these elements can be a diagnostic tool in the identification of Miocene and Carboniferous deposits. Sr, Ca, and also Mn, and Mg, are generally associated with carbonate minerals, mainly siderite, calcite, and dolomite (Pearce et al. 2010). Strontium can also be associated with minerals such as gypsum, anhydrite, strontianite and celestite, in addition to calcite and aragonite (Playter 2018). This is confirmed by the lithology of the Miocene deposits, where marly claystone and clays, as well as gypsum interlayers, were observed.

Table 4. Geochemical ratios for the samples from the Carboniferous and the Miocene deposits from WSx borehole (USCB, Poland)

Tabela 4. Wskaźniki geochemiczne dla próbek osadów karbonu i miocenu z otworu wiertniczego WSx (GZW, Polska)

	Carboniferous			Miocene		
	average value (n = 120)	range of results		average value (n = 51)	range of results	
		min.	max.		min.	max.
Th/U	2.8	1.4	4.1	3.2	0.5	5.8
Th/Ta	13.4	5.0	40.0	14.8	4.2	30.0
Nb/Ti	30.1	24.8	35.0	32.5	16.6	37.6
Th/Nb	1.0	0.4	2.7	1.0	0.2	1.8
Zr/Th	8.9	5.4	17.3	7.1	3.8	17.3
Ti/Zr	0.0041	0.0014	0.0060	0.0049	0.0020	0.0091
Cr/Zr	1.0	0.2	2.9	1.2	0.2	4.0
Cr/Sc	8.0	2.7	44.0	7.6	3.7	33.5
Sc/Th	1.3	0.3	3.2	1.1	0.4	1.7
Sc/Zr	0.1	0.0	0.5	0.2	0.0	0.2
TiO <sub>2</sub> /K <sub>2</sub> O	0.30	0.11	0.45	0.86	0.14	21.17
TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.049	0.023	0.062	0.102	0.034	2.048
Sr/CaO	785.5	34.8	2,162.5	204.7	21.2	1,009.1
MgO/CaO	8.6	0.9	23.8	1.4	0.0	8.2
Fe <sub>2</sub> O <sub>3</sub> /CaO	27.0	3.9	74.6	5.6	0.1	35.7

Many studies have used various elemental ratios to detect the detrital input, sediment recycling, and provenance, redox condition and palaeoproductivity, and paleogeographic changes, as well as in order to distinguish units with different geochemical features (e.g. Pearce et al. 1999, 2005, 2010; Weissert et al. 2008; Ramkumar et al 2015, 2021; Craigie et al. 2016; Ratcliffe et al. 2016; Bayon et al. 2020). In this study, elemental indicators connected with terrigenous components such as Th/U, Th/Ta, Nb/Ti, Th/Nb, Zr/Th, Ti/Zr, Cr/Zr, Cr/Sc, Sc/Th, Sc/Zr,  $\text{TiO}_2/\text{K}_2\text{O}$ , and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  have been tested (Table 4).

The average values of these ratios, as well as the ranges of the results, are very similar for the Carboniferous and Miocene series. Additionally, the distribution of most of these indicators in the profile did not show significant differences in individual parts of the Miocene and Carboniferous profiles. Only indices such as Th/U, Zr/Th, Ti/Zr,  $\text{TiO}_2/\text{K}_2\text{O}$ , and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  make it possible to separate packages with different geochemical records in the stratigraphic profile (Fig. 5). Variations in these parameters are largely dependent on changes in source/provenance, which affects the relative concentrations of detrital heavy minerals (Craigie et al. 2016).

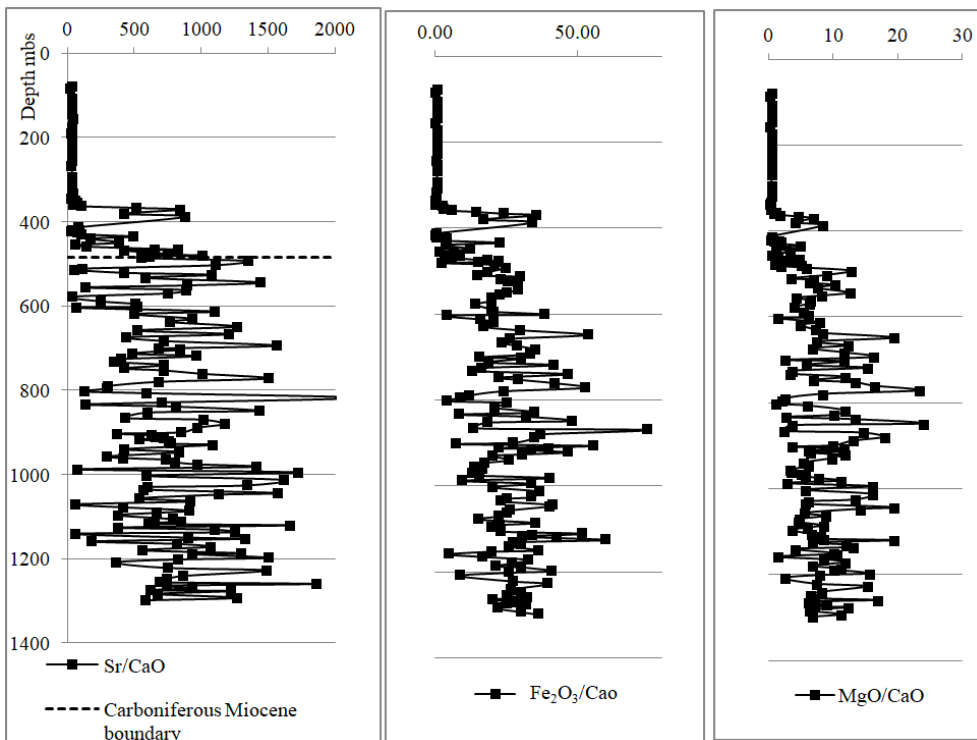


Fig. 5. Stratigraphical variability of the selected geochemical ratios

Rys. 5. Zmienność stratygraficzna wybranych wskaźników geochemicznych

Geochemical indicators such as Sr/CaO, MgO/CaO, and Fe<sub>2</sub>O<sub>3</sub>/CaO based on the share of elements related to carbonate minerals were also tested. The Sr/CaO, MgO/CaO, and Fe<sub>2</sub>O<sub>3</sub>/CaO ratios show significantly lower values for Miocene deposits. This is particularly visible in the upper part of the Miocene, i.e. in the Skawina Formation. According to [Hsiung et al. \(2021\)](#), the correlation between Ca and Sr intensities indicates that biogenic carbonates are the primary source of Ca, with a small contribution from terrigenous sources, despite the absence of biogenic material. The Fe<sub>2</sub>O<sub>3</sub>/CaO ratio is suggested as a useful proxy for terrigenous components in sediments. Deposits with lower Fe/Ca with high concentrations of Co are primarily composed of biogenic carbonate material rather than material from terrigenous sources ([Bayon et al. 2020](#)). Based on the Sr/CaO and Fe<sub>2</sub>O<sub>3</sub>, it can be stated that in the Carboniferous series, Ca is sourced from biogenic carbonates as well as from terrigenous sources. By contrast, biogenic carbonate material is dominant in the Miocene deposits. The indices presented above have shown their applicability in the chemostratigraphy of the analyzed material.

## Conclusion

Geochemical studies have shown slightly different geochemical features of the samples from the Carboniferous coal-bearing series and the Miocene cover within the USCB. The major oxides SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the predominant constituents, with average contents of 60.60 and 18.708%, respectively, in the Carboniferous, and 55.45 and 13.87%, respectively, in the Miocene. Other major oxides, such as MgO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, MnO and Cr<sub>2</sub>O<sub>3</sub>, are present in lower concentrations. Moreover, a significant enrichment in CaO in the Miocene deposits and the presence of horizons with Fe<sub>2</sub>O<sub>3</sub> enriched in the entire profile have been stated. Based on the chemical composition of siliciclastic rocks, most of the samples, both Carboniferous and Miocene, can be classified as claystones (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> < 4%), including Fe-rich claystones. (Fe<sub>2</sub>O<sub>3</sub> > 10%). The remaining samples can be classed as siltstones and Fe-rich siltstones, argillaceous sandstones and Fe-rich argillaceous sandstones, and sandstones.

The concentrations of trace elements associated with the detrital fraction, such as Zn, Cr, Co, Ba, Ti, Zr, Nb and Sc show slightly higher concentrations in Carboniferous sediments. The analysis of geochemical profiles has shown levels with different concentrations of these elements. Based on the high presence of Ti, Zr and Nb in both Carboniferous and Miocene deposits, units with a higher detrital input can be identified. Additionally, elemental indicators connected with terrigenous components such as Th/U, Zr/Th, Ti/Zr, and TiO<sub>2</sub>/K<sub>2</sub>O show similar patterns in the analyzed profile. Geochemical indicators such as Sr/CaO, MgO/CaO, and Fe<sub>2</sub>O<sub>3</sub>/CaO based on the share of elements related to carbonate minerals allow the conclusion that in the Carboniferous series, Ca is sourced from biogenic carbonates as well as from terrigenous sources, while in the Miocene deposits, biogenic carbonate material is dominant.

The paper shows that chemostratigraphy can be used as a stratigraphic tool and is able to provide new insights into the correlation of barren sequences of the USCB.

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#### GEOCHEMISTRY OF THE CARBONIFEROUS COAL-BEARING SERIES AND THE MIOCENE COVER WITHIN THE UPPER SILESIA COAL BASIN – A CASE STUDY

#### Keywords

Miocene, carboniferous, USCB, chemostratigraphy

#### Abstract

This paper presents geochemical data for 171 core samples of the Carboniferous coal-bearing series and the Miocene cove from the central part of the Upper Silesian Coal Basin. Major oxide concentrations ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ , and  $\text{Cr}_2\text{O}_3$ ) were obtained using XRF. Trace and major elements (Mo, Cu, Pb, Zn, Ni, Co, U, Cr, V, Mn, As, Th, Sr, Cd, Sb, Bi, Ba, Ti, W, Zr, Ce, Nb, Ta, Be Sc) were analysed ICP-MS.

The main goals of this study were to demonstrate the distribution, as well as the stratigraphical variability, of the selected elements and to determine whether chemostratigraphy tools could be effectively applied to analyze Carboniferous and Miocene deposits of the USCB. Geochemical studies have shown showed different geochemical features of the samples from the Carboniferous and the Miocene. The diversity is mainly expressed in the enrichment of Miocene sediments in Ca and Sr related to biogenic carbonate material. It was also stated that the concentrations of trace elements associated with the detrital fraction, such as Zn, Cr, Co, Ba, Ti, Zr, Nb, and Sc show slightly higher values in Carboniferous sediments. On the basis of the content of Ti, Zr, and Nb, as well as ratios such as Th/U, Zr/Th, Ti/Zr, and  $\text{TiO}_2/\text{K}_2\text{O}$ , units with different inputs of the terrigenous fraction can be identified in both Carboniferous and Miocene formations. The paper shows that chemostratigraphy can be used as a stratigraphic and correlation tool for the Carboniferous and the Miocene deposits of the USCB.

**GEOCHEMIA KARBONU PRODUKTYWNEGO I MIOCENU GÓRNOŚLĄSKIEGO  
ZAGŁĘBIA WĘGLOWEGO – STUDIUM PRZYPADKU**

## Słowa kluczowe

GZW, karbon, miocen, chemostratygrafia

## Abstract

W pracy przedstawiono dane geochemiczne dla 171 próbek skał osadowych z karbońskiej serii węglonośnej i pokrywy miocenińskiej z centralnej części Górnośląskiego Zagłębia Węglowego. Udziały głównych tlenków ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{TiO}_2$  i  $\text{Cr}_2\text{O}_3$ ) oznaczono za pomocą XRF. Pierwiastki główne i śladowe (Mo, Cu, Pb, Zn, Ni, Co, U, Cr, V, Mn, As, Th, Sr, Cd, Sb, Bi, Ba, Ti, W, Zr, Ce, Nb, Ta, Be i Sc) analizowano przy pomocy ICP-MS. Głównym celem badań była analiza koncentracji i zmienności stratygraficznej wybranych pierwiastków głównych i śladowych, jak również ocena możliwości stosowania chemostratygrafii w analizie karbońskich i miocenijskich osadów GZW. Badania geochemiczne wykazały odmienne właściwości geochemiczne próbek z karbonu produktywnego oraz miocenu. Zróżnicowanie to wyraża się głównie wzbogaceniem osadów miocenu w Ca i Sr, związane z biogenicznym materiałem węglanowym. Stwierdzono również, że stężenia pierwiastków śladowych, związanych z frakcją detrytyczną, takich jak: Zn, Cr, Co, Ba, Ti, Zr, Nb, Sc, wykazują nieco wyższe wartości w osadach karbonu. Na podstawie koncentracji pierwiastków Ti, Zr i Nb oraz wskaźników geochemicznych Th/U, Zr/Th, Ti/Zr,  $\text{TiO}_2/\text{K}_2\text{O}$  można zidentyfikować jednostki o różnym udziale frakcji terygeniczej, zarówno w osadach karbonu i miocenu. W pracy wykazano, że chemostratygrafia może być z powodzeniem wykorzystywana jako narzędzie stratygraficzne i korelacyjne dla utworów karbonu i miocenu Górnośląskiego Zagłębia Węglowego.