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**STRONTIUM AND BARIUM IN THE TRIASSIC LIMESTONE OF
THE OPOLE SILESIA DEPOSITS****STRONT I BAR W WAPIENIACH TRIASOWYCH ZŁÓŻ OBSZARU ŚLĄSKA OPOLSKIEGO**

This article presents the results of studies of strontium and barium content in Triassic (Muschelkalk) carbonate rock samples taken from the area of the Polish part of the Germanic Basin (the area of Opole Silesia). Sr and Ba were determined in the rocks of all formations of the Lower Muschelkalk – Gogolin Beds, Górażdże Beds, Dziewkowice (Terebratula) Beds and Karchowice Beds. Strontium and barium are chemical elements characteristic for aragonite carbonate phase. Aragonite is unstable calcium carbonate phase which is transformed such as high-Mg calcite into low magnesium calcite during diagenesis. So as Sr and Ba indicate the presence of aragonite in the primary carbonate material. Now these elements concentrate in low-Mg calcite crystal structure. The Triassic rocks of Lower Muschelkalk which are mined in different quarries of the Opole Silesia area are mainly built of low-Mg calcite with lower amounts of high-Mg calcite, protodolomite, ordered dolomite and huntite. There are smaller addition of non-carbonate minerals – quartz, chalcedony, muscovite, feldspars and iron minerals. The presence of Sr and Ba now bound in a structure of low-Mg calcite will indicate the occurrence of aragonite in the primary carbonate material. The Triassic rocks from the area of Opole Silesia were studied to determine the rocks enriched in Sr and Ba. Selected rock samples were examined using ICP AES spectrometry, XRF analysis and microprobe measurements. The results of studies show that strontium and barium occur in rocks of all Lower Muschelkalk formations. The lowest contents of these elements were determined in rocks of Gogolin Beds, higher – in rocks of other formations. The results of studies show that Sr and Ba concentrate in low-Mg calcite which dominates in Lower Muschelkalk rocks. Limestone built mainly of low-Mg calcite or “pure” calcite without substitution of other elements, especially Mg, Fe, Si and Al could be applied in lime industry or in other branches of industry, where pure quality raw material, without substitutions is needed.

Keywords: strontium, barium, Triassic limestone, Opole Silesia Deposits

W artykule przedstawiono wyniki badań zawartości strontu i baru w próbkach skał węglanowych triasu (wapienia muszlowego), pobranych w obszarze polskiej części zbiornika germańskiego (rejon Śląska Opolskiego). Stront i Bar oznaczono w skałach wszystkich formacji dolnego wapienia muszlowego –

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w warstwach gogolińskich, górażdzańskich, dziewkowickich (terebratulowych) i karchowickich. Stront i bar są charakterystyczne dla aragonitowej fazy węglanowej. Aragonit stanowi niestabilną fazę węglanu wapnia, która, podobnie jak kalcyt wysokomagnezowy ulega przeobrażeniu w niskomagnezowy kalcyt podczas diagenety. Zatem obecność Sr i Ba wskazuje na występowanie aragonitu w pierwotnym materiale węglanowym. Obecnie pierwiastki te występują w strukturze niskomagnezowego kalcytu. Skąły triasowe dolnego wapienia muszlowego, eksploatowane w różnych kamieniołomach obszaru Śląska Opolskiego są zbudowane głównie z niskomagnezowego kalcytu przy mniejszym udziale kalcytu wysokomagnezowego, protodolomitu, dolomitu uporządkowanego i huntytu. W skałach tych występują niewielkie domieszki minerałów niewęglanowych – kwarcu, chalcedonu, muskowitu, skaleni i minerałów żelaza. Obecność Sr i Ba, związanych w strukturze niskomagnezowego kalcytu będzie wskazywać na występowanie aragonitu w pierwotnym materiale węglanowym.

Skąły triasowe z obszaru Śląska Opolskiego analizowano w celu określenia, które wapienie są wzbogacane w Sr i Ba. Wybrane próbki skał poddano następującym analizom: spektrometrii ICPAES, analizie XRF oraz badaniom w mikroobszarach. Wyniki badań wykazały, że stront i bar występują w skałach wszystkich formacji dolnego wapienia muszlowego. Najniższe zawartości tych pierwiastków oznaczono w skałach warstw gogolińskich, wyższe w skałach pozostałych formacji. Wyniki badań wskazują, że Sr i Ba koncentrują się w niskomagnezowym kalcycie, który dominuje w skałach dolnego wapienia muszlowego. Wapienie zbudowane z niskomagnezowego kalcytu lub „czystego” kalcytu bez podstawień innych pierwiastków, głównie Mg, Fe, Si i Al, mogą być stosowane w przemyśle wapienniczym lub innych gałęziach przemysłu, w których wymagany jest surowiec „czysty” jakościowo, bez domieszek.

Słowa kluczowe: stront, bar, wapienie triasowe, złoża Śląska Opolskiego

1. Introduction

The Opole Silesia region is a zone of the eastern part of the epicontinental Germanic Basin (Assmann, 1944; Szulc, 2000). Deposits of the Germanic Basin are made of Triassic carbonate rocks, including Muschelkalk rocks (Middle Triassic). Triassic limestones are mined in various quarries of the Opole region. They constitute the material used in various industries, mainly as raw material for lime and cement production, for flue gas desulfurization, as well as an additive to animal feed and a fertilizer ingredient. It is used in various branches of industry as a raw material of suitable geochemical composition. That determines, among other things, the need for selective operation in various quarries, which is usually carried out using blasting. The problem has been the subject of many studies, including, *inter alia*: the issue of costs and the best layout of the mine pit, cracking of rocks as an adverse effect of blasting and the analysis of the fineness of the material before blasting work commences in quarries, conducted in order to determine the effectiveness of shooting (Bazzazi & Esmaeili, 2012; Mikaeil et al., 2011). Thus, the geochemical composition of limestone will affect its mechanical properties analyzed during the planning stage of blasting.

The limestones of the Opole Silesia region are diverse in terms of content of Ca and Mg and ingredients such as Fe, Mn, Si, Al, as well as Sr and Ba (Stanienda, 2011, 2013a, b, 2014). Strontium and barium are elements whose content would determine decisively the quality of the raw material limestone, such as, eg. the amount of Ca, Mg, or impurity of Fe, Mn, Si and Al. They usually occur in small amounts, similarly to rare elements in the mineral substance of coal in coal seams, such as Ti, Zr, Cr, P and others, which are part of the heavy minerals present in the rocks surrounding coal deposits (Stanienda, 2015), or radon present often in coal deposits (Ball & Wysocka, 2011), which, however, in contrast to Sr and Ba found in limestone, is toxic. The diversity of shell limestone deposits, including geochemical variability of their composi-

tion, is a result of the sedimentation conditions of the Germanic Basin (Szulc, 1990, 1993, 2000, 2007). Lower Muschelkalk deposits formed in changing environments of marine transgression and regression. In addition, the diversity of the geochemical composition was also influenced by diagenetic processes that led to changes in the mineral composition of the original carbonate material, including the transformation of unstable carbonate phases into stable ones. As a result of diagenesis, high magnesium calcite and aragonite was transformed into low magnesium calcite (Ali et al., 2010; Althoff, 1977; Boggs, 2010; Fairchild et al., 2000; Mackenzie & Andersson, 2013; Morse et al., 2006; Stanienda, 2013a, b). Dolomite appeared as a result of dolomitization. Dolomite was transformed into calcite during dedolomitization, and silica concretions occurred as a result of the process of silicification. Additionally, mineral carbonates underwent dissolution during diagenesis and spaces left by the dissolved carbonates were filled with mineral iron, forming stylolites (Bodzioch, 2005; Boggs, 2010; Stanienda, 2013a, b). Carbonate rocks of the Opole Silesia area are mostly limestone, dolomitic limestone, in some places marl limestone built in majority with low magnesium calcite, and in minority with high magnesium calcite, ordered dolomite, protodolomite and huntite. Possible additives include: siderite, ankerite and non-carbonate minerals: quartz, chalcedony, mica, clay minerals, feldspar, as well as Fe oxides and sulphides (Stanienda, 2011, 2013a, b).

This article presents the results of research on strontium and barium marked in Triassic deposits of Lower Muschelkalk, whose profile includes (counting from its bottom): the Gogolin Beds, then the Górażdże, Dziewkowice (Terebratula) and Karchowice Beds, with the last one deposited at the top of the profile. Strontium and barium indicate the presence of aragonite in the original carbonate sediment, which is an unstable phase of calcium carbonate, and which is transformed into low magnesium calcite during diagenesis. Thus, Sr and Ba are currently present in low magnesium calcite.

2. Methodology of study

2.1. Field study

Samples for the study were collected from the area of Opole Silesia, in the quarries of Strzelce Opolskie, Ligota Dolna, Szymiszów, Wysoka, Tarnów Opolski and in the area of Mount St. Anne (Fig. 1), from all of lower shell limestone formations: the lower and upper Gogolin Beds, the Górażdże, Dziewkowice (Terebratula) and Karchowice Beds.

Samples from the lower Gogolin Beds were taken in the Gogolin quarry, from the upper Gogolin Beds – in the Gogolin and Ligota Dolna quarries, from the Górażdże Beds – in the Strzelce Opolskie, Ligota Dolna and Wysoka quarries and from an exposure in the amphitheater at Mount St. Anne, from the Dziewkowice Beds – in the Strzelce Opolskie, Szymiszów quarries and an exposure in the area of Mount St. Anne, from the Karchowice Beds – in the Strzelce Opolskie and Tarnów Opolski quarries and from the exposures in the area of Mount St. Anna (Stanienda, 2011, 2013a).

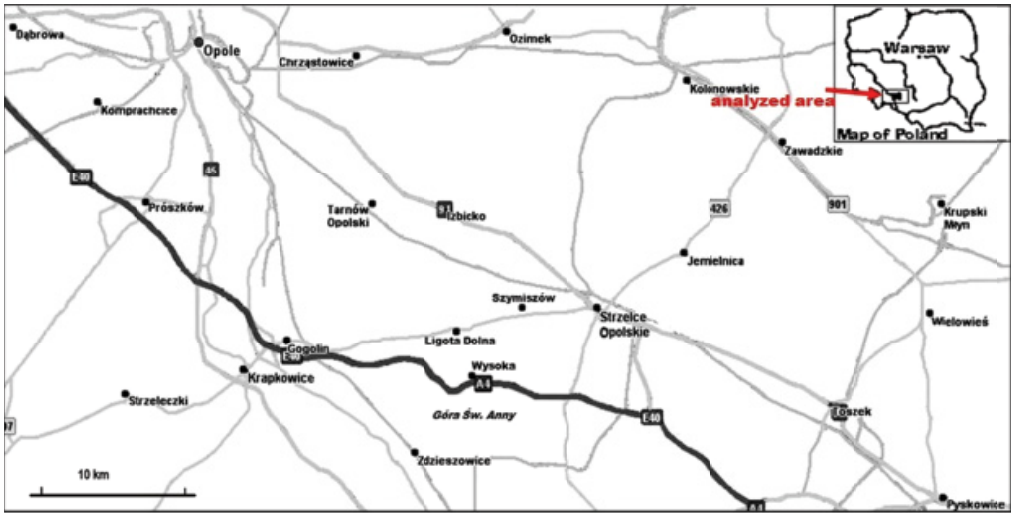


Fig. 1. Location of the analyzed area (Stanienda, 2013a)

2.2. Laboratory study

The research of Triassic limestones of the Opole Silesia area included ICP AES spectrometry, an XRF analysis and an examination of microareas (microprobe measurements). AES ICP spectrometry was carried out at the Institute of Applied Geology of the Silesian University of Technology. The analysis was performed using a type JY 2000 emission spectrometer with excitation of inductively coupled plasma (ICP-AES), which is used for measuring contents of elements in solid and liquid samples. The measurement is based on the phenomenon of atomic emission. 19 samples of limestone taken from all formations of lower shell limestone were analyzed. Two samples (G1, G4) were taken in the Gogolin quarry, 4 – in the Ligota Dolna quarry, 4 – in the area of Mount St. Anne, 5 – in the Strzelce Opolskie quarry and 4 – in the Tarnów Opolski quarry. The XRF analysis was performed in the Refractory Materials Division in Gliwice, a branch of the Institute of Ceramics and Building Materials in Warsaw. This analysis was executed during the implementation phase of a research on carbonate phases of Triassic limestone from the Opole region, diagenetic processes and possibilities of using limestone containing magnesium in the flue gas desulfurization process (Stanienda, 2013a). This method was used to determine the amount of strontium. The analysis was carried out on ten samples. One sample from the quarries in Gogolin (G1) and Ligota Dolna (LD11), two samples from Wysoka (W1, W5), three from Mount St. Anne (SA2, SA5 and SA12) and three from Strzelce Opolskie (SO1, SO17 and SO20) were chosen. The tests were performed using a WDXRF PW 2424 sequential X-ray fluorescence spectrometer (PANalytical). An X-ray spectral microanalysis (research in microareas – microprobe measurements) was performed at the Institute of Non-Ferrous Metals, also during the implementation phase of a research on carbonate phases of Triassic limestones of the Opole region, diagenetic processes and possibilities of using limestone containing magnesium in a desulphurization process (Stanienda, 2011, 2013a, b, 2014). The study involved a total of 10 samples. Analyses were performed with use of EPMA X-ray microanalysis techniques using

a JXA-8230 X-ray microprobe (JEOL). Tests were conducted on sample specimens which were sputtered with a layer of carbon. The quantitative analysis of Sr and Ba, conducted using WDS spectrometers, was performed in microareas of samples G1, LD11, SA12, SO1, SO14, SO17, SO20, W1, W5 and S2.

3. Results of study

3.1. Results of ICP AES spectrometry

The biggest number of samples from all formations of lower Muschelkalk was subjected to ICP AES Spectrometry. 5 samples from the Gogolin Beds, 4 samples from Górażdże Beds, 4 – from Dziewkowice (Terebratula) Beds and 6 – from the Karchowice Beds were analyzed. The results are given in Table 1.

TABLE 1

Results of ICP AES spectrometry

No.	Formation	Sample number	Sr		Ba	
			[ppm]	[% mass]	[ppm]	[%mass]
1	Gogolin Beds	G1	185	0.0185	150	0.015
2		G4	175	0.0175	167	0.0167
3		LD4	210	0.021	197	0.0197
4		LD9	245	0.0245	240	0.024
5		LD11	250	0.025	239	0.0239
6	Górażdże Beds	LD14	198	0.0198	188	0.0188
7		SA7	310	0.031	298	0.0298
8		SA10	305	0.0305	285	0,0285
9		SA12	320	0.032	303	0.0303
10	Dziewkowice (Terebratula) Beds	SA15	305	0.0305	287	0.0287
11		SO6	210	0.021	215	0.0215
12		SO9	225	0.0225	220	0.022
13		SO30	254	0.0254	223	0.0223
14	Karchowice Beds	SO7	198	0.0198	165	0.0165
15		SO22	230	0.023	205	0.0205
16		TO7	135	0.0135	120	0.012
17		TO41	120	0.012	105	0.0105
18		TO15	175	0.0175	155	0.0155
19		TO62	190	0.019	170	0.17

Gogolin Beds limestone

The strontium content in Gogolin Beds limestone varies from 175 ppm to 250 ppm, whereas a lower amount of Sr was determined in rocks from Gogolin and a higher amount in limestone from the quarry in Ligota Dolna. A similar pattern was observed for barium, which is higher in the rocks of Ligota Dolna and lower in limestone of Gogolin. The content of Ba in Gogolin Beds limestone varies from 150 ppm to 240 ppm.

Górażdże Beds limestone

Górażdże limestone is generally characterized by higher values of strontium and barium when compared with Gogolin limestone. The amount of Sr in the rocks of this formation ranges from 198 ppm to 320 ppm. Higher levels of Sr > 300 ppm were determined in limestone from the area of Mount St. Anne, lower Sr < 200 ppm in rocks from the quarry in Ligota Dolna. The content of Ba varies from 188 ppm to 303 ppm, the amount of Ba < 200 ppm is characteristic of the rocks from Ligota Dolna, while the content of Ba > 280 ppm is found in the rocks in the area near Mount St. Anne.

Dziewkowice (Terebratula) Beds limestone

The content of Sr in this formation of limestone ranges from 210 ppm to 305 ppm. The amount of Sr > 300 ppm is characteristic of the rocks from Mount St. Anne, while values of less than 260 ppm were found in limestone from the quarry in Strzelce Opolskie. The amount of barium varies from 215 ppm to 287 ppm, with a value of 287 ppm (the highest) characteristic of the rocks from Mount St. Anne and lower values – for limestone from the quarry in Strzelce Opolskie.

Karchowice Beds limestone

The limestone samples of the Karchowice Beds were collected from the quarries in Strzelce Opolskie and Tarnów Opolski. Overall strontium content ranges from 120 ppm to 230 ppm. The amount of Sr < 195 ppm is characteristic for the rocks from Tarnów Opolski, while higher than 195 ppm – for limestone from the quarry in Strzelce Opolskie. The content of barium varies in the Karchowice Beds limestone from 105 ppm to 205 ppm.

Summing up the results of ICP AES spectrometry, it can be concluded that the Gogolin and Karchowice Beds limestone generally have a lower strontium content than the Górażdże and Dziewkowice Beds rocks. A similar pattern was also observed for the amounts of barium. However, there are exceptions. The amount of Sr in sample LD14 is much lower than the amount of this element in other samples from the Górażdże formation and even lower than the amount of Sr in some samples from the Gogolin Beds (LD4, LD9 and LD11). In case of barium there are even more exceptions. One example is sample LD14, where the determined amount of Ba was lower than in some limestone samples of the Gogolin Beds (samples LD4, LD9 and LD11). Also some samples from the Dziewkowice Beds (SO6, SO30 SO9) have a lower content of Ba than the aforementioned samples from the Gogolin Beds.

3.2. Results of XRF analysis

An XRF analysis of strontium content was carried out to complement the results of ICP AES spectrometry. The results are given in Table 2. Most samples analyzed by this method were not spectrometrically tested (an ICP AES analysis). Exceptions are sample G1 and LD11, in which Sr content was determined using both methods.

The content of Sr determined using XRF method in the Gogolin Beds limestone varies from 319.6 ppm to 434.1 ppm. Sr content is higher than that obtained as a result of the measurement with an emission spectrometer. In the case of limestone samples from other formations, the results of the XRF analysis cannot be compared with the results of ICP AES spectrometry as different

samples from these formations were analyzed. The amount of Sr in the Góraźdze Beds rock varies from 287 ppm to 334.6 ppm, in the Dziewkowice (Terebratula) Beds rock – from 301.2 ppm to 312.9 ppm, and in limestone from the Karchowice Beds – from 87.8 ppm to 137.8 ppm. The results of the XRF analysis indicate that the lowest amount of strontium is in limestone of the Karchowice Beds, while higher Sr content was determined in the rocks of other formations.

TABLE 2

Results of XRF analysis of Sr and Ba in selected samples (Stanienda, 2013a)

Sample origin and its number	Gogolin Beds		Góraźdze Beds			Dziewkowice Beds		Karchowice Beds			
	LD11	G1	SA5	W1	W5	SA12	SO1	SA2	SO17	SO20	
Type of analyzed sample	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	
Sr	[ppm]	434.1	319.6	320.0	287.0	334.6	312.9	301.2	99.0	137.8	87.8
	[%mass]	0.04341	0.03196	0.032	0.0287	0.03346	0.03129	0.03012	0.0099	0.01378	0.00878

3.3. Results of microprobe measurements

The tests showed the greatest differentiation in the amounts of Sr and Ba as a result of measurements of selected points of microareas in the analyzed samples. This diversity confirms the variability of the chemical composition of individual micro-areas within each of the tested limestone. Designation of Sr and Ba was performed in the areas where carbonate base of limestone or allochem bonding cement (bioclasts) were present.

Gogolin Beds limestone

Sr content in the Gogolin Beds limestone changes in each microarea of the test samples (G1 and LD11) (Figs. 2 and 3) from 100 to 1000 ppm, and barium – from 300 to 2000 ppm (Tabs. 3 and 4). In both cases of Sr and Ba, higher content of these elements is characteristic of the rocks of Ligota Dolna, while lower content – of limestone from Gogolin. The results show significant differences in the content of both Sr and Ba in the Gogolin Beds rock.

TABLE 3

Microprobe chemical analyses of Sr and Ba in microarea of sample G1 (Stanienda 2013a, 2014)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.09	900	0.07	700
2	0.03	300	0	0
3	0.01	100	0	0
4	0.05	500	0	0
5	0.02	200	0	400
6	0.05	500	0.03	300
7	0	0	0	0
8	0.01	100	0	0

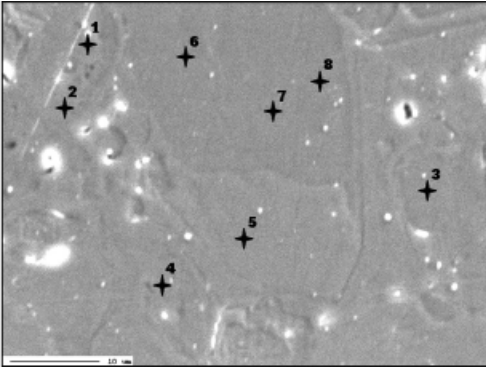


Fig. 2. BSE image of a sample G1 (Upper Gogolin limestone from Gogolin) (Stanienda, 2013a, 2014). Magn. 2000×. Light grey – calcite. 1-8 – points of chemical analysis

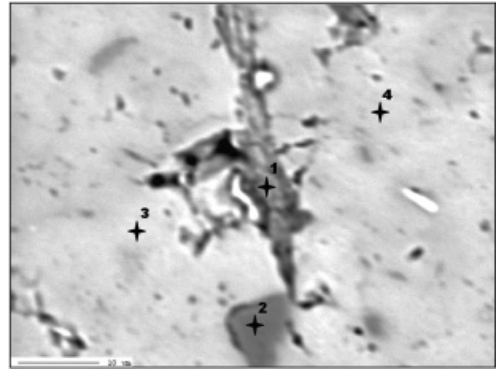


Fig. 3. BSE image of a sample LD11 (Upper Gogolin limestone from Ligota Dolna) (Stanienda, 2013a). Magn. 2000×. Light grey – calcite; dark grey – carbonate phase rich in magnesium. 1-4 – points of chemical analysis

TABLE 4

Microprobe chemical analyses of Sr and Ba in microarea of sample LD11 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0	0	0	0
2	0	0	0.10	1000
3	0.10	1000	0	0
4	0.10	1000	0.20	2000

Górażdże Beds limestone

Sr content in the Górażdże Beds limestone changes in each microarea of the test samples (W5 and SA5) (Figs. 4 and 5) from 100 to 1200 ppm, and barium – from 300 to 800 ppm (Tabs. 5 and 6). In both cases of samples: from the quarry in Wysoka (W5) and limestone from the area of Mount St. Anne (sample SA5) a variation of Sr at various points of the examined microareas can be observed. Barium was found at only one microarea point of a sample from the Wysoka quarry (W5), while in case of a rock from Mount St. Anne (sample SA5) – in six of the seven analyzed points. The results show significant differences in the content of Sr in the Górażdże Beds rock, while the diversity of barium content is significantly lower.

TABLE 5

Microprobe chemical analyses of Sr and Ba in microarea of sample W5 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	2	3	4	5
1	0.01	100	0.04	400

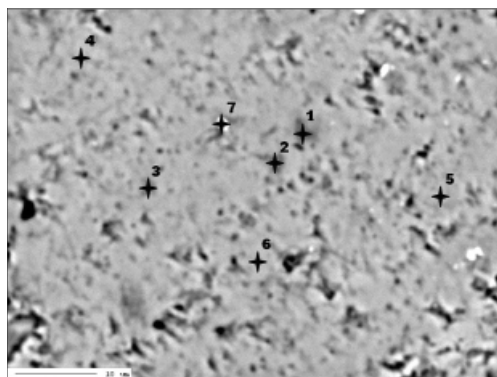


Fig. 4. BSE image of a sample W5 (Góraźdze limestone from Wysoka) (Stanienda, 2013a). Magn. 2000 \times . Light grey – calcite; dark grey – carbonate phase rich in magnesium. 1-7 – points of chemical analysis

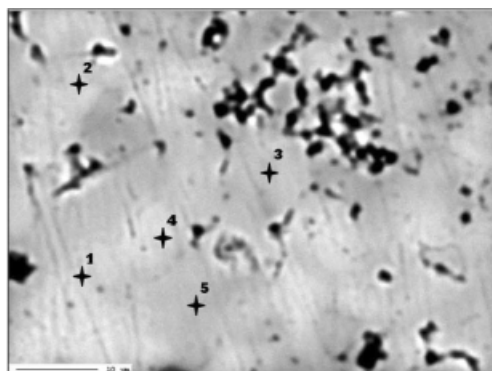


Fig. 5. BSE image of a sample SA5 (Góraźdze limestone from Mount St. Anne) (Stanienda, 2013a). Magn. 2000 \times . Light grey – calcite; dark grey – carbonate phase rich in magnesium. 1-5 – points of chemical analysis

1		2		3		4		5
2		0		0		0.03		300
3		0.07		700		0		0
4		0		0		0.08		800
5		0.05		500		0.03		300
6		0.05		500		0.04		400
7		0.06		600		0.03		300

TABLE 6

Microprobe chemical analyses of Sr and Ba in microarea of sample SA5 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.07	700	0	0
2	0.09	900	0.05	500
3	0.04	400	0	0
4	0.05	500	0	0
5	0.12	1200	0	0

Dziewkowice (Terebratula) Beds limestone

Sr content in the Dziewkowice Beds limestone changes in each microarea of the test samples (SA12, S2 and SO1) (Figs. 6, 7 and 8) from 100 to 1200 ppm, and barium – from 100 to 56900 ppm (Tabs. 7, 8 and 9). Like in the case of the Góraźdze Beds rock, limestone of the Dziewkowice Beds shows considerable variation in the content of strontium, with the highest value observed in a sample from Mount St. Anne (SA12). In addition, the Dziewkowice limestone also demonstrates differences in the content of barium, which is higher than in the previous two rock formations. The highest amount of Ba was determined in a sample from Szymiszów (S2).

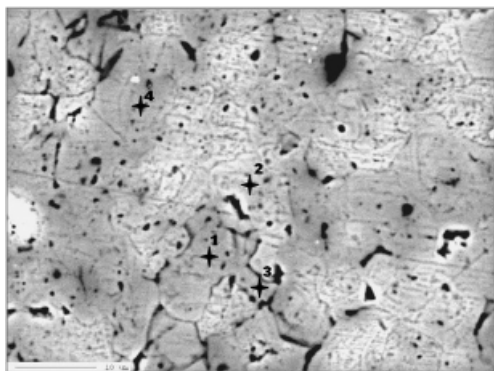


Fig. 6. BSE image of a sample SA12 (Dziewkowiec limestone from Mount St. Anne) (Stanienda, 2013a).
Magn. 2000 \times . Light grey – calcite.
1-4 – points of chemical analysis

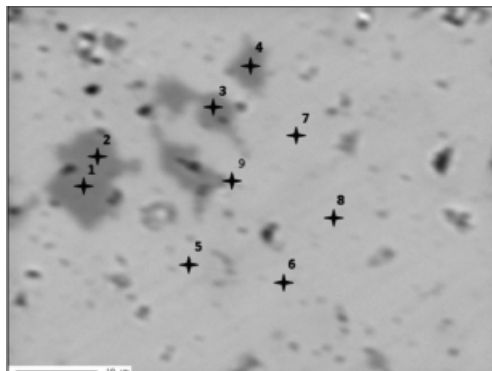


Fig. 7. BSE image of a sample S2 (Dziewkowiec limestone from Szymiszów) (Stanienda, 2013b).
Magn. 500 \times . Light grey – calcite.
1-9 – points of chemical analysis

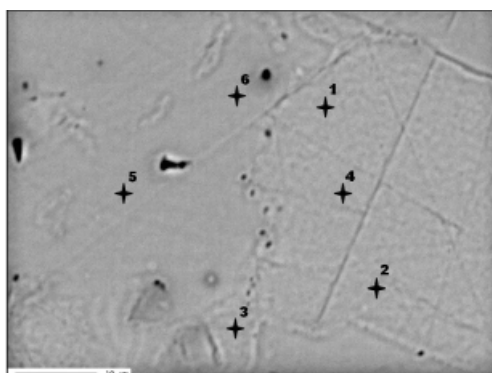


Fig. 8. BSE image of a sample SO1 (Dziewkowiec limestone from Strzelce Opolskie) (Stanienda, 2013a).
Magn. 2000 \times . Light grey – calcite. 1-6 – points of chemical analysis

TABLE 7

Microprobe chemical analyses of Sr and Ba in microarea of sample SA12 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.04	400	0	0
2	0.08	800	0.08	800
3	0	0	0	0
4	0.12	1200	0	0

TABLE 8

Microprobe chemical analyses of Sr and Ba in microarea of sample S2 (Stanienda, 2013b)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0	0	0.84	8400
2	0.02	200	0.01	100
3	0.01	100	0	0
4	0	0	5.69	56900
5	0	0	0.02	200
6	0	0	0	0
7	0	0	0.01	100
8	0.03	300	0	0
9	0	0	0.01	100

TABLE 9

Microprobe chemical analyses of Sr and Ba in microarea of sample SO1 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.04	400	0	0
2	0	0	0	0
3	0.04	400	0.02	200
4	0	0	0.03	300
5	0.02	200	0	0
6	0	0	0	0

Karchowice Beds limestone

Sr content in the Dziewkowice Beds limestone changes in each microarea of the test samples (SO14, SO17, SO20, TO5 and to15) (Figs. 5, 6 and 7) from 200 to 2900 ppm, and barium – from 100 to 36600 ppm (Tabs. 10, 11, 12, 13 and 14). For the samples of the quarry in Strzelce Opolskie (SO14, SO17 and SO20), Sr contents varies slightly in different points of the tested micro-areas from 200 to 580 ppm. Larger differences in the quantities were observed in case of Ba: from 10 to 410 ppm. A significant variability of both Sr and Ba was shown by the results of the analysis of samples from the quarry in Tarnów Opolski. The amount of Sr changes in those samples from 200 to 2900 ppm, and the amount of Ba – from 200 to 36600 ppm. The test results indicate that a higher content of both strontium and barium was determined in the microarea points of the samples from the Tarnów Opolski deposit and a lower content was found in limestone from the deposit of Strzelce Opolskie. Moreover, the results of the spectral microanalysis indicate that Karchowice limestone exhibits the largest variation in the content of both Sr and Ba while compared with the previous rock formations.

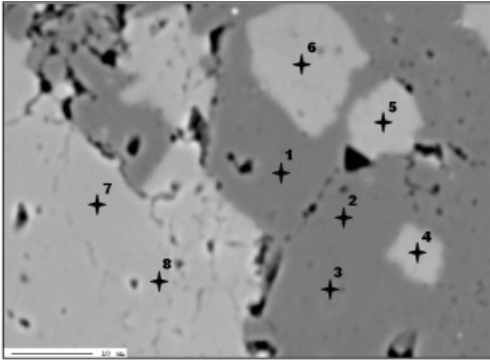


Fig. 8. BSE image of a sample SO14 (Karchowice limestone from Strzelce Opolskie) (Stanienda, 2013a). Magn. 2000×. Light grey – calcite; dark grey – carbonate phase rich in magnesium. 1-8 – points of chemical analysis

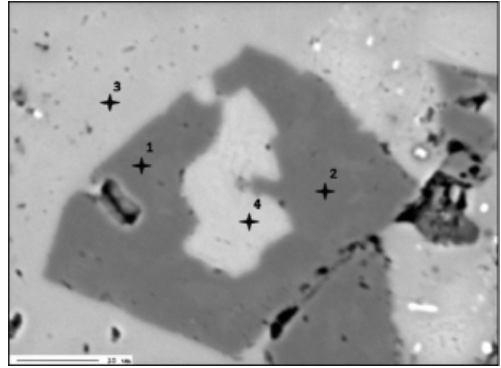


Fig. 9. BSE image of a sample SO17 (Karchowice limestone from Strzelce Opolskie) (Stanienda, 2013b). Magn. 2000×. Light grey – calcite; dark grey – carbonate phase rich in magnesium. 1-4 – points of chemical analysis

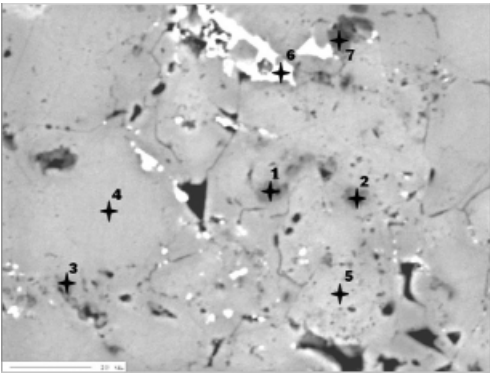


Fig. 10. BSE image of an SO20 sample (Karchowice limestone from Strzelce Opolskie) (Stanienda, 2013a). Magn. 2000×. Light grey – calcite; dark grey – carbonate phase rich in magnesium; light – silicates. 1-7 – points of chemical analysis

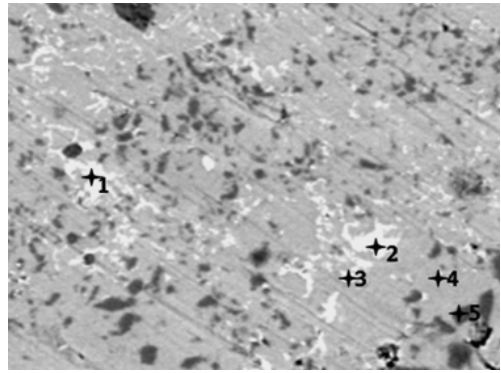


Fig. 11. BSE image of an TO5 sample (Karchowice limestone from Tarnów Opolski) (Stanienda, 2011). Magn. 1000×. Light grey – calcite; dark grey – carbonate phase rich in magnesium; white – Mn-Fe concretions. 1-5 – points of chemical analysis

TABLE 10

Microprobe chemical analyses of Sr and Ba in microarea of sample SO14 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	2	3	4	5
1	0	0	0.001	10
2	0	0	0.013	130
3	0	0	0.020	200
4	0.049	490	0.007	70

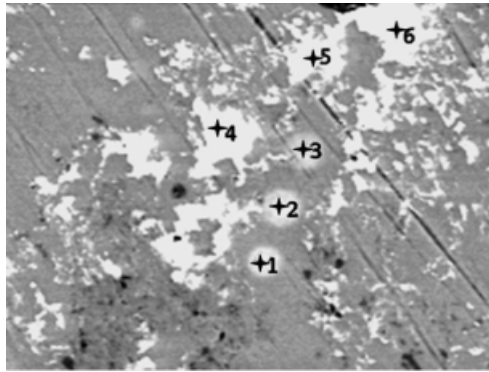


Fig. 12. BSE image of a sample TO15 (Karchowice limestone from Tarnów Opolski) (Stanienda, 2011). Magn. 1000 \times . Light grey – calcite; dark grey – carbonate phase rich in magnesium; white – Fe oxides. 1-6 – points of chemical analysis

1	2	3	4	5
5	0.058	580	0.024	140
6	0	0	0.006	60
7	0.053	530	0.026	260
8	0	0	0.041	410

TABLE 11

Microprobe chemical analyses of Sr and Ba in microarea of sample SO17 (Stanienda, 2013b)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.03	300	0.01	100
2	0.04	400	0.01	100
3	0	0	0	0
4	0	0	0	0

TABLE 12

Microprobe chemical analyses of Sr and Ba in microarea of sample SO20 (Stanienda, 2013a)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0	0	0.01	100
2	0.02	200	0.01	100
3	0	0	0	0
4	0.03	300	0	0
5	0.05	500	0	0
6	0	0	0.04	400
7	0	0	0	0

TABLE 13

Microprobe chemical analyses of Sr and Ba in microarea of sample TO5 (Stanienda, 2011)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.05	500	3.66	36600
2	0.27	2700	1.51	15100
3	0.04	400	0.04	400
4	0.03	300	0.11	1000
5	0.10	1000	0.02	200

TABLE 14

Microprobe chemical analyses of Sr and Ba in microarea of sample TO15 (Stanienda, 2011)

Point number	Sr		Ba	
	[%mass]	[ppm]	[%mass]	[ppm]
1	0.04	400	0.08	800
2	0.09	900	0.08	800
3	0.06	600	0.06	600
4	0.02	200	0.04	400
5	0.29	2900	0.15	1500
6	0.22	2200	0.02	200

4. Conclusions

The results of research presented in this article showed the presence of strontium and barium in the limestone of the Opole Silesia region. These elements were marked in rocks of all lower Muschelkalk formations (Middle Triassic), originating in various areas of Opole Silesia. Differences in the content of strontium and barium characterizes not only deposits of different formations but the variability is also observed in limestone within each of these formations. Differentiation of the amount of Sr, and Ba is also reflected in the rocks of the same formations, from different areas of Opole Silesia.

AES ICP spectrometry results indicate that the Gogolin and Karchowice limestones are the least rich in Sr, and Ba, while higher contents of these elements can be found in the Górażdże and Dziewkowice (Terebratula) Beds. The data obtained as a result of a strontium XRF analysis showed that higher amounts of Sr was determined in the Gogolin, Górażdże and Dziewkowice limestones, while the lowest content of the element characterized the Karchowice limestone. Results of ICP AES spectrometry and the XRF analysis showed the presence of varying strontium content in samples LD11 and G1 of the Gogolin Beds. This may be due to the fact that the marking of Sr was conducted using two different testing methods. Furthermore, strontium is present in varying amounts in low magnesium calcite crystals formed possibly due to the transformation of aragonite during the processes of diagenesis, which is an unstable variety of calcium carbonate, and with which strontium is associated. Thus, performing an analysis on a material taken from the same averaged sample containing various types of calcite, including grains of primary, low magnesium calcite and high magnesium calcite, and marking the presence

of elements such as Sr and Ba, which appear there in small amounts, can yield varying results, which is associated with varying calcite concentration in a sample subjected to a particular analysis. For this study, due to the fact that the ICP AES method was applied to more samples than the XRF method, the results of the ICP AES tests are assumed to be more reliable than the results obtained during the XRF analysis. The results of the tests, which show the variability of amounts of strontium and barium in microareas of the sample, confirm the differences in Sr and Ba content even within the same sample. Varying amounts of Sr and Ba in samples of each formation are related to the specificity of the method, as the measurements of the elements are made at selected points of microareas in a sample. The differentiation of Sr and Ba was observed within the same microarea. A possible reason for that is different varieties of calcite building the microareas of the analyzed sample. During the measurements in microareas, the highest content of Sr was determined in the samples from the Karchowice Beds, and the highest content of Ba was found in the Dziewkowice and Karchowice Beds limestone. The results of those tests confirmed the lowest content of Sr, and Ba present in the microareas of the Gogolin Beds limestone.

While analyzing the presence and diversity of Sr and Ba in Triassic limestones of the Opole Silesia region, which are raw materials used in various sectors of the economy, the genesis of these elements should be explained. Strontium is an element of high ionic radius, focused in the Earth's crust, especially in the continental zone. The size of the ionic radius of Sr^{2+} is 0.13 nm and represents an intermediate between the radii of Ca^{2+} and K^+ ions, so Sr connects to isoivalent diadochy of Ca and heterovalent diadochy of K (Polański, 1988b). Thus, almost the entire amount of strontium found in the Earth's crust is concentrated in the minerals of the rock-forming calcium and potassium (Polański, 1988b). The results of the tests in microareas made within the carbonate mass of the analyzed rocks show that Sr and Ba are present in the carbonate mineral phases. Therefore, these elements also occur in some of the carbonate minerals. According to the literature, strontium occurs in aragonite skeletons and shells of marine organisms (Boggs 2010; Mackenzie & Andersson, 2013; Morse & Mackenzie 1990; Polański, 1988b; Stanienda, 2013a & 2014). Its presence in aragonite stems from the fact that Sr has a larger ionic radius than the ionic radius of Ca. Therefore, it enters the structure of aragonite, which is analogous to strontianite, more easily than calcite. In turn, the mineral material made of aragonite is richer in strontium than a calcitic material (Boggs, 2010; Polański, 1988b; Stanienda, 2014). However, aragonite is an unstable calcium carbonate phase, because during the process of diagenesis it is transformed into low magnesium calcite. Only the presence of strontium shows that the initial phase of calcium carbonate was just aragonite. Barium, like strontium, has a large ionic radius of approx. 0.16 nm, so its geochemical behavior in the Earth's crust is directed by diadochy of potassium, which has a similar ionic radius (Polański, 1988). Accordingly, the greater part of Ba is collected in the rock-forming potassium minerals. Moreover barium, like strontium, is an ingredient of aragonite shells of many lower marine organisms and after their death it passes to the bottom sediments (Boggs, 2010; Morse & Mackenzie, 1990; Polański, 1988b; Stanienda, 2014). A strontium-barium compound is a results of similarly sized ionic radii of Sr^{2+} and Ba^{2+} (Boggs 2010; Polański, 1988b; Stanienda, 2014). Just like in the case of strontium, barium enters the structure of aragonite easier than the structure of calcite. Its presence, like the presence of strontium, attests to the presence of aragonite, an unstable phase of calcium carbonate, in the original carbonate material, which was transformed into low magnesium calcite during the diagenesis.

The results of the strontium and barium studies and the analysis of the genesis of these elements indicate that Sr and Ba are present in low magnesium calcite crystals. Thus, limestone enriched in Sr and Ba is predominantly composed of low magnesium calcite. However, it is assumed that, in addition to low magnesium calcite crystals containing strontium and barium, crystals of that phase of calcium carbonate which do not contain Sr and Ba may also be present. These are probably low magnesium calcite crystals of the original carbonate material or low magnesium calcite crystals which were transformed into low magnesium calcite during the diagenesis with aragonite. Strontium and barium are not expected to occur in phases enriched in magnesium carbonate, such as high magnesium calcite, dolomite or huntite. The presence of Sr and Ba may then indicate the uniformity of the composition of geochemical limestone which is predominantly composed of low magnesium calcite. This can be a valuable piece of information in the conduct of selective mining, allowing to acquire limestone built predominantly with low magnesium calcite, a small percentage of Mg and Fe and other elements, especially in the aspect of using this type of raw material in the lime industry and the industries in which raw limestone of “pure” quality is required or where the acceptable levels of dopants are minimal.

The research results should be analyzed in terms of the impact of Sr and Ba on the environment due to the use of limestone from the area of Opole Silesia in different economic sectors, e.g. in the lime and agricultural industries or as a sorbent in the flue gas desulfurization. The results of the ICP AES and XPS analyzes show that the average content of strontium in the Gogolin Beds limestone varies from 175 to 434.1 ppm, in the Górażdże Beds limestone – from 198 to 334.6 ppm, in the Terebratula (Dziewkowice) Beds rocks – from 210 to 312.9 ppm and in the Karchowice Beds rocks – from 120 to 230 ppm. The results of the tests of microareas indicate that the strontium content measured in the selected points of the microareas changes in the Gogolin Beds limestone from 100 to 1000 ppm, in the Górażdże Beds limestone from 100 to 1200 ppm, in the Terebratula Beds limestone also from 100 to 1200 ppm and in the Karchowice Beds limestone from 200 to 2900 ppm. Sr values obtained from the ICP AES and XRF measurements fall within the strontium content typical of limestone sediments, shallow and deep water sediments, as well as tertiary and older ones (Polański, 1988a, b). Higher content of strontium, from 1000 to 2900 ppm, determined at the microarea points, is typical of current sediments. In deep contemporary sedimentary limestone, Sr content is 2000 ppm (Polański, 1988a, b), while in shallow water Holocene limestone it reaches 6500 ppm. Strontium is also present in skeletons of various marine organisms. Its content in calcite building mussel shells is from 75 to 3000 ppm, in aragonite from 750 to 5500 ppm. In corals, the amount of aragonite is from 4000 to 170,000 ppm of strontium, while calcite of urchins comprises from 750 to 2200 ppm of Sr (Polański, 1988b). This data indicates that in some cases the strontium content in the natural environment can exceed even 150,000 ppm, therefore the amount indicated in the limestone of Opole Silesia area that does not exceed 2900 ppm, should be considered as traces which do not represent a threat to the environment, even after the limestone is processed during its application in various industries. The results of ICP AES showed that the average content of barium in the Gogolin Beds limestone is from 150 to 240 ppm, in the Górażdże Beds limestone it is from 188 to 303 ppm, in the Terebratula Beds limestone – from 215 to 287 ppm and in the Karchowice Beds limestone – from 105 to 205 ppm. The content of Ba marked in the selected points of microareas in the samples is: in the Gogolin Beds limestone from 300 to 2000 ppm, in the Górażdże Beds limestone from 300 to 800 ppm, in the Dziewkowice (Terebratula) Beds

limestone from 100 to 56,900 ppm and the Karchowice Beds rock from 10 to 36,600 ppm. The amount of barium in marine limestone sediments averages from 90 to 190 ppm (Polański, 1988a, b). Thus, the obtained results exceed the values of Ba typical of limestone deposits, especially in case of the amount of Ba obtained from single points of microareas. When analyzing the possibility of the presence of barium in the environment, it should be added that the content of this element in deep-sea clay sediments can be up to 4200 ppm. The content of Ba is also higher in manganese nodules, as it amounts to 3000 ppm (Polański, 1988b). Therefore, concentrations of Ba found in the environment are higher than those characteristic of carbonate rocks and marked in limestone from the area of Opole Silesia during the ICP AES analysis of the average content of this element. Thus, despite the increased amount of Ba marked during the single point analyses of microareas in the samples, it should be assumed that the overall, average content of barium in the limestone deposits from the region of Opole Silesia will not pose a threat to the environment and at the same time will not limit the use of limestone from this area in the various fields of economy.

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