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Article

# Geochemical and Mineralogical Features of Triassic Dolomites from the Area of Upper Silesia in Poland

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**Abstract:** Detailed description of carbonate minerals different in magnesium content of Triassic dolomites were presented in this article. The tests were carried out to determine geochemical and mineralogical features in the terms of their geoengineering properties. The following carbonate phases were identified: a low-Mg calcite, a high-Mg calcite, a proto-dolomite, an ordered dolomite and a huntite. The following research methods were used: microscopic analysis, X-Ray Diffraction, X-Ray Fluorescence and Electron probe microanalysis. The samples were collected from the Tarnowice formation which is the lower part the profile of the Upper Muschelkalk. On the basis of the results the chemical formulas of carbonate phases were calculated. The ranges of Mg and Ca content were presented in formulas. The results indicate of Mg in low-Mg calcite ranges from 0.6 to 1.2%, in high-Mg calcite from 7.47 to 10.41%. In proto-dolomite it ranges from 10.96 to 11.78%. In ordered dolomite Mg content is stoichiometric value for dolomite – 13.18%. Due to the reduced Mg content in identified huntite (the value ranges from 13.62% to 17.76), this carbonate phase was named as de-huntite.

**Keywords:** dolomites; microscopic analysis; X-Ray Diffraction; X-Ray Fluorescence; Electron microprobe analysis; geochemical properties

## 1. Introduction

The area of Upper Silesia, including the area of Bytom and Piekary Śląskie, is an area where Triassic carbonate rocks occur, including Lower, Middle and Upper Muschelkalk formations [1,2]. These rocks in contrast to the limestone deposits of the area of Opole Silesia [3–15] have not been thoroughly investigated in terms of the presence of carbonate phases with different magnesium content. In the limestones of Opole Silesia, five carbonate phases were identified, characterized by different Mg content: low-magnesium calcite, high-magnesium calcite, proto-dolomite, ordered dolomite and huntite.

The Middle Muschelkalk deposits, including the Tarnowice Unit [16], have not been the subject of detailed research in the term of identifying carbonate phases with different magnesium content. However, due to the probability of the presence of carbonate phases with different amounts of Mg in them, mainly high-magnesium calcite, which was identified in the rocks of the lower Muschelkalk of the area of Opole Silesia, rocks of the Tarnowice Unit were chosen as the subject of the study.

During earlier studies of the Triassic carbonate rocks from the area of Opole Silesia, which are formations of the lower and partly middle Muschelkalk, the presence of the following carbonate phases was identified: low-magnesium calcite, high-magnesium calcite, proto-dolomite, ordered dolomite and huntite. The presence of these phases made it possible to determine the conditions of carbonate rocks' sedimentation and the diagenetic processes that these rocks underwent. Due to the probability of the presence of these mineral phases in the rocks of the Tarnowice Unit, which are formation of the upper part of the Middle Muschelkalk [16–18], it was worth undertaking research that allowed to obtain new data on the presence of carbonate phases with different magnesium content and geochemical composition of the carbonate rocks. Based on the research results, it was also possible to determine the sedimentation conditions in which the rocks of the Tarnowice Unit were formed and the diagenetic processes that influenced the final structure of the carbonate rocks.

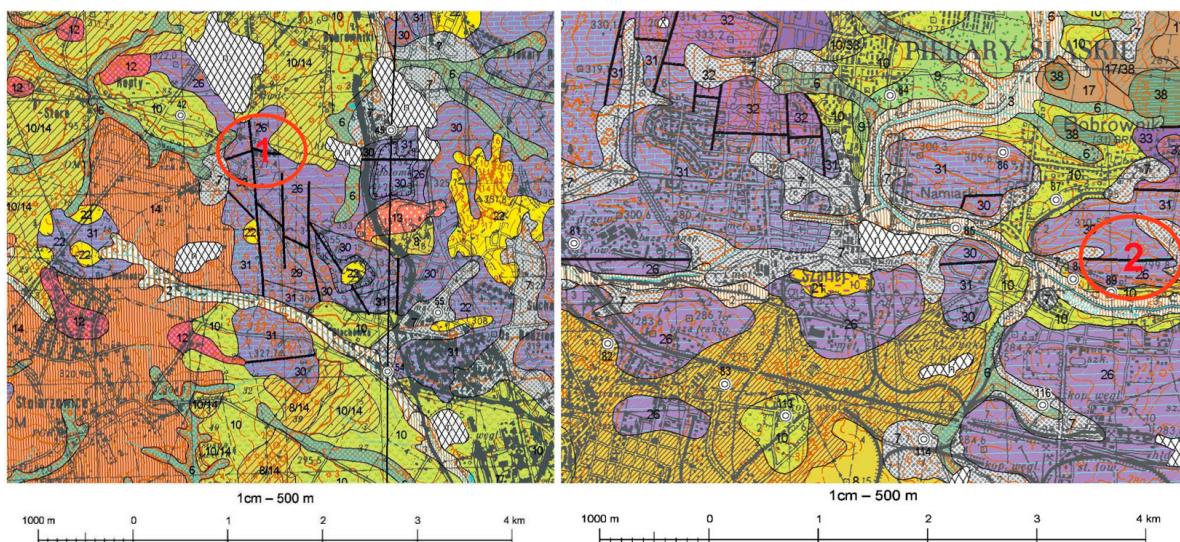


The results of the research and the conclusions formed on the basis of the results will be a source of new data on the mineral composition and genesis of the rocks of the Tarnowice Unit.

## 2. Materials and Methods

### 2.1. Materials

The subject of this project are carbonate rocks of the Tarnowice Unit from selected areas of the Upper Silesia (Silesian Voivodeship). The study zone includes the area of Piekary Śląskie and Bytom (Figure 1). The samples were given symbols depending on the sampling location: LZ- Lazarówka Quarry (area of Bytom – Sucha Góra City), PSK- Piekary Śląskie City, Mieczysław Karłowicz Street, PSZ- Piekary Śląskie City, Zawisza Czarny Street.



**Figure 1.** Location of the research area. Fragment of a detailed geological map of Poland [19]. Original scale 1: 50,000. Sheet - 910 - Bytom (M-34-50-D). 1 – Lazarówka Quarry (Lazarówka street - LZ), 2 – Piekary Śląskie area (Karłowicz - PSK and Zawisza Czarny - PSZ streets). **Numbering on a geological map:** 26 - Middle Triassic - dolomites and limestones (Jemielnica and Tarnowice stratas).

### 2.2. Methods

Microscopic observations in transmitted light, were made in the Laboratory of the Department of Applied Geology, using the Zeiss Axioscope, cooperating with the K 300 image analyzer. Thin plates were made from six carbonate rock samples. Observations were made at  $\times 100$  and  $\times 200$  magnifications. Phase identification by X-ray diffraction (XRD) was done in the laboratory of the Solid State Department, in Institute of Physics, Faculty of Mathematics, Physics and Chemistry of the University of Silesia. The tests were performed using the EMPIRIAN diffractometer by PANALYTICAL. The XRF analysis was also performed in the laboratory of the Solid State Department, Institute of Physics, Faculty of Mathematics, Physics and Chemistry of the University of Silesia. The X-Ray Fluorescence Spectrometer (XRF), model ZSX Primus II by Rigaku, was used for the research. It uses wavelength dispersion for measurements. The maximum lamp voltage is 60 kV (rhodium lamp). Measuring range Be - U. Measurements are non-standard (fundamental parameters method). Microprobe measurements were carried out at the Institute of Non-Ferrous Metals in Gliwice. Three samples were delivered in the form of polished sections, made of rocks with numbers: PSK2, PSZ3 and LZ1. The content of the following elements were measured: C, O, Mg, Al, Si, Ca, Mn and Fe. The tests were performed by X-ray microanalysis using the JXA 8230 X-ray microprobe made by JEOL. The accelerating voltage was 15kV, the electron beam current was 20nA. Quantitative analyzes of the chemical composition were carried out using the wavelength dispersion (WDS) method. The size of the analyzed area, resulting from the characteristics of the electron beam and the

X-ray excitation area, is of the order of  $1\mu\text{m}^3$ . The maps of the element distribution were made using the energy dispersive method (EDS). The standards used were: pure metals for Fe, Mn and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) as the standard for aluminum and oxygen, calcium silicate ( $\text{CaSiO}_3$ ) as the standard for silicon and calcium, iron sulfide ( $\text{Fe}_2\text{S}$ ) as the standard for sulfur (for sample LZ1), diamond as the standard and magnesium oxide ( $\text{MgO}$ ) as a magnesium standard. The supplied samples were sputtered with a gold layer.

### 3. Results

#### 3.1. Mineralogical and petrographic characteristics of samples

During this project two types of rocks were studied: lime dolomites and dolomites. Photographs of the samples are shown in the figure below (Figure 2).

Samples taken from the Lazarówka quarry are characterized by a dark brown color and low compactness, especially the LZ3 sample. It could be probably the effect of weathering processes. The rocks show a sparite texture and a chaotic, compact, in places porous structure. The exception is the LZ3 sample – it is unconsolidated rock. Reaction with hydrochloric acid, either weak or occurring after pulverization, strongly indicates dolomite predominance. It can therefore be concluded that these are probably dolomitic limestones or lime dolomites. The data obtained by applying X-ray Diffraction and X-Ray Fluorescence (XRF) will provide more detailed information about these rocks. In the case of rocks taken from the area of Piekary Śląskie, from Karłowicz and Zawisza Czarny Streets, the reaction with hydrochloric acid occurs after pulverization, which indicates the dolomite dominance. Thus, these rocks can be defined as dolomites. The rocks taken from the area at Zawisza Czarny Street present a brown or light brown color, a dolosparite texture and a compact, chaotic structure. The rocks taken from the area of Karłowicz Street are characterized by a gray color, a dolosparite texture and a compact, disordered structure.

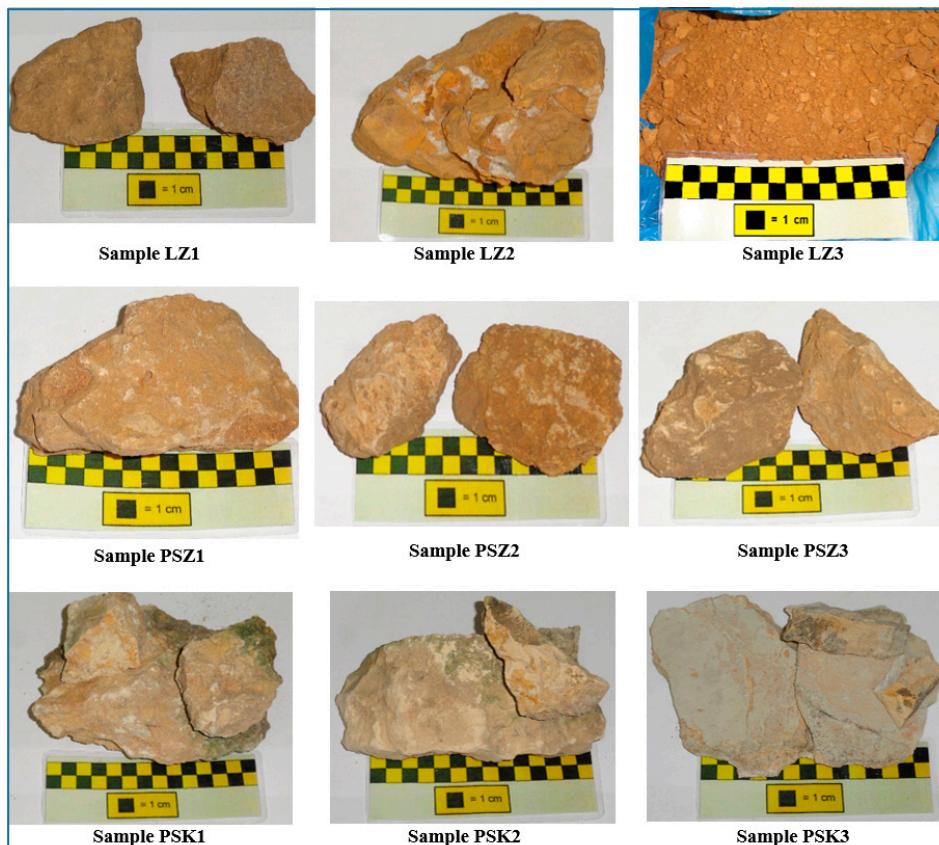


Figure 2. Photographs of the samples.

Six samples of carbonate rocks were subjected to microscopic examination.

The rocks from the Lazarówka Quarry in the microscopic images have a sparite texture (samples LZ2, LZ3 - Figure 3a, c, d, e), in some places biomorphic (Sample LZ2 - Figure 3b). The structure is chaotic, compact. Sparite rocks contain veins built of coarse-crystalline calcite (Figure 3a, d, e), as well as euhedral, rhombohedral dolomite crystals (Figure 3c, e). Dolomite crystals are often filled with iron compounds (Figure 3c), so they can be treated as dolomite pseudomorphs. Rocks with a biomorphic texture include oval bioclasts, bonded with contact cement, with pores in some places (Figure 3b). In the mineral composition, dolomite and calcite as well as admixtures of Fe compounds were determined. The samples from Piekary Śląskie have a biomorphic (samples PSK1, PSZ1, PSZ2 - Figure 3f, g, h, l, m, o) or sparite (samples PSK3, PSZ2 - Figure 3i, j, k, n) texture. The structure is compact, chaotic. Samples with a biomorphic texture similar to rocks from the Lazarówka Quarry include oval or elongated bioclasts, bonded with microsparite or sparite cement. The cement is porous or contact (Figure 3f, g, h, l, m, o). Some bioclasts have a rim made of iron compounds (Figure 3f, g). The interior of some bioclasts is filled with micrite or microsparite (Figure 3f, g, h, l, m, o). Rocks with a sparite texture are built of a rock mass. Concentrations of iron compounds are present here (Figure 3k, n), stylolites filled with Fe compounds can also be observed (Figure 3k). In addition, single, fine grains of chalcedony (Figure 3j) and quartz (Figure 3k) were identified in some samples. In the mineral composition carbonate minerals dominate. Iron compounds, chalcedony and quartz are present in smaller amounts.

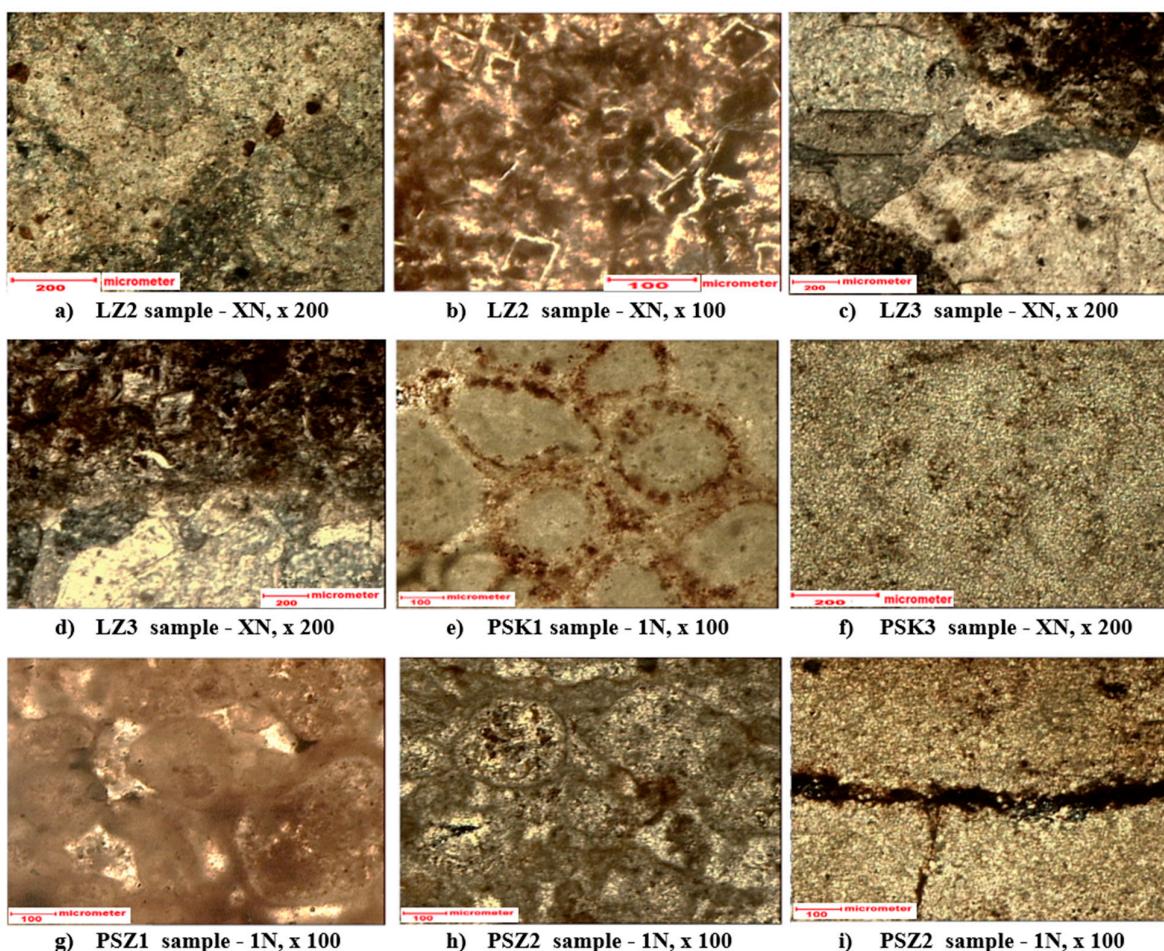


Figure 3. Microscopic photographs of carbonate rock samples.

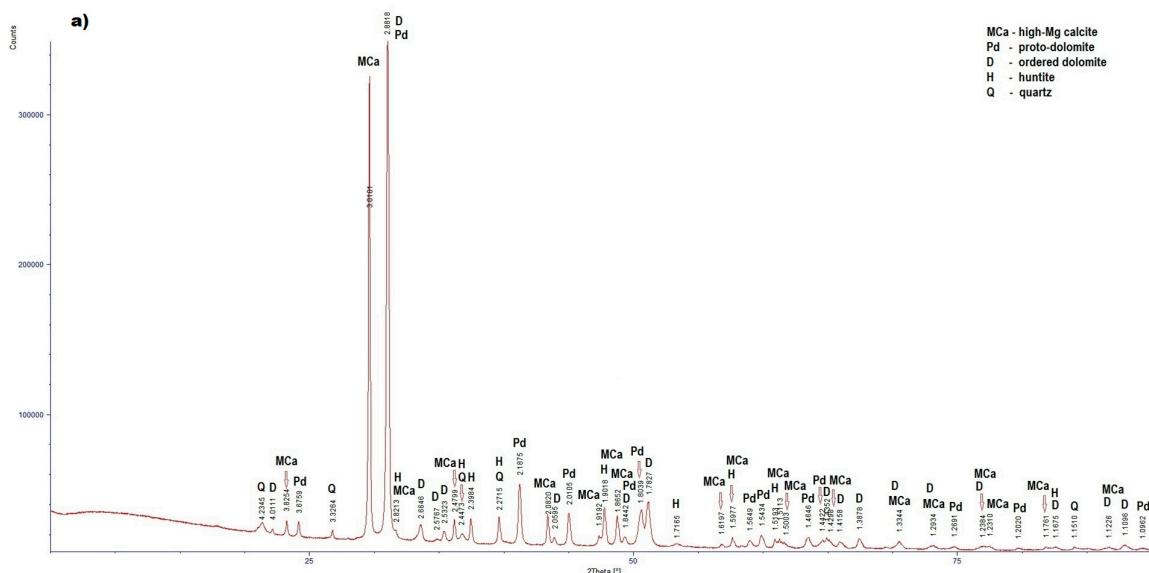
### 3.2. Results of X-Ray Diffraction

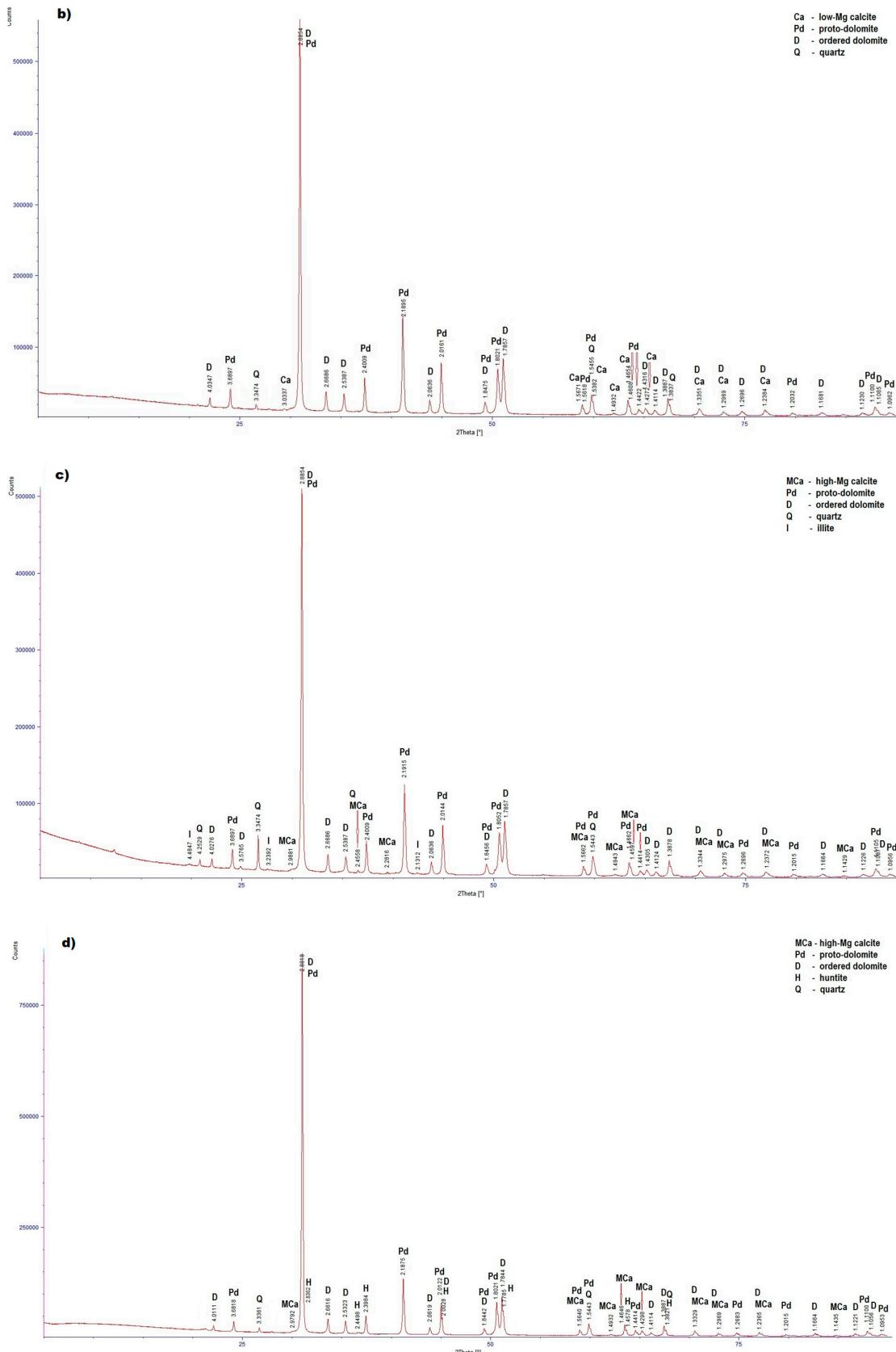
The Table 1 and Figure 4 present the results of X-ray diffraction of the examined carbonate rocks of the Tarnowice Unit. The results of X-ray diffraction show that dolomite dominate in the examined rocks. Low-magnesium calcite was determined only in the PSK1 sample (Figure 4b). In this rock, apart from the dominant dolomite and the lesser amount of low-magnesium calcite, quartz was also determined. In the samples, apart from dolomite, high-magnesium calcite is present. Huntite was identified in the LZ2 and PSZ1 samples (Figure 4a, d). From non-carbonate minerals, quartz was determined in the diffraction patterns of all the samples (Figure 4), and additionally illite in the sample PSK3 (Figure 4c). The X-ray diffraction results indicate that the dominant calcite phase in the examined rocks is high-magnesium calcite. Based on the results of X-ray diffraction, it can be concluded that the rocks the rocks from the Lazarówka quarry can be described as calcareous dolomites, while the rocks from the area of Piekary Śląskie represent dolomites, with a small amounts of calcite or, in the case of some rocks, huntite.

**Table 1.** Results of X-Ray diffraction.

Type of Sample	Type of Mineral	d <sub>hkl</sub> - index of the lattice intervals of exposed parallel lattice planes system Å intensity of diffraction lines
LZ2 (Figure 4a)	High-Mg calcite	3.8254 (12), 3,0101 (100), 2,8213 (2), 2.4799 (14), 2,0820 (16), 1.9182 (7), 1.9018 (21), 1.8652 (23), 1.6197 (4), 1.5977 (11), 1.5193 (6), 1.5113 (3), 1.5003 (3), 1.4298 (8), 1.3344 (3), 1,2934 (4), 1.2384 (1), 1.2310 (1), 1.1761 (3), 1.1226 (3)
	Proto-dolomite	3.6759 (4), 2.8818 (100), 2.1875 (30), 2.0105 (15), 1.8442 (5), 1.8039 (17), 1.5649 (4), 1.5434 (10), 1.4646 (7), 1.4422 (3), 1.2691 (3), 1.2020 (1), 1.0962 (2)
	Ordered dolomite	4.0111 (1), 2.8818 (100), 2.6648 (4), 2.5767 (3), 2.5323 (2), 2.0595 (3), 1.8442 (5), 1.7827 (21), 1.4352 (3), 1.4158 (3), 1.3878 (9), 1.3344 (4), 1.2934 (2), 1.2384 (3), 1.1675 (2), 1.1226 (2), 1.1096 (8)
	Huntite	2,8213 (100); 2,4473 (9); 2,3984 (10); 2,2715 (5); 1,9018 (1); 1,7165 (3); 1,5977 (10); 1,5193 (1); 1,5113 (1); 1,1675 (1);
LZ3	Quartz	4,2345 (19); 3,3264 (100); 2,4473 (7); 2,2715 (7); 1,1510 (2)
	High-Mg calcite	3,8468 (8); 3,0284 (100); 2,7931 (2); 2,4860 (14); 2,2787 (21); 2,0886 (16); 1,9052 (21); 1,8685 (23); 1,3344 (3); 1,2975 (4); 1,2384 (1); 1,1236 (3)
	Proto-dolomite	3.6957 (4), 2.8854 (100), 2.4041 (13), 2.1915 (30), 2.0161 (15), 1.8475 (5), 1.8039 (17), 1.5662 (3), 1.5465 (10), 1.4654 (7), 1.4440 (3), 1.2704 (3), 1.2020 (1), 1.1105 (8), 1.0962 (2)
	Ordered dolomite	4.0276 (1), 2.8854 (100), 2.6686 (4), 2.5387 (2), 2.0636 (3), 1.8475 (5), 1.4305 (3), 1.4131 (1), 1.3894 (8), 1.3344 (3), 1.2975 (2), 1.2384 (3), 1.1681 (2), 1.1236 (2), 1.1073 (8)
PSK1 (Figure 4b)	Quartz	4,2529 (19); 3,3425 (100); 2,4558 (7); 2,2787 (7); 1,5412 (10); 1,3844 (6)
	Low-Mg calcite	3.0337 (100), 1.5671 (1), 1.5382 (9), 1.4932 (5), 1.4654 (2), 1.4272 (5), 1.3351 (3), 1.2969 (5), 1.2384 (2)
	Proto-dolomite	3.6897 (4), 2.8854 (100), 2.4009 (13), 2.1895 (30), 2.0161 (15), 1.8475 (5), 1.8021 (17), 1.5618 (3), 1.5455 (10), 1.4608 (7), 1.4422 (3), 1.2696 (3), 1.2032 (1), 1.1100 (8), 1.0962 (2)
	Ordered dolomite	4.0347 (1), 2.8854 (100), 2.6686 (4), 2.5387 (2), 2.0636 (3), 1.8475 (5), 1.7857 (21), 1.4316 (3), 1.4114 (1), 1.3887 (8), 1.3351 (3), 1.2969 (2), 1.2384 (3), 1.1681 (2), 1.1230 (2), 1.1065 (8)
	Quartz	3.3474 (100), 1.5455 (10), 1.3837 (6)

PSK3 (Figure4c)	High-Mg calcite	2.9881 (100), 2.4558 (14), 2.2816 (21), 1.5662 (1), 1.4933 (3), 1.4662 (3), 1.4597 (2), 1.3344 (3), 1.2975 (4), 1.2372 (1), 1.1429 (4)
	Proto-dolomite	3.6897 (4), 2.8854 (100), 2.4009 (13), 2.1915 (30), 2.0144 (15), 1.8456 (5), 1.8052 (17), 1.5662 (3), 1.5443 (10), 1.4662 (7), 1.4414 (3), 1.2696 (3), 1.2015 (1), 1.1105 (8), 1.0956 (2)
	Ordered dolomite	4.0276 (1), 3.5710 (4), 2.8854 (100), 2.6686 (4), 2.5387 (2), 2.0636 (3), 1.8456 (5), 1.7857 (21), 1.4305 (3), 1.4124 (1), 1.3878 (8), 1.3344 (3), 1.2975 (2), 1.2372 (3), 1.1664 (2), 1.1226 (2), 1.1087 (8)
	Quartz	4.2529 (19), 3.3474 (100), 2.4558 (7), 1.5443 (10)
PSZ1 (Figure4d)	Illite	4.4847 (100), 3.2392 (65), 2.1312 (31)
	High-Mg calcite	2.9792 (100), 1.5640 (1), 1.4932 (3), 1.4646 (3), 1.4298 (8), 1.3329 (3), 1.2969 (4), 1.2365 (1), 1.1435 (4)
	Proto-dolomite	3.6818 (4), 2.8818 (100), 2.1875 (30), 2.0122 (15), 1.8442 (5), 1.8021 (17), 1.5640 (3), 1.5443 (10); 1.4414 (3), 1.2683 (3), 1.2015 (1), 1.1100 (8); 1.0953 (2)
	Ordered dolomite	4.0111 (1), 2.8818 (100), 2.6616 (4), 2.5323 (2), 2.0619 (3), 2.0028 (15); 1.8442 (5), 1.7844 (21), 1.4114 (1); 1.3887 (8), 1.3329 (3), 1.2969 (2), 1.2365 (3), 1.1664 (2), 1.1221 (2); 1.1056 (8)
PSZ3	Huntite	2.8362 (100), 2.4498 (9), 2.3984 (10), 2.0028 (7), 1.7785 (15), 1.4578 (2), 1.3821 (1)
	Quartz	3.3361 (100), 1.5443 (10), 1.3821 (6)
PSZ3	High-Mg calcite	3.0101 (100), 1.5627 (1), 1.5382 (9), 1.4895 (3), 1.4578 (3), 1.4262 (8), 1.3269 (3), 1.2946 (4), 1.2352 (1), 1.1435 (4)
	Proto-dolomite	3.6681 (4), 2.8688 (100), 2.3928 (13), 2.1829 (30), 2.0066 (15), 1.8410 (5), 1.7978 (17), 1.5627 (3), 1.5403 (10), 1.2670 (3), 1.2015 (1), 1.0944 (2)
	Ordered dolomite	3.9947 (1), 2.8688 (100), 2.6545 (4), 2.5224 (2), 2.0578 (3), 1.8410 (5), 1.7797 (21), 1.4396 (3), 1.4089 (1), 1.3861 (8), 1.3320 (3), 1.2946 (2), 1.2352 (3), 1.1655 (2), 1.1211 (2), 1.1082 (8)
	Quartz	3.3264 (100), 1.5403 (10), 1.3804 (6)





**Figure 4.** X-ray diffraction patterns of the dolomite samples: (a) LZ2, (b) PSK1, (c) PSK3, (d) PSZ1.

### 3.3. Results of X-Ray Fluorescence

By XRF analysis, the elements present in the studied carbonate rocks were determined. The dolomites' test results are given in Tables 2–4. The results of the study of the elemental composition indicate that the highest percentage present the elements building carbonate minerals, i.e. Ca, Mg, C, O (Table 2). These elements are part of carbonate phases such as: low-magnesium calcite, high-magnesium calcite, dolomite phases and huntite. In smaller amounts, the following elements were determined: Na, Al, Si, K, Mn, Fe, F, P, S, Cl, Ti, Cr, Ni, Cu, Zn, Sr, Ba and Pb, and in some samples Rb, Br, Co, As and Cd.

**Table 2.** Composition of the studied samples elements.

Element	Unit	Detection limit	Sample number					
			LZ2	LZ3	PSK1	PSK3	PSZ1	PSZ2
Main elements								
C	mass%	0.02437	6.53	8.06	8.16	7.69	8.45	8.36
O	mass%	0.15465	52.5455	3556.5456	5456.3456	39		
Na	mass%	0.01456	0.62	0.24	0.13	0.10	0.14	0.13
Mg	mass%	0.00861	7.23	9.48	10.95	10.50	10.78	10.98
Al	mass%	0.00161	0.33	0.18	0.26	0.70	0.15	0.15
Si	mass%	0.00276	3.42	1.22	1.31	2.78	0.83	0.72
K	mass%	0.00139	0.05	0.02	0.08	0.19	0.03	0.03
Ca	mass%	0.00454	18.95	22.66	21.80	20.66	21.75	21.80
Mn	mass%	0.00142	0.78	0.45	0.06	0.04	0.09	0.06
Fe	mass%	0.00148	8.39	2.18	0.33	0.51	1.12	0.84
Trace elements								
F	ppm	577,45	BDL	BDL	776	475	BDL	BDL
P	ppm	4.03	222	55	64	87	94	69
S	ppm	6.98	891	359	1491	544	719	869
Cl	ppm	37.72	564	500	613	531	620	633
Ti	ppm	24.43	113	68	100	292	70	56
Cr	ppm	15,87	22	7	13	27	BDL	BDL
Co	ppm	15.25	31	BDL	19	23	BDL	BDL
Ni	ppm	8.08	26	26	17	15	20	18
Cu	ppm	7.5	22	12	362	545	16	17
Zn	ppm	6.6	6803	290	5	9	1248	3455
As	ppm	16,8	BDL	BDL	BDL	BDL	23	41
Rb	ppm	3.8	BDL	BDL	5	9	BDL	BDL
Br	ppm	5.07	BDL	13	BDL	BDL	5	5
Ba	ppm	66.5	BDL	BDL	99	233	BDL	BDL
Sr	ppm	4.2	50	46	117	81	81	78
Cd	ppm	15.05	BDL	BDL	BDL	BDL	29	37
Pb	ppm	13.27	2818	74	73	36	151	178

BDL – below detection limit.

Manganese and iron can be substitutions for Ca and Mg in carbonate minerals. Strontium and barium are elements originally present in aragonite, an unstable phase of calcium carbonate, which, like high-magnesium calcite, is transformed into low-magnesium calcite during diagenesis. Ni, K, Si, Al, as well as some Fe, Br and Cd will be included in the composition of aluminosilicates - mainly feldspars and clay minerals. S, Ti, Cr, some Fe, Ni, Cu, Zn Pb will probably be bound in sulfides and oxides. During sedimentation processes, Ni is incorporated into the structures of clay minerals. Nor can it form sulfides and arsenides. What appear together with Fe and Mn in smithsonite. Chlorine is bound in chlorides and phosphorus is present in organic matter.

The content of individual elements, basic oxides included in the minerals of the examined rocks,  $\text{MgCO}_3$  content and the value of the ratio of Ca to Mg were calculated (Table 3).

**Table 3.** Contents of basic elements, oxides,  $\text{MgCO}_3$  and value of Ca/Mg ratio.

Sample number	Content of basic elements [%]							
	Ca	Mg	Fe	Mn	Si	Al	Na	K
LZ2	18.95	7.23	8.39	0.78	3.42	0.33	0.62	0.05
LZ3	22.66	9.48	2.18	0.45	1.22	0.33	0.24	0.02
PSK1	21.80	10.95	0.33	0.06	1.31	0.26	0.13	0.08
PSK3	20.66	10.50	0.51	0.04	2.78	0.70	0.10	0.19
PSZ1	21.75	10.78	1.12	0.09	0.83	0.15	0.14	0.03
PSZ2	21.80	10.98	0.84	0.06	0.72	0.15	0.13	0.03
Content of basic oxides [%]								
	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	MnO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
LZ2	26.51	11.99	11.99	1.01	7.32	0.62	0.84	0.06
LZ3	31.70	15.72	3.12	0.58	2.61	0.62	0.32	0.02
PSK1	30.50	18.16	0.47	0.08	2.80	0.49	0.17	0.09
PSK3	28.91	17.41	0.73	0.05	5.95	1.32	0.13	0.23
PSZ1	30.43	17.87	1.60	0.12	1.77	0.28	0.19	0.04
PSZ2	30.50	18.21	1.20	0.07	1.54	0.28	0.17	0.04
MgCO <sub>3</sub> content and Ca/Mg ratio								
	Ca [%]	CaO [%]	Mg [%]	MgO [%]	MgCO <sub>3</sub> [%]	Ca/Mg		
LZ2	18.95	26.51	7.23	11.99	25.78	2.62		
LZ3	22.66	31.70	9.48	15.72	33.80	2.39		
PSK1	21.80	30.50	10.95	18.16	39.04	1.99		
PSK3	20.66	28.91	10.50	17.41	37.43	1.97		
PSZ1	21.75	30.43	10.78	17.87	38.42	2.02		
PSZ2	21.80	30.50	10.98	18.21	39.15	1.98		

Based on the obtained data, the position of the studied carbonate rocks was presented according to the classification of Chilingar [20] and Pettijohn [21] (Table 4).

The data presented in Table 4 indicate that the studied carbonate rocks represent lime dolomites, some samples LZ2, LZ3 and PSZ1, in the classification of Pettijohn [21] – calcareous dolomites. Therefore, these rocks, apart from the mineral dolomite, also contain calcite phases, including high-magnesium calcite. This confirms the results of X-Ray diffraction.

**Table 4.** Position of the analyzed rocks in classifications based on Ca/Mg ratios and MgO and MgCO<sub>3</sub> contents [%].

Specimen name	Sample number	Ca/Mg	MgO [%]	MgCO <sub>3</sub> [%]	Rock name in the Chilingar G.V. (1957) classification	Rock name in the Pettijohn F.J. (1975) classification
Rocks of the Lazarówka Quarry	LZ2	2.62	11.99	25.31	Lime Dolomite	Calcerous dolomite
	LZ3	2.39	15.72	33.18	Lime Dolomite	Calcerous dolomite
Rocks from the area of Piekary Śląskie City	PSK1	1.99	18.16	38.33	Lime Dolomite	Lime Dolomite
	PSK3	1.97	17.41	36.75	Lime Dolomite	Lime Dolomite
	PSZ1	2.02	17.87	37.74	Lime Dolomite	Calcerous dolomite
	PSZ2	1.98	18.21	38.43	Lime Dolomite	Lime Dolomite

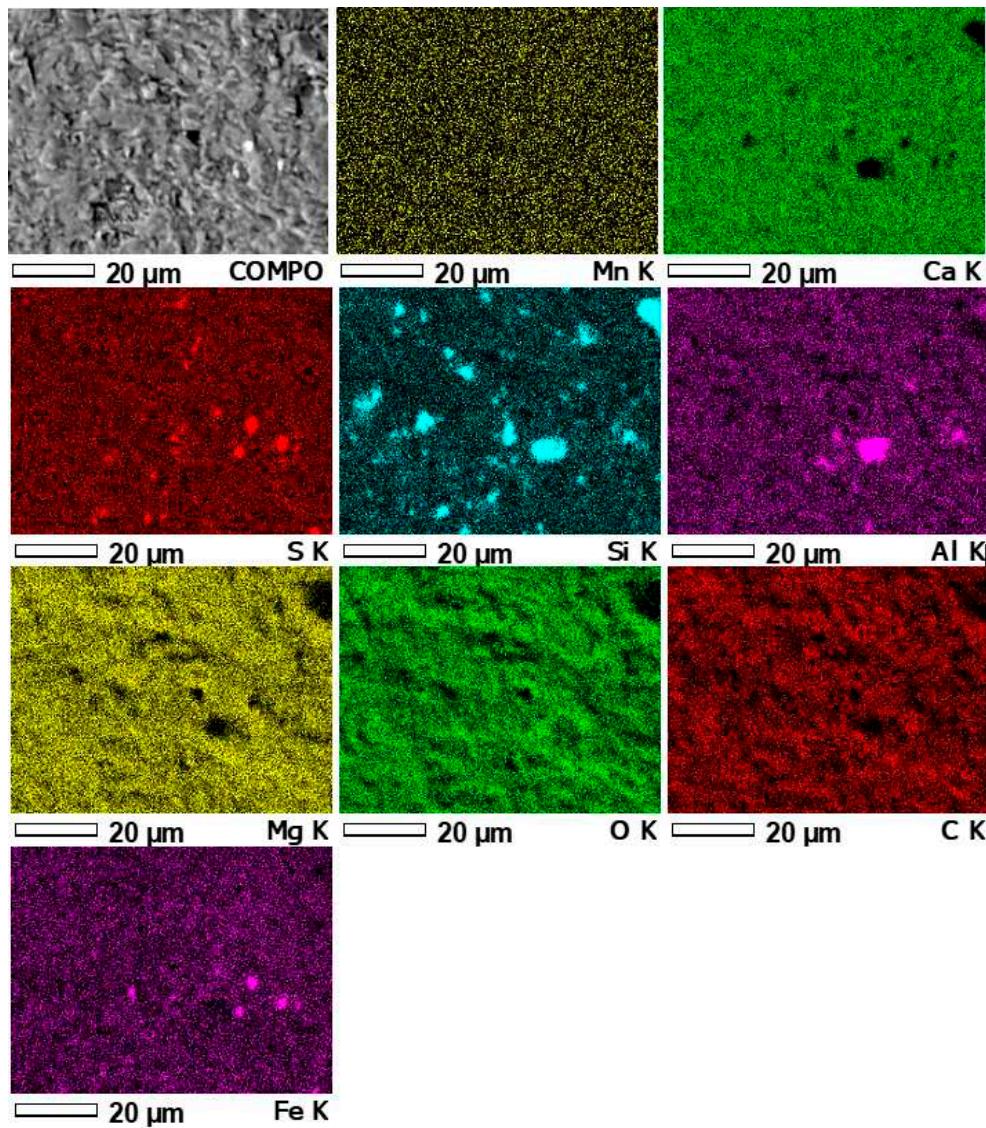
### 3.4. Results of microprobe measurements

Three samples in the form of polished sections made of rocks were tested – LZ1, PSK2 and PSZ3. Quantitative measurements of the following elements were carried out: C, O, Mg, Al, Si, Ca, Mn and

Fe. As part of the EDS microprobe analysis, maps of distribution of elements were made. Moreover, quantitative analysis using the EDS method and quantitative analysis at points using the WDS method were done. The results were normalized to 100%. On the basis of the measured Ca, Mg, C and O contents of carbonate phases building the examined dolomites were identified. Furthermore chemical formulas of studied carbonate phases were calculated. Other elements, such as Si, Al, Fe, Mn, are probably bound in silicates and aluminosilicates. Fe and S could be bound in pyrite. Because these elements occur in small amounts, the formulas of the minerals they form have not been determined.

Sample LZ1 - rock from the Lazarówka quarry

In the first stage of microprobe analysis, the distribution of the following elements was measured: Mn, Ca, S, Si, Al, Mg, O, C and Fe in the first micro-area of the LZ1 sample (Figure 5).

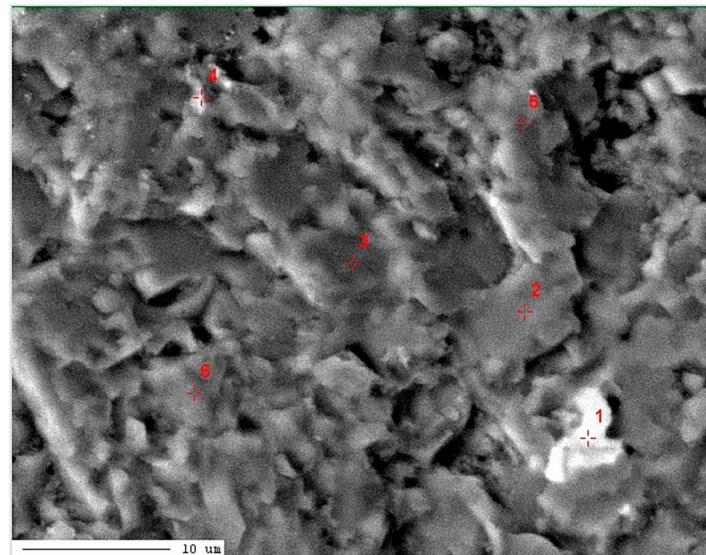


**Figure 5.** Maps of the distribution of EDS elements in micro-area 1 of the LZ1 sample, magnification x1500.

Superposition of Ca and Mg images distribution allows to determine the presence of these elements in the same areas, which indicates the presence of calcium-magnesium carbonate phases. The superposition of Fe and S images distribution allows to determine the presence of iron sulfides

– pyrite in the sample. And the occurrence of Si and Al in the same areas of Si nad Al images indicate the presence of aluminosilicates. The rest of Si is probably connected with silicate mineral – quartz.

In the second micro-area of the LZ1 sample, measurements of the elemental content were done using the WDS method (Figure 6, Table 5).



**Figure 6.** Image of the composition of sample LZ1 micro-area 2, with marked points of quantitative analysis, magnification x2500.

**Table 5.** Results of the WDS analysis at the points of LZ1 sample micro-area.

Point Number	Element Content [mass%]	Element								MgO [%]
		C	O	Mg	Si	Al	Ca	Fe	Mn	
1 / low-Mg calcite (Ca <sub>0.95</sub> ,Mg <sub>0.05</sub> )CO <sub>3</sub>	10.5852.10	1.20	0.740	0.0525.441.471.057.37						100.00 2.00
2 / high-Mg calcite (Ca <sub>0.57</sub> ,Mg <sub>0.43</sub> )CO <sub>3</sub>	10.9354.1910.37	BDL	0.0720.962.870.600.01							100.00 17.28
3 / high-Mg calcite (Ca <sub>0.69</sub> ,Mg <sub>0.31</sub> )CO <sub>3</sub>	12.0755.99	7.47	0.010	0.0621.292.650.46	BDL					100.00 12.45
4 / high-Mg calcite (Ca <sub>0.57</sub> ,Mg <sub>0.43</sub> )CO <sub>3</sub>	11.9053.4710.41	0.050	0.0521.961.890.250.02							100.00 17.35
5 / proto-dolomite (Ca <sub>0.53</sub> ,Mg <sub>0.47</sub> )CO <sub>3</sub>	11.2053.4911.39	0.050	0.0820.922.250.610.01							100.00 18.98
6 / proto-dolomite (Ca <sub>0.51</sub> ,Mg <sub>0.49</sub> )CO <sub>3</sub>	11.2953.4411.71	0.010	0.1120.692.170.560.02							100.00 19.52

BDL – below detection limit.

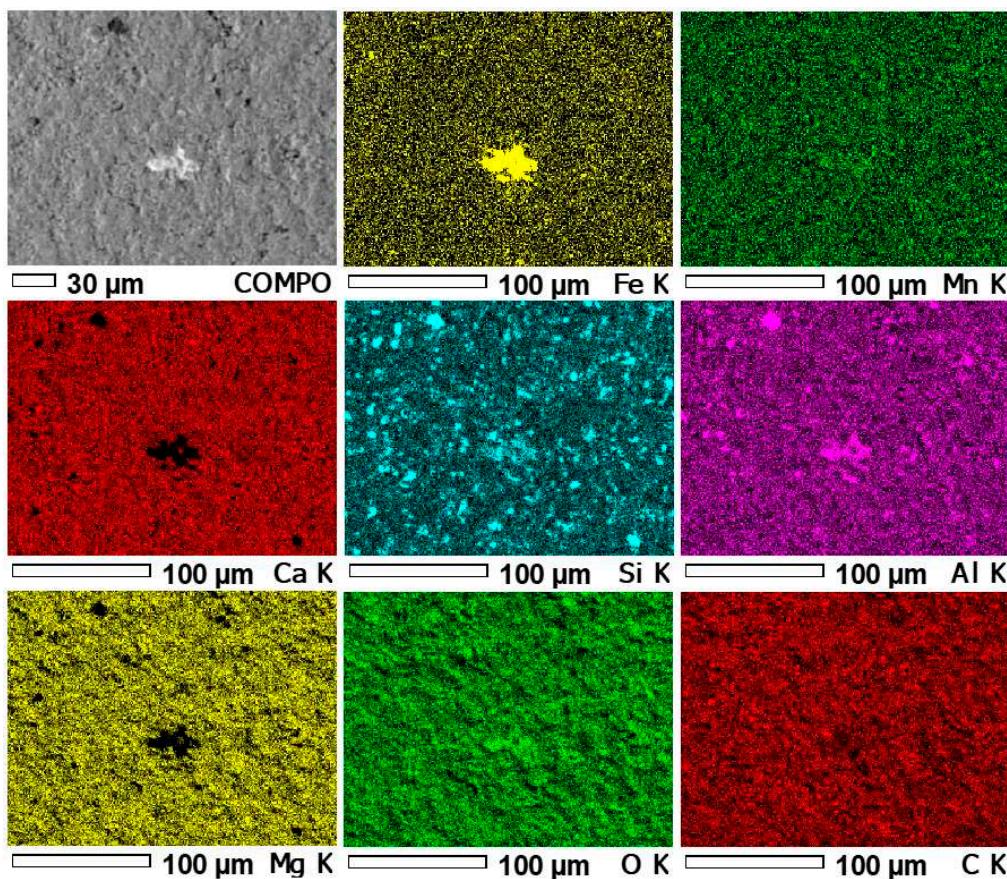
The results of measurements in micro-area 2 of the LZ1 sample indicate the presence of three carbonate phases with different Mg content: low-magnesium calcite (point 1), high-magnesium calcite (points 2, 3 and 4) and proto-dolomite (points 5 and 6) (Figure 6, Table 5). Proto-dolomite of

the sample LZ1 is characterized by a lower MgO content than the stoichiometric value for dolomite (MgO – 21.86 %, Mg – 13.18 %).

Sample PSK2 - rock from the area of Piekary Śląskie (Karłowicz Street)

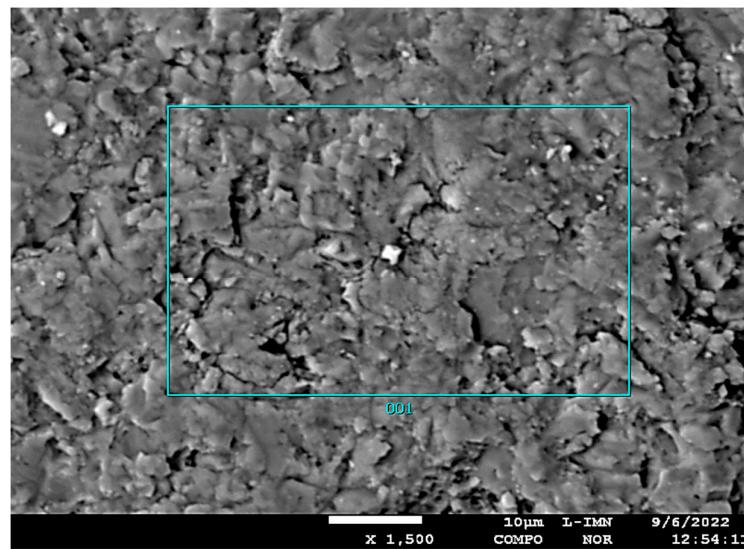
In the first stage of the study of the PSK2 sample, in micro-area 1 of this sample the distribution of the following elements was measured: Mn, Ca, Si, Al, Mg, O, C and Fe (Figure 7).

Superposition of Ca and Mg images distribution (Figure 7) allows to determine the presence of these elements in the same areas, which indicates the presence of calcium-magnesium carbonate phases. The superposition of Ca, Mg and Fe distribution images allows to determine the presence of carbonate phases rich in Mg with substitution of Fe (dolomite phases). And the occurrence of Si and Al in the same areas of Si and Al images indicate the presence of aluminosilicates. The rest of Si is like in the sample LZ1 probably connected with presence of quartz.



**Figure 7.** Maps of the distribution of EDS elements, in the micro-area 1 of PSK2 sample, magnification x500.

In micro-area 2 of the PSK2 sample, the content of basic elements was measured using the EDS method (Figure 8, Table 6).



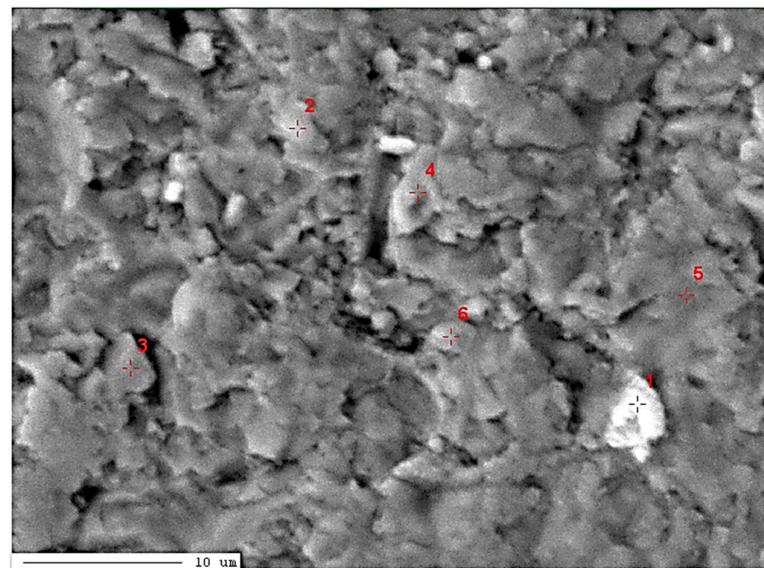
**Figure 8.** The result of the quantitative analysis performed by the EDS method for micro-area 2 of the PSK2 sample.

The results of measurements using EDS method in micro-area 1 of the PSK2 sample indicate the presence of a carbonate phase with an increased magnesium content, higher than typical for dolomite, but lower than stoichiometric value for huntite ( $\text{MgO} - 34.25\%$ ,  $\text{Mg} - 20.65\%$ ). This may indicate the presence of huntite carbonate phase, transformed during the dehunitization process. During this process the part of the magnesium ions was removed from the huntite crystal. Because of it the content of  $\text{MgO}$  is definitely lower than the stoichiometric value for huntite. Therefore this mineral phase was named as de-huntite.

**Table 6.** Results of the EDS analysis at the points of micro-area 1 of the PSK2 sample.

Point Number	Element							$\text{MgO}$ [mass%]
	C	O	Mg	Si	Al	Ca	Fe	
1 / huntite ( $\text{Ca}_{0.41}\text{Mg}_{0.59}\text{CO}_3$ ) <sub>7.95</sub>	1.06	14.211	14.030	4.424	2.860	0.060	0.43	100.00 23.68

In the third micro-area of the PSK2 sample, measurements of the elemental content were done using the WDS method (Figure 9, Table 7).



**Figure 9.** Image of the composition of micro-area 3 of the PSK2 sample with marked points of quantitative analysis, magnification x2500.

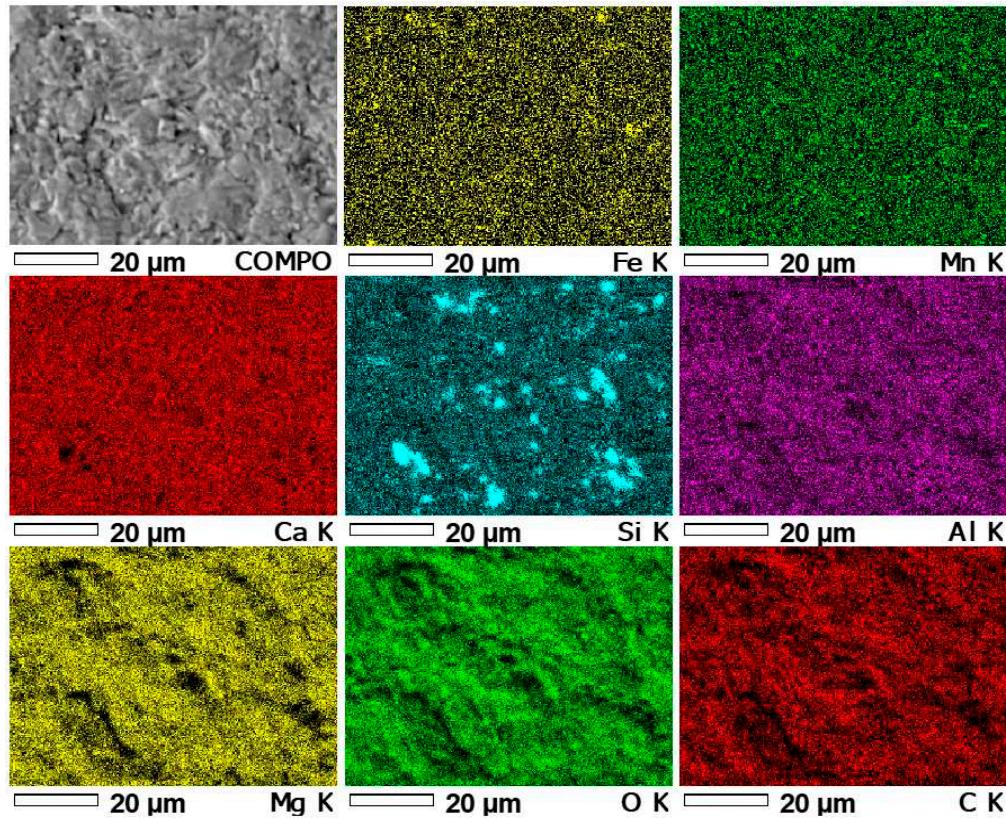
**Table 7.** The results of the WDS analysis in the micro-area 2 zone of the PSK2 sample.

Point Number	Element [mass%]	Element [mass%]							MgO [%]	
		C	O	Mg	Si	Al	Ca	Fe		
1 / Fe-Si oxyhydroxide	3.01	16.90	0.63	41.18	0.05	2.65	35.24	0.34	100.00	1.05
2 / proto-dolomite (Ca <sub>0.41</sub> ,Mg <sub>0.59</sub> )CO <sub>3</sub>	11.41	55.23	11.77	0.13	0.05	21.34	0.06	0.01	100.00	19.62
3 / high-Mg calcite (Ca <sub>0.41</sub> ,Mg <sub>0.59</sub> )CO <sub>3</sub>	11.33	52.39	9.53	0.38	6.00	20.21	0.15	0.01	100.00	15.88
4 / proto-dolomite (Ca <sub>0.41</sub> ,Mg <sub>0.59</sub> )CO <sub>3</sub>	11.00	54.63	11.16	1.29	0.61	21.15	0.14	0.02	100.00	18.60
5 / high-Mg calcite (Ca <sub>0.41</sub> ,Mg <sub>0.59</sub> )CO <sub>3</sub>	11.34	56.15	8.54	0.64	0.16	21.62	1.51	0.04	100.00	14.23
6 / proto-dolomite (Ca <sub>0.41</sub> ,Mg <sub>0.59</sub> )CO <sub>3</sub>	11.35	56.15	10.96	0.13	0.07	21.30	0.03	0.01	100.00	18.27

The results of measurements in micro-area 2 of the PSK2 sample indicate the presence of two carbonate phases with different Mg content – high-magnesium calcite (points 3 and 4) and proto-dolomite (points 2, 4, 6) (Figure 9, Table 7). A little variability of Mg content was observed in high-Mg calcite. Proto-dolomite like in the sample LZ1 is characterized by a lower MgO content than the stoichiometric value for dolomite. In point 1 increased content of Si and Fe were measured. The mineral phase determined in point 1 could be Fe-Si oxyhydroxide with some minor contributions of carbonate to the beam: about 25% based on comparison of C concentration with pure carbonate spots. In point 3 the increased content of Al was measured. It is probably bound in illite. This mineral was determined by X-ray diffraction.

PSZ3 sample - rock from the area of Piekary Śląskie (Zawisza Czarny Street)

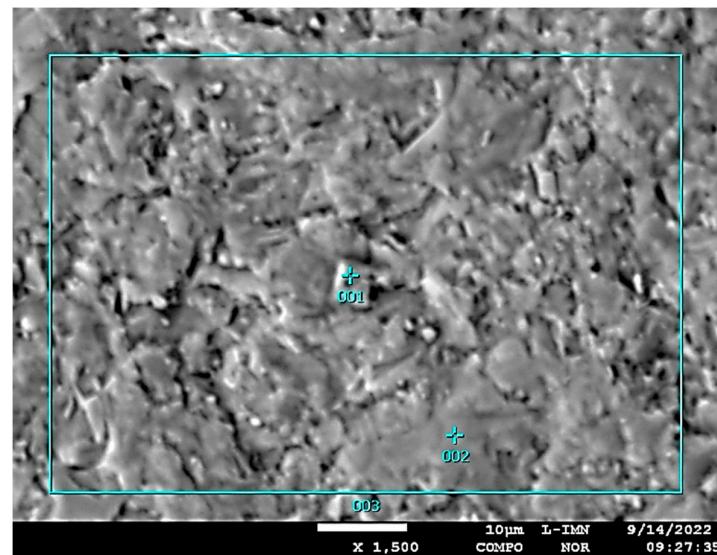
In the first stage of the study of the PSK2 sample like in the case of previous samples, the distribution of the following elements was measured: Mn, Ca, S, Si, Al, Mg, O, C and Fe in micro-area 1 of this sample (Figure 10).



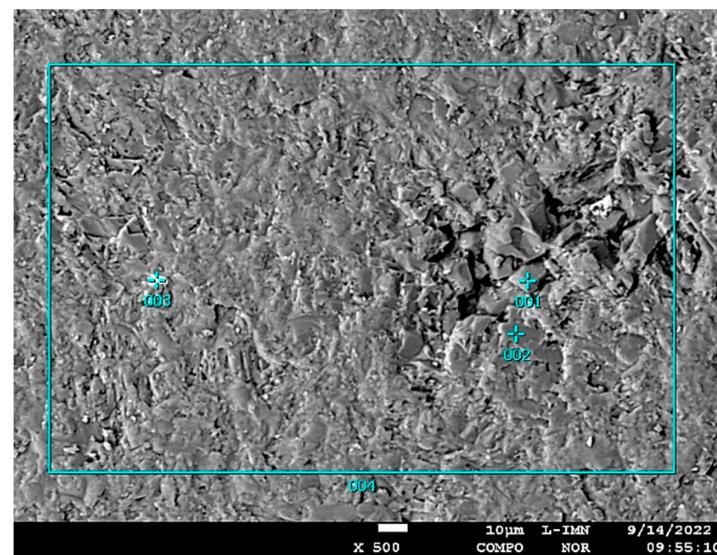
**Figure 10.** Maps of the distribution of EDS elements in microarea 1 of the PSZ3 sample, magnification x1500.

Superposition of Ca and Mg images distribution (Figure 10) allows to determine the presence of these elements in the same areas, which indicates the presence of calcium-magnesium carbonate phases. The superposition of Ca, Mg and Fe distribution images allows to determine in some areas of the sample the presence of carbonate phases rich in Mg with substitution of Fe (dolomite phases). The occurrence of Si and Al in the same areas of Si nad Al images indicate like in the previous samples the presence of aluminosilicates. The rest of Si is probably connected like in previous samples with quartz.

In micro-areas 1 and 2 of the PSZ3 sample, the content of elements: C, O, Mg, Al, Si, Ca, Mn and Fe was measured using EDS method (Figures 11 and 12, Table 8).



**Figure 11.** Image of the composition of micro-area 1 of the PSZ3 sample with marked places of EDS quantitative analysis.



**Figure 12.** Image of the composition of the micro-area 2 of PSZ3 sample with marked places of EDS quantitative analysis.

The results of microprobe measurements made in micro-area 1 using EDS method indicate the dominance of carbonate phases with an increased magnesium content, higher than typical for dolomite, but slightly lower than the stoichiometric value of huntite. As in the case of the PSK2 sample also in this sample de-huntite is present. Thus the crystals of original huntite were probably transformed during dehunitization. As in the case of micro-area 1 of the PSZ3 sample, also in micro-area 2 de-huntite phase dominates.

**Table 8.** EDS analysis results in micro-areas 1 and 2 of the PSZ3 sample.

Point Number	Element							MgO [mass%] [%]
	C	O	Mg	Si	Al	Ca	Fe	
Contents of elements in micro-area 1 (Figure11)								
1 / huntite	7.71	51.44	15.24	1.14	0.12	24.12	0.03	100.00 25.40

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$(\text{Ca}_{0.41}, \text{Mg}_{0.59})\text{CO}_3$

2 / huntite  
 $(\text{Ca}_{0.41}, \text{Mg}_{0.59})\text{CO}_3$  5.3744.1117.760.280.2432.000.160.08 100.00 29.60

Total area / huntite

$(\text{Ca}_{0.41}, \text{Mg}_{0.59})\text{CO}_3$  7.4352.1214.240.600.1125.110.280.11 100.00 23.73

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Contents of elements in micro-area 2 (Figure12)

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1 / huntite  
 $(\text{Ca}_{0.42}, \text{Mg}_{0.58})\text{CO}_3$  9.5757.1713.62BDL0.0918.800.690.06 100.00 22.70

2 / huntite

$(\text{Ca}_{0.31}, \text{Mg}_{0.69})\text{CO}_3$  6.1247.9316.500.020.0929.170.090.08 100.00 27.50

3 / huntite

$(\text{Ca}_{0.49}, \text{Mg}_{0.61})\text{CO}_3$  4,5042.6714.630.300.1333.833.780.16 100.00 24.38

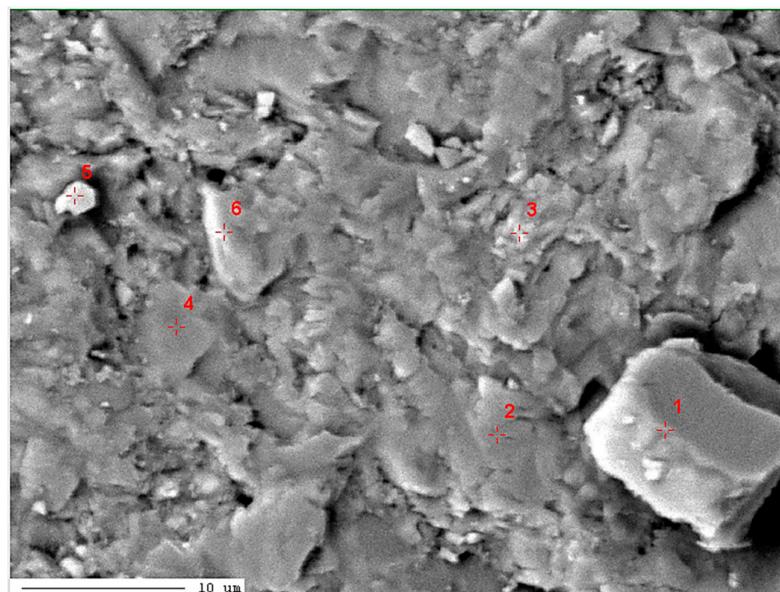
Total area / huntite

$(\text{Ca}_{0.43}, \text{Mg}_{0.57})\text{CO}_3$  7.6052.0013.760.530.1625.000.830.12 100.00 22.93

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BDL – below detection limit.

In the third micro-area of the PSZ3 sample, measurements of the elemental content using the WDS method were done (Figure 13, Table 9).



**Figure 13.** Image of the composition of the micro-area 4 of PSZ3 sample with marked points of quantitative analysis, magnification x2500.

**Table 9.** Results of WDS analysis in micro-area 3 of the PSZ3 sample.

Point Number	C	O	Element						MgO Content [mass%]	
			Mg	Si	Al	Ca	Fe	Mn		
1 / low-Mg calcite (Ca <sub>0.98</sub> ,Mg <sub>0.02</sub> )CO <sub>3</sub>	10.09	55.47	0.60	0.020	0.023	33.72	0.070	0.01	100.00	1.00
2 / proto-dolomite (Ca <sub>0.51</sub> ,Mg <sub>0.49</sub> )CO <sub>3</sub>	12.65	55.20	11.78	BDL	0.022	0.32	BDL	0.03	100.00	19.63
3 / high-Mg calcite (Ca <sub>0.68</sub> ,Mg <sub>0.32</sub> )CO <sub>3</sub>	11.52	55.82	7.66	0.300	0.082	0.53	3.93	0.16	100.00	12.77
4 / proto-dolomite (Ca <sub>0.52</sub> ,Mg <sub>0.48</sub> )CO <sub>3</sub>	11.82	55.57	11.52	0.050	0.022	0.86	0.150	0.01	100.00	19.20
5 / proto-dolomite (Ca <sub>0.51</sub> ,Mg <sub>0.49</sub> )CO <sub>3</sub>	11.31	56.14	11.75	BDL	0.012	0.63	0.130	0.03	100.00	19.58
6 / proto-dolomite (Ca <sub>0.51</sub> ,Mg <sub>0.49</sub> )CO <sub>3</sub>	13.05	56.67	11.68	0.030	0.041	8.41	0.080	0.04	100.00	19.47

BDL – below detection limit.

The results of measurements carried out in micro-area 3 of the PSZ3 sample indicate the presence of three carbonate phases: low-magnesium calcite (point 1), high-magnesium calcite (point 3) and proto-dolomite (points 2, 4, 5 and 6) (Figure 13, Table 9). In the point 3 the increased content of Fe was determined. Fe substitute for Mg in a high-Mg calcite crystal. It is possible that Fe likely forms a solid solution with ankerite or siderite. However these minerals were not identified by X-ray diffraction.

#### 4. Discussion

The subject of this project was to study carbonate rocks of the Tarnowice Unit of selected areas of the Upper Silesia (Silesian Voivodeship) in terms of determination their geochemical and mineralogical properties. This topic was undertaken due to the probability of the presence of carbonate phases with different magnesium content in these rocks, mainly the occurrence of high-magnesium calcite, which was identified in the rocks of the Lower Muschelkalk of the area of Opole Silesia. The Tarnowice Unit, which are the Middle Muschelkalk Formation, have not been studied in detail in this aspect so far. The research zone includes the areas of Piekary Śląskie and Bytom. Samples of carbonate rocks were collected in the Lazarówka Quarry (area of Bytom City) and in the area of Piekary Śląskie, at Mieczysław Karłowicz Street and at Zawisza Czarny Street.

##### 4.1. Mineral phases and the trace elements of the Triassic dolomites

Macroscopically examined carbonate rocks differ slightly, mainly in terms of color. The rocks from the Lazarówka Quarry show a brownish color, while the rocks of the area of Piekary Śląskie have colors from light brown to gray, a sparite texture, and a chaotic, compact, in some areas of rock porous structure. Rocks from the Lazarówka Quarry are characterized by reduced compactness. A weak reaction with hydrochloric acid indicates dolomite dominance in rocks. Microscopic images often reveal a biomorphic texture. The rocks are made of oval or elongated bioclasts bonded with contact or pore cement. Sparite, euhedral, rhombohedral dolomite crystals have also been observed in microscopic images. Some crystals are filled with iron compounds. These crystals are probably pseudomorphs after dolomite.

Additionally, detailed data on the examined rocks were provided by the results of X-Ray diffraction. Five carbonate phases, differentiated in terms of magnesium content, were marked on the diffraction patterns of the samples: low-magnesium calcite (however, only in one sample), high-magnesium calcite, proto-dolomite, ordered dolomite and huntite. Among the non-carbonate minerals, quartz was identified and illite in one sample (PSK3). The results of X-Ray diffraction showed that dolomite phases and high-magnesium calcite dominate in the rocks.

Many interesting data were provided by the results of X-Ray Fluorescence (XRF). Based on the results of the analysis, the basic oxide composition of the rocks, the Ca to Mg ratio and the  $MgCO_3$  content were calculated. Based on the obtained data, the position of the studied carbonate rocks in the classifications of Chilingar [20] and Pettijohn [21] was presented. The results of study indicate that the carbonate rocks represent lime dolomites, in the Chilingar [20] classification. In Pettijohn [21] classification samples PSK1, PSK3 and PSZ2 represent lime dolomites and samples LZ2, LZ3 and PSZ1 – calcerous dolomites. Therefore, these rocks, apart from the mineral dolomite, also contain calcite phases, including high-magnesium calcite. This was confirmed by the X-Ray diffraction results.

Moreover, the results of the XRF analysis showed, apart from the high content of elements such as Ca, Mg, C and O, also the presence, in trace amounts, elements characteristic for minerals such as silicates, aluminosilicates, oxides and sulfides, which, apart from Sr and Ba, are not basic components of carbonate rocks. These are: Al, Si, Fe, K, Na, Ti, Cr, Mn, Zr, Co, Cd, Ni, Cu, Zn, Pb, As, Rb, Br and Cl. These elements are most often supplied from the outside to the sea basin where carbonate sedimentation takes place. Some of them may occur in minerals formed during diagenetic processes. Manganese and iron can be substitutions for Ca and Mg in carbonate minerals.

Strontium and barium are elements originally present in aragonite, an unstable phase of calcium carbonate, which, like high-magnesium calcite, is transformed into low-magnesium calcite during diagenesis. Sr and Ba often appear in the carbonate phases. According to literature data, Sr occurs in the skeletons of marine organisms [6,8,22–35]. Its presence in aragonite is associated with a larger ionic radius compared to the ionic radius of Ca, therefore it easily enters the structure of aragonite, more similar to the structure of strontianite than to the structure of calcite. Therefore, aragonite contains a higher amount of Sr than calcite [8,22]. However, aragonite is an unstable phase of calcium carbonate, similarly to high-magnesium calcite, and during diagenesis it is transformed into low-magnesium calcite. Thus, only the presence of strontium indicates that the primary phase of calcium carbonate was aragonite. Ba, like Sr, is found in the skeletons of marine organisms. Ba has a similar ionic radius to Sr [8,20,24,25,27], so it will be easier to enter the aragonite structure than calcite. Thus, only the presence of Sr and Ba indicates that the primary phase of calcium carbonate was aragonite.

Ni, K, Si, Al, as well as some Fe, are included in the aluminosilicates – mainly feldspars and clay minerals. S, Ti, Cr, some Fe, Ni, Cu, Zn Pb will probably be bound in sulfides and oxides. Some of the samples contain high Pb-Zn amounts. It supports the hypothesis that ore-forming and dolomitization fluids are related. Therefore probably there were taking place the similar to processes which caused the mineralization with zinc and lead ores during the diagenesis in the Śląsko-Krakowski Region.

During sedimentation processes, Ni is incorporated into the structures of clay minerals. Nor can it form sulfides and arsenides. Cd is usually found in zinc sulfides. It can also appear together with Fe, Mn and Co in smitsonite. Chlorine is bound in chlorides and phosphorus is present in organic matter.

Detailed data were provided by the results of microprobe measurements. Based on the content of elements, mainly Ca and Mg, determined during the measurements made in the micro-areas of the samples, the following carbonate phases with different Mg content were determined: low-magnesium calcite, high-magnesium calcite, proto-dolomite, ordered dolomite and huntite. On the basis of microprobe measurements results, the chemical formulas of the carbonate phases were calculated. The results of studies in samples' micro-areas have shown that high-magnesium calcite has a Mg content higher than "pure" (low-magnesium) calcite, but lower than proto-dolomite. The proto-dolomite is characterized by a lowered content of magnesium in relation to the stoichiometric

value for dolomite, but the higher than that of high-magnesium calcite. Ordered dolomite has a content of Mg close to the stoichiometric value. Huntite determined by microprobe measurements is characterized by lower Mg content than the stoichiometric value for this carbonate phase. Therefore this mineral phase was named as de-huntite. Reduced magnesium content in de-huntite is probably the effect of the process of advance stage of diagenesis – dehunization. It cannot exclude the theory which assumes that determined de-huntite phase may represent a huntite-dolomite solid solution or mixture.

The results of the microprobe measurements confirmed the data obtained by previous analytical methods.

The results of the executed tests show that dolomite phases (proto-dolomite and ordered dolomite – around 90%) dominate in studied rocks. Increased content of high-Mg calcite (circa 8%) occurs in most of rocks. Low-Mg calcite (circa 5 to 8%) is present only in three rocks. Moreover, in three rocks also huntite (around 5%) phase was determined. The content of Mg allowed to name this phase as de-huntite. Quartz occurs in most of rocks (circa 1 to 2%). Illite was identified by X-ray diffraction only in one sample (PSK3). The estimate relative proportions of the mineral phases confirmed the classification of the studied rocks into the dolomite group.

#### 4.2. Dolomites' formation during sedimentary and diagenetic processes

On the basis of the research results, a theory about the rocks of the Tarnowice Beds formation and the diagenetic processes that influenced the final structure of these rocks was formed.

During the Upper Muschelkalk in Triassic Basin a development of fauna was observed, which was stopped during the Middle Muschelkalk. The development of the fauna was a result of wide connections with the Alpine Sea during the sea transgression. The East Carpathian Gate was probably active then, and further into the West, the Rhine and Burgundy Gates. At the beginning of the transgression, the sea bottom was inhabited by crinoids, which skeletons after crinoids' dying formed trochite layers. These layers create the lower part of the Upper Muschelkalk. Layers with Myophoria Transversa Bornemann and Pecten discites (Schlotheim) are also characteristic here [30–32,34,35]. There are also limestones with glauconite. On the basis of the fauna which occurs here it is possible to distinguish these deposits from the formations of the Middle Muschelkalk. In the upper part there are limestones with a greater content of marls, locally claystones, dolomites, and sometimes sandy limestones and calcareous sandstones. The Tarnowice Unit are deposited above the Diplopora dolomites. They are also called lamellar dolomites [8]. They were formed during the marine regressions of the Upper Muschelkalk, when another complex of limestone deposits was formed [18]. This was mainly due to uplift movements, which led to the shallowing of the sea and then emergence of the Silesian-Cracow area [6,36,37]. Accordingly, mixed carbonate-clastic deposits of the Upper Muschelkalk were formed at that time [36,37]. There was also erosion of older sediments, which lasted until the beginning of the Late Triassic, i.e. the Carnian [18].

Thus, the Tarnowice Unit are typical sediments of a drying, shallow sea [32,33]. Probably the sediments of the Tarnowice Unit were originally limestones, which were analogous to the deposits and Middle Muschelkalk dolomitized during diagenetic processes. The dolomites in the Śląsko-Krakowski Region, were mineralized with zinc and lead ores during the diagenesis. They were the subject of exploitation. The dolomites of the Tarnowice Unit could probably have been formed in the same way as the ore-bearing dolomites as a result of metasomatic processes. Because of this they may include the carbonate phases with different magnesium content.

On the basis of the research results it can be stated that the rocks of the Tarnowice Unit are built not only of the dolomite phases, but also of other carbonate phases with different Mg content. Among them high-magnesium calcite dominates, which has not been studied in detail in this formation before. It is an unstable phase of calcium carbonate, which is usually not preserved in older sediments such as Triassic but is usually transformed like aragonite into low magnesium calcite during diagenetic processes. Another novelty is the presence of huntite, a carbonate phase with magnesium content higher than that of dolomite. It can be defined as magnesium-calcium carbonate. This carbonate phase has not been identified in the rocks of the Tarnowice Unit before. This carbonate

phase is characterized by lower Mg content than stoichiometric value for huntite. Because of it this phase was named as de-huntite.

## 5. Conclusions

Based on the obtained test results and their interpretation, the following conclusions were formulated:

1. The results of the research indicate that the studied carbonate rocks are lime dolomites according to the Chilingar classification. Three of them in Pettijohn classification represents calcareous dolomites.
2. The analyzed rocks apart from the dolomite phases, contain also calcite phases, including the dominant high-magnesium calcite.
3. The results of X-Ray diffraction showed that five carbonate phases with different magnesium content occur in the examined rocks: low-magnesium calcite, high-magnesium calcite, proto-dolomite, ordered dolomite and huntite.
4. X-Ray Fluorescence (XRF) results showed the presence of elements, not only those typical of carbonate minerals, but also elements such as: Al, Si, Fe, K, Na, Ti, Cr, Cd, Br, Cr, As, Mn, Zr, Co, Ni, Cu, Zn, Pb and Cl. Some of them may occur in minerals formed during diagenetic processes.
5. The results of the microprobe measurements showed that there are two types of dolomite in the studied rocks: proto-dolomite and ordered dolomite. Proto-dolomite is characterized by a reduced magnesium content compared to the stoichiometric value for dolomite, but higher than that of high-magnesium calcite, while ordered dolomite has a Mg content close to the stoichiometric value.
6. The results of microprobe measurements have shown that high-magnesium calcite has a Mg content higher than "pure" (low-magnesium) calcite, but lower than proto-dolomite.
7. During microprobe measurements the magnesium-calcium carbonate phase was determined. The Mg content of this phase is higher than in ordered dolomite, but lower than typical for huntite. That's why this mineral was named as de-huntite. The reduced content of Mg in this phase is probably the effect of dehunitization – the process of advance stage of diagenesis.
8. The achievement of the project is the identification of carbonate phases rich in magnesium, which have not been studied so far in the formation of the Tarnowice Unit, such as: high-magnesium calcite, proto-dolomite, ordered dolomite and de-huntite.
9. On the basis of the obtained data, a theory connected with the formation of the studied rocks was formed. According to the data the rocks of the Tarnowice Unit are the sediments of the drying, shallow, epicontinental sea. They were re-flooded by seawater during the regressions of the Upper Muschelkalk period.
10. The original sediments of the Tarnowice Unit were probably limestones which were dolomitized during metasomatic processes. This may be evidenced by the presence of carbonate phases that differ in terms of magnesium content.

The test results therefore provide new data on the mineral composition and geochemistry of the Tarnowice Unit. They will be used for further studies of Triassic carbonate rocks, in particular in terms of the possibility of their practical use.

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## References

1. Matysik, M. Reefal environments and sedimentary processes of the Anisian Karchowice Beds In Upper Silesia, Southern Poland. *Annales Societatis Geologorum Poloniae* **2010**, *80*, 123–145.
2. Senkowiczowa, H. Possibilities of formalizing the lithostratigraphic division of the Middle and Upper Triassic of the Silesian-Cracow Upland. *Geological Quarterly* **1980**, *24* (4), 787–804.
3. Niedźwiedzki, R. Lithostratigraphy of the Górażdże Formation of the Dziewkowice Information in Opole Silesia. *Geological and Mineralogical Works of Wrocław University LXXI* **2000**, Wrocław.
4. Niedźwiedzki, R.; Szulc, J.; Zarankiewicz, M. Stone treasures of the Saint Anne Land. Geological Guide 2013. [www.annaland.pl](http://www.annaland.pl)
5. Stanienda K. *Effects of dolomitization processes in the Triassic limestone of Tarnów Opolski Deposit*. Silesian University of Technology Press, Gliwice, Poland 2011. ISBN: 978-83-7880-071-2
6. Stanienda K. *Diagenesis of the Triassic limestone from the Opole Silesia in the aspect of magnesian calcite presence*. Silesian University of Technology Press, Gliwice, Poland 2013. ISBN: 978-83-7335-872-0
7. Stanienda, K. Huntite in the Triassic limestones of Opolski Silesia. *Mineral Resources Management* **2013**, *9* (3), 79–98. DOI 10.2478/gospo-2013-0036
8. Stanienda, K. Mineral phases in carbonate rocks of the Gogolin Beds from the area of Opole Silesia. *Mineral Resources Management* **2014**, *30* (3), 17–42. DOI 10.2478/gospo-2014-0026
9. Stanienda, K. Carbonate phases rich in magnesium in the Triassic limestones of the East part of Germanic Basin. *Carbonates and Evaporites* **2016**, *31*, 387–405. DOI 10.1007/s13146-016-0297-2
10. Stanienda, K. Mineral phases in carbonate rocks of the Górażdże Beds from the area of Opole Silesia. *Mineral Resources Management* **2016**, *32* (3), 67–92. DOI 10.1515/gospo-2016-0023
11. Stanienda-Pilecki, K. Carbonate minerals with magnesium in Triassic Terebratula limestone in the term of limestone with magnesium application as a sorbent in desulfurization of flue gases. *Archives of Mining Sciences* **2017**, *62* (3), 459–482. DOI 10.1515/amsc-2017-0035
12. Stanienda-Pilecki, K. Magnesium calcite in Muschelkalk limestones of the Polish part of the Germanic Basin. *Carbonates and Evaporites* **2018**, *33* (4), 801–821. <https://doi.org/10.1007/s13146-018-0437-y>
13. Stanienda-Pilecki, K. The Use of Limestones Built of Carbonate Phases with Increased Mg Content in Processes of Flue Gas Desulfurization. *Minerals* **2021**, *11*, 1044, 1–21. <https://doi.org/10.3390/min11101044>
14. Szulc J. International Workshop – Field Seminar The Muschelkalk- Sedimentary Environments, Facies and Diagenesis- Excursion Guidebook and Abstracts. Kraków- Opole, Poland, 1990, 1–32.
15. Szulc, J. Early alpinie tectonics and lithofacies succesion in the Silesian part of the Muschelkalk Basin. In *Muschelkalk*, H. H. Haggdorn and A. Seilacher (eds.). Goldschnecke, Stuttgart, Germany, 1993, 19–28.
16. Szulc, J. Middle triassic evolution of the Northern Peri-Tethys area is influenced by early opening of the Tethys Ocean. *Annales Societatis Geologorum Poloniae* **2000**, *70*, 1–48.
17. Szulc, J. Stratigraphy and correlation with Tethys and other Germanic subbasins. International Workshop on the Triassic of Southern Poland. Pan-European Correlation of Epicontinental Triassic 4<sup>th</sup> Meeting, Fieldtrip Guide, September 3–8, 2007, 26–28.
18. Szulc J. Triassic of the Silesia-Cracow area. Materials of the 42nd Speleological Symposium, 9–10, Kraków, Poland 2008.
19. Biernat, S. Reamble: Wilanowski S., Lewandowski J. (2016) Detailed geological map of Poland. Sheet 910 – Bytom (M-34-50-D). Polish Geological Institute. National Research Institute, Poland 1954.
20. Chilingar, G.V. Classification of limestones and dolomites on basis of Ca/Mg ratio. *J. Sed. Petrol.* **1957**, *27*, 187–189.
21. Pettijohn, F.J. *Sedimentary rocks. III ed.* New York, USA, 1975.
22. Boggs S. Jr. *Petrology of sedimentary rocks. Second Edition*. Cambridge University Press, London, 2010.
23. Mackenzie, F.T., Andersson, A.J. The Marine carbon system and ocean acidification during Phanerozoic Time. *Geochemical Perspectives* **2013**, *2* (1).
24. Mavromatis, V., Götschl, K.E., Grengg, C., Konrad, F., Purgstaller, B., Dietzel, M. Barium partitioning in calcite and aragonite as a function of growth rate. *Geochimica et Cosmochimica Acta* **2018**, *237*, 65 – 78. <https://doi.org/10.1016/j.gca.2018.06.018>
25. Morse, J.W., Mackenzie, F.T. Geochemistry of sedimentary carbonates. *Elsevier* **1990**, *33*, 707.
26. Morse, J.W., Andersson, A.J., Mackenzie, F.T. Initial responses of carbonate-rich shelf sediments to rising atmospheric pCO<sub>2</sub> and “ocean acidification”: Role of high Mg-calcites. *Geochimica et Cosmochimica Acta* **2006**, *70*, 5814 – 5830
27. Polański, A. *Basics of geochemistry*. Geological Publishing House, Warsaw, 1988.
28. Tucker, M. E., Wright, V. P. *Carbonate sedimentology*. Blackwell Scientific Publications, Oxford London, Edinburgh Boston Melbourne, 1990, 366–372. doi.org/10.1002/97814443 14175
29. Zhang, S., Zhou, R., DePaolo, D.J. The Seawater Sr/Ca ratio in the past 50 Myr from Bulk Carbonate Sediments Corrected for Diagenesis. Elsevier
30. Zhang, S., DePaolo, D.J. Equilibrium calcite-fluid Sr/Ca partition coefficient from marine sediment and pore fluids. *Geochimica et Cosmochimica Acta* **2020**, *289*, 33 – 46. <https://doi.org/10.1016/j.gca.2020.08.017>

31. Zhong, S., Mucci, A. Calcite and aragonite precipitation from seawater solutions of various salinities: Precipitation rates and overgrowth compositions. *Chemical Geology* **1989**, *78*, 283 – 299. [https://doi.org/10.1016/0009-2541\(89\)90064-8](https://doi.org/10.1016/0009-2541(89)90064-8)
32. Makowski, H. Historical Geology. Geological Publishing House, Warsaw, Poland, 1977.
33. Senkowiczowa, H., Szyperko-Śliwińska, A. Stratigraphy and palaeogeography of the Triassic. *Geological Institute* **1972**, 252.
34. Czermiński, J. (Editor) *Geological Structure of Poland, Volume II, Catalog of Fossils, Part 2, Mesozoic*. Geological Publishing House, Warsaw, Poland 1970.
35. Bujoczek, M., Gładysz, K., Stępień, A. Tarnowskie Góry Underground - a living organism on a selected fragment of the mine of the Fryderyk Mine (Blachówka – Western – Urban Glückhilfe). Project Report, Tarnowskie Góry Cave Mountain Club, Poland 2013.
36. Migaszewski, Z. Origin of the dolomites. *Geological Quarterly* **1990**, *34* (1), 202.
37. Migaszewski Z. Current views on the genesis of dolomites. *Geological Quarterly* **1990**, *3*, 111-117.

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