

Scanning electron microscopy – a highly selective and sensitive tool for the determination of carbonate minerals with different Mg content

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ABSTRACT:

Stanienda-Pilecki, K. and Jonczy, I. 2025. Scanning electron microscopy – a highly selective and sensitive tool for the determination of carbonate minerals with different Mg content. *Acta Geologica Polonica*, **75** (3), e52.

In this article, using a scanning electron microscope with EDS, the results of the identification of carbonate minerals differing in magnesium content in Precambrian magnesites and Triassic limestones and dolomites are presented. This technique enables the identification of mineral phases whose chemical composition differs only slightly in the content of individual elements. This is important in the case of carbonate minerals containing magnesium, because as the amount of Mg increases, successive carbonate phases are formed, starting with low-magnesium calcite and ending with magnesite. The following carbonate phases: low-Mg calcite, high-Mg calcite, proto-dolomite, ordered dolomite, de-huntite, huntite and magnesite were identified in samples collected from the Precambrian magnesite rock of the Braszowice deposit of Lower Silesia and the Triassic, Muschelkalk limestones and dolomites of Opole Silesia and Upper Silesia in Poland. Based on the results of the study, the chemical formulas of low-magnesium calcite, high-magnesium calcite, proto-dolomite, ordered dolomite, de-huntite, huntite and magnesite were formulated. The data obtained made it possible to determine the range of magnesium content in the chemical formulas of the identified carbonate phases. In addition, schematic crystal structures of the studied carbonate phases were also developed.

Key words: Scanning electron microscopy; Carbonate minerals; Magnesium.

INTRODUCTION

Carbonate minerals (MCO_3) include different phases that differ in Mg content: calcite phases (high-Mg calcite, low-Mg calcite) [CaCO_3], dolomite phases [$\text{CaMg}(\text{CO}_3)_2$], huntite phases [$\text{CaMg}_3[\text{CO}_3]_4$] and magnesite [MgCO_3]. It is very important to determine the magnesium-rich carbonate phases, especially when there is little variation in the magnesium content of individual phases. Scanning electron microscopy is a precise and sensitive tool for determining elements in various materials and is therefore widely used in various fields of research. SEM allows the operator to obtain microimages characterized by

high resolution and appropriate sharpness. (Koga *et al.* 2021; Ali *et al.* 2023; Łydźba-Kopczyńska *et al.* 2024), and at present, it is one of the most popular observational techniques. As already mentioned, SEM is widely used in many fields of science when testing various materials, and amongst others Jonczy and Filipowicz (2024) and also Nocoń *et al.* (2023) have shown that scanning electron microscopy is an important research method used in the analysis of waste materials. SEM allows the identification of the mechanisms of wear of materials, e.g. steel, during wear tests (Wieczorek *et al.* 2021; Nadeau and Herguth 2004), and also SEM is used in the characterization of micro- and nanomaterial microstructures (Liu *et*



al. 2010), during mineralogical researches of fly ash (Zdera 2013) or different aggregates, based on different kinds of rocks (Wu *et al.* 2017).

The aim of this research was to qualitatively and quantitatively identify carbonate phases (occurring in selected magnesites and limestones) the classification of which is based on the proportion of the magnesium content in their chemical composition. Given that the differences in the amount of magnesium, which determine the affiliation of a given phase to a specific carbonate group, are quite subtle, it is important to use an appropriate research technique. SEM was used in this research, indicating that this technique is an alternative to X-ray spectral analysis in micro-areas.

GEOLOGICAL SETTING

Magnesium is one of the main components, along with calcium, in the following carbonate phases: low-Mg calcite, high-Mg calcite, proto-dolomite, ordered dolomite, huntite and also magnesite. The studied carbonate phases occur in the Precambrian magnesites of Lower Silesia (Brasowice deposit) (Krzyżanowski *et al.* 2010; Stefanicka *et al.* 2016) and in the Triassic limestones of Opole Silesia and also Upper Silesia (Stanienda 2011, 2013a, b, 2014, 2016a, b; Stanienda-Pilecki 2017–2019, 2021). Magnesite is one of the minerals that are rarely found in Poland, and it occurs only in Lower Silesia (in the area of the Sudetes foreland). Magnesite deposits in the Brasowice area are associated with dislocation, hydrothermal and weathering processes in the metamorphic rock serpentinite. Magnesite occurs in two forms, as veins and in the form of a more dispersed “network”. Veins were the main subject of underground mining. The geological structure of the Brasowice Hills, especially in the western part, differs significantly from the structure of the northern deposits of the serpentinite massif. The serpentinite rock is diversely cut by a fine network of magnesite inclusions. Magnesite veins are common in some serpentinite zones, varying in thickness from a few millimetres to 20 cm. These are mainly occurrences of yellow (ferrous) and brown (non-ferrous) magnesite (Stefanicka *et al.* 2016).

The Triassic carbonate rocks from the area of the Polish fragment of the Central-European Basin (Opole and Upper Silesia) are the sediments of the eastern part of this epicontinental basin. This area is the eastern zone of the Central European Triassic intracratonic basin (Szulc 2000). Carbonate phases characterized by variable magnesium content oc-

cur in limestones covering the Lower Muschelkalk sediments. These are the following units: Gogolin, Góraždze, Dziewkowice (Terebratula), Karchowice, Tarnowice and Boruszowice. The names of the units are related to regional nomenclature and refer to the names of towns. The Muschelkalk carbonate rocks of Poland contain carbonate phases with different Mg contents – low-Mg calcite, high-Mg calcite, proto-dolomite, ordered dolomite and de-huntite (Stanienda 2013a, b, 2014, 2016a, b; Stanienda-Pilecki 2017–2019, 2021, 2023; Stanienda-Pilecki and Jendruś 2024).

Low-Mg calcite can be considered to be the main component of the limestone. Dolomite phases are common, but high-magnesium calcite and de-huntite are rather rare in the Muschelkalk sedimentary rocks. High-Mg-calcite and dolomite phases are the main components of dolomites. High-magnesium calcite, like aragonite, is unstable and usually, at an early stage of diagenesis, transforms into low-magnesium calcite. It is characteristic of sediments of younger geological periods. Huntite occurs in various rocks, but in sedimentary rocks it usually represents the vadose zone. In Muschelkalk carbonate rocks de-huntite has been found (Stanienda 2014; Stanienda-Pilecki 2023; Stanienda-Pilecki and Jendruś 2024).

The study of carbonate phases with different amount of magnesium is very important in the study of the formation of carbonate minerals in the analysed part of the Central-European Basin sediments, as well as in the stability and solubility of the mineral phases (Stanienda 2011, 2013a, b, 2014, 2016a, b; Stanienda-Pilecki 2017, 2018, 2021, 2023; Stanienda-Pilecki and Jendruś 2024).

MAGNESIUM IN CARBONATE MINERALS

Magnesium is primarily associated with seawater, less often with freshwater. This element can also be released from carbonate and siliceous rocks during their weathering on land, and when it migrates to seawater in the shelf zone, it forms dolomite phases, sometimes it is a component of high-Mg calcite (Mackenzie and Andersson 2013; Morse and Mackenzie 1990; Morse *et al.* 2006; Tucker and Wright 1990). Carbonate phases rich in Mg are characterized by instability, which is related to the different size of the Ca and Mg cations, the strength of the ionic bonds as well as the length of the ionic radius. It should be noted that the strength of the ionic bond between two Ca ions is higher than that between Ca and Mg ions. (Morse and Mackenzie 1990; Bertram *et al.* 1991; Böttcher *et al.* 1997; Morse

et al. 2006; Boggs 2010; Böttcher and Dietzel 2010). The crystals of high-Mg calcites tend to be less stable than pure calcite (without Mg substitution) and also stoichiometric dolomite or huntite – those in which magnesium is a permanent element, not a substitute (Faust 1953; Cole and Lancucki 1975; Althoff 1977; Graf and Goldsmith 1982; Dollase and Reeder 1986; Paquette and Reeder 1990; Tsipursky and Buseck 1993; Nürnberg *et al.* 1996; Böttcher *et al.* 1997; Titiloye *et al.* 1998; Kralj *et al.* 2004; Atay and Çelik 2010; Böttcher and Dietzel 2010; Nash *et al.* 2011). High-Mg calcite is unstable and over time, transforms into low-Mg calcite quite easily (Bertram *et al.* 1991; Böttcher *et al.* 1997; Boggs 2010; Böttcher and Dietzel 2010). Pure water rich in magnesium may cause high-magnesium calcite to be replaced by dolomite (Morse *et al.* 2006). At temperatures between 25 and 64°C, a calcite phase containing 1.9 mol% MgCO₃ is stable compared to both low-Mg calcite and aragonite. High-Mg calcite containing up to 15 mol% MgCO₃ is stable relative to low-Mg calcite at temperatures above 42°C (up to 60°C). (Morse and Mackenzie 1990). Mg substitution also affects the solubility of calcite phases. It rises with the increase of MgCO₃ (Mackenzie and Andersson 2013). High-Mg calcite containing up to 40% MgCO₃ (Yavuz *et al.* 2006) is commonly observed in many natural low temperature environments (Bertram *et al.* 1991; Zahng and Dave 2000; Boggs 2010). In dolomite phases and in huntite, magnesium does not replace calcium (Stanienda 2011, 2013a, 2014). It is the chemical element that, together with Ca, forms these carbonate phases in a fixed ratio. The dolomite phase and huntite are therefore stable carbonate phases. The formation of dolomite phases mainly depends on the Mg/Ca ratio, temperature, CO₂ content and reaction time (Szulc 2000; Zhang *et al.* 2010; Delmann 2011). Proto-dolomite is a non-stoichiometric, poorly ordered carbonate phase which is created in the early stages of diagenesis during sediment compaction. It usually forms euhedral, rhombohedral crystals (Morse *et al.* 2006; Zhang *et al.* 2010; Deelman 2011, 2021). Dolomite is characteristic of the advanced stages of diagenesis in water environments rich in magnesium (Szulc 2000; Zhang *et al.* 2010; Deelman 2011). Huntite is the carbonate phase rich in Mg which is formed under conditions of hydrothermal processes, weathering of dolomite or it could be a product of the transformation of high-Mg calcite under high temperature conditions. It occurs in vadose zone sediments in carbonate rocks (Cole and Lancucki 1975; Althoff 1977; Atay and Çelik 2010; Deelman 2011). The crystal structure of magnesite is

similar to that of calcite (Oh *et al.* 1973; Markgraf and Reeder 1985; Fiquet *et al.* 2002; Bromiley *et al.* 2007; Scott *et al.* 2013). Magnesite is stable in the presence of MgO under the pressure-temperature conditions of the lower mantle (Fiquet *et al.* 2002; Schroll 2002; Bromiley *et al.* 2007; Scott *et al.* 2013; Deelman 2021; Grieco *et al.* 2023). Therefore it is formed mainly in magmatic and metamorphic environments. Large magnesite deposits occur in the Precambrian, and thick magnesite-dominated sequences are unknown in the Phanerozoic (Schroll 2002). Precipitation of these magnesite deposits seems unlikely. Some of the Mg-rich carbonates could be transformed into sparse magnesite (Schroll 2002). Cryptocrystalline magnesite is commonly found in ultramafic rocks (Grieco *et al.* 2023). Magnesite – magnesium carbonate – is usually homogeneous (Markgraf and Reeder 1985). It rarely contains substitutions of other elements.

MATERIALS AND METHODS

Samples for laboratory testing were taken from various locations in southern Poland: Lower Silesia – Braszowice deposit (M1, M2), Opole Silesia – Gogolin quarry (G) and Upper Silesia – Tarnowskie Góry area (TGO), Piekary Śląskie (PSK, PSZ), Radzionków (Rd) (Text-fig. 1). A total of samples were investigated: two from the Precambrian Serpentine Massif – samples M1 and M2, one from the Lower Muschelkalk (Middle Triassic) – Gogolin Unit (G), three – from the Upper Muschelkalk (Middle Triassic) – three from the Tarnowice Unit (PSK, PSZ, Rd) and one from the Boruszowice Unit (TGO) (Text-fig. 1).

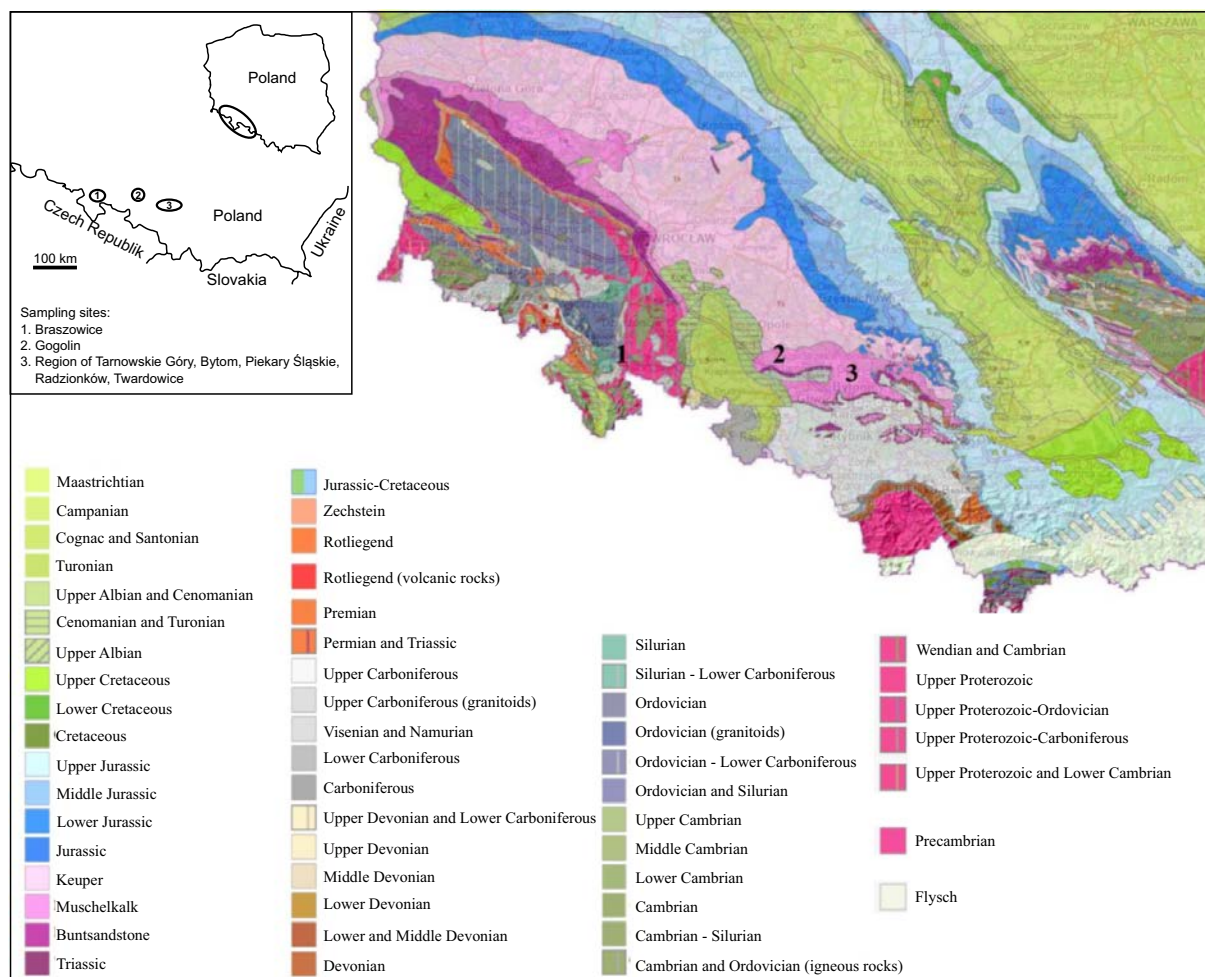
The investigations were carried out using a Thermo Fisher Scientific AXIA ChemiSEM scanning electron microscope integrated with an EDS spectrometer. The samples provided were sputtered with a conductive gold layer using a sputter metal coating machine type SPT-20, COXEM. Measurement parameters: voltage 15kV, tungsten sources were used.

RESULTS OF STUDY

The results of the microscopic observations are presented in Figures 2 to 10 and Tables 1 to 9.

M1 sample – Magnesite from Braszowice Deposit

The results of the measurements indicate the dominance of magnesite in this sample (Text-fig. 2). This carbonate phase is dark grey in color. The Mg



Text-fig. 1. Schematic map with location of sampling places (own study) and geological map of studied area, scale 1:1000000 (https://geologia.pgi.gov.pl/karto_geo/)

content is very high, slightly above the stoichiometric value for magnesite – 28.83%. The calculated value of MgO is given in Table 1. It is also higher than typical for stoichiometric magnesite – 47.80%. Ordered dolomite (Text-fig. 2 – point 2 and Table 1) and huntite (Text-fig. 2 – point 4 and Table 1) have also been identified. These carbonate phases are light grey in color. The Mg contents of these carbonate phases are also typical of stoichiometric values for ordered

dolomite (13.18%) and huntite (20.62%) (see Table 1), as in the case of magnesite. The elevated Si content at some points indicates the presence of silicates in this rock, probably quartz or chalcedony. In the tested sample from Braszowice, SEM-EDS analysis showed the dominance of stoichiometric magnesite (51.57–55.38% MgO), and less abundant: stoichiometric dolomite (22.22% MgO) and huntite (37.31% MgO (see Table 1).

Point number / Mineral chemical formula	Content [%wt]									Total [%wt]	MgO* [%wt]
	C	O	Mg	Ca	Al	Si	Fe	Na			
1/magnesite/Mg(CO ₃)	9.7	52.9	31.1	2.2	0.2	3.9	–	–		100.00	51.57
2/dolomite/Ca _{0.49} Mg _{0.51} (CO ₃) ₂	5.5	52.6	13.4	20.5	0.8	6.3	–	0.9		100.00	22.22
3/magnesite/Mg(CO ₃)	9.3	53.0	33.4	1.8	0.1	1.7	0.7	–		100.00	55.38
4/huntite/ CaMg ₃ (CO ₃) ₂	9.3	52.9	22.5	1.2	0.6	12.6	0.9	–		100.00	37.31

Table 1. Chemical composition in micro-area of sample M1. * MgO content was calculated based on EDS results, note refers to Tables 2–9.

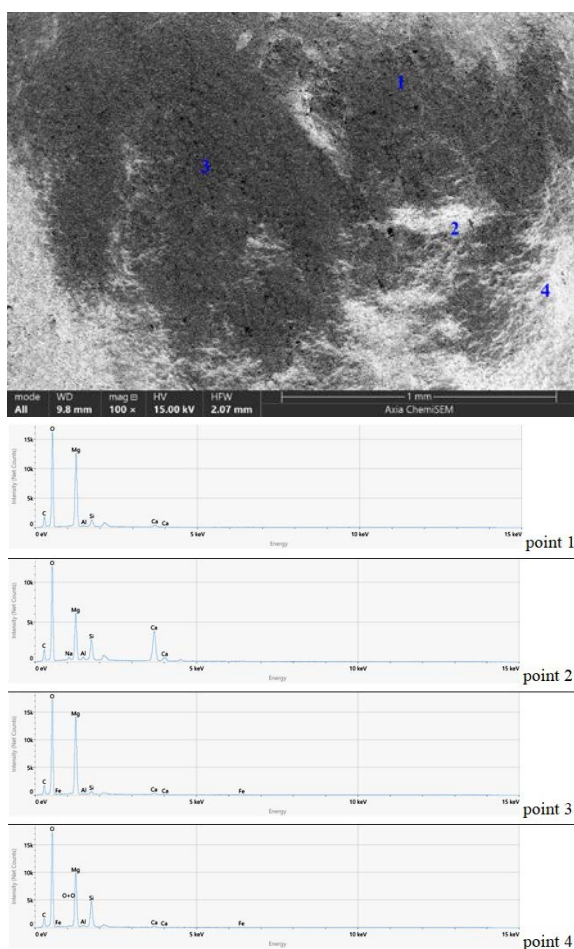
Point number / Mineral chemical formula	Content [%wt]										Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Fe	Na	K	S		
1/magnesite/Mg _{0.88} Ca _{0.22} (CO ₃)	12.8	37.1	25.4	9.4	0.4	4.2	10.1	—	0.6	—	100.00	42.12
2/pyrite/FeS ₂	19.9	10.5	1.5	—	—	0.7	32.4	—	—	35.0	100.00	0.90
3/magnesite/Mg(CO ₃)	15.1	51.2	30.8	—	—	0.6	2.3	—	—	—	100.00	51.07
4/ magnesite/Mg _{0.98} Ca _{0.02} (CO ₃)	15.7	52.6	28.2	0.8	—	0.7	2.0	—	—	—	100.00	46.76
5/magnesite/Mg(CO ₃)	14.6	38.5	29.6	0.7	—	1.1	15.3	0.2	—	—	100.00	49.08

Table 2. Chemical composition in micro-area 1 of sample M2.

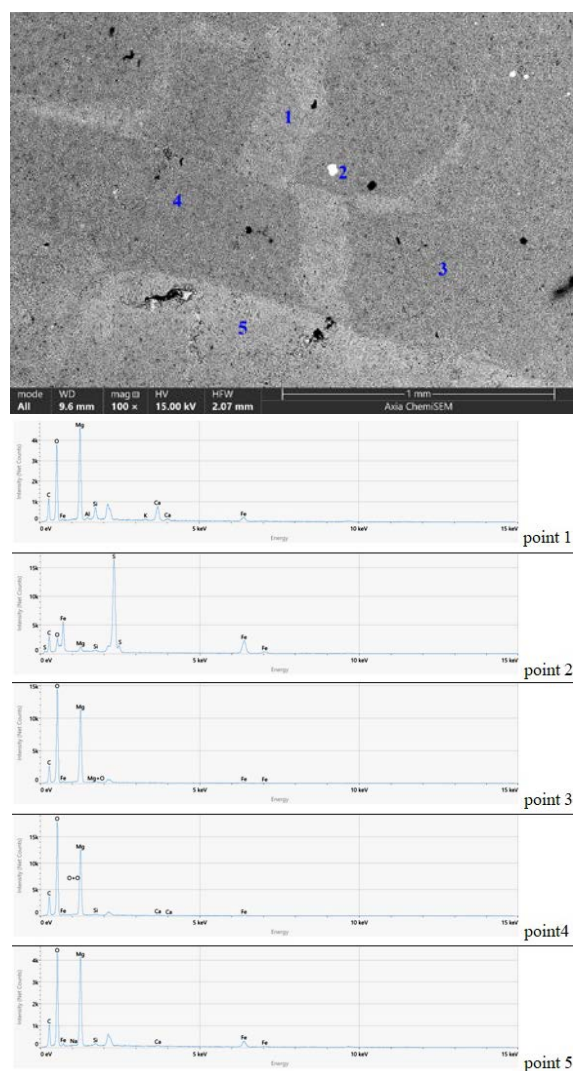
M2 sample – Magnesite from Braszowice Deposit

The results of the measurements in the first micro-area indicate the dominance of magnesite in this sample (Text-fig. 3 and Table 2). This carbonate phase is grey in colour. However, there are two types of magnesite. One is characterised by an Mg content similar to the stoichiometric value for magnesite (Text-fig. 3 – points 3, 5 and Table 2) and the other has a lower Mg content than the stoichiometric value (Text-fig. 3 – points 1, 4 and

Table 2). It shows the differentiation of magnesite phases in micro-area 1 of sample M2. Pyrite has also probably been identified (Text-fig. 3 – point 2 and Table 2). The elemental values measured in microarea 2 (Text-fig. 4) of sample M2 show the purity of the magnesite phase in this micro-area (Table 3). The Mg content values are higher than the



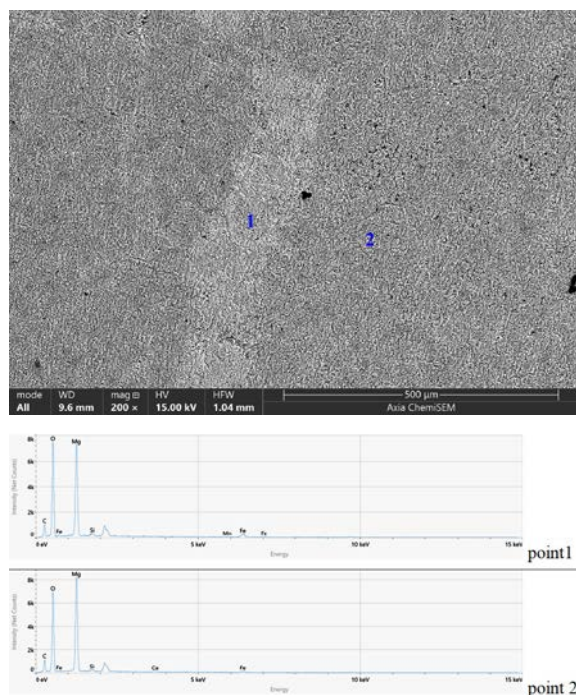
Text-fig. 2. Microphotography of the M1 sample with points of analysis, BSE and EDS spectra.



Text-fig. 3. Microphotography (1) of the M2 sample with points of analysis, BSE and EDS spectra.

Point number / Mineral chemical formula	Content [%wt]							Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Si	Fe	Mn		
1/magnesite/Mg(CO ₃)	11.00	42.1	34.1	–	1.5	10.5	0.8	100.00	56.54
2/magnesite/Mg(CO ₃)	12.00	43.9	37.9	0.9	1.3	4.0	–	100.00	62.84

Table 3. Chemical composition in the second micro-area of sample M2.



Text-fig. 4. Microphotography (2) of the M2 sample with points of analysis, BSE and EDS spectra.

typical stoichiometric values for magnesite (28.83% Mg) which may indicate an admixture of brucite. The elevated Si content in some points of the micro-areas indicates the presence of silicates in this rock, probably quartz or chalcedony. According to the measurement results, the tested rock could be classified as magnesite. In this tested sample (M2) analysis showed the dominance of stoichiometric magnesite (42.12–62.84% MgO) (Tables 2 and 3).

G sample – Gogolin limestone from Gogolin Quarry

Low magnesium calcite dominates in this sample (Text-fig. 5 and Table 4). However, the Mg content varies from 1.1% to 6.1%. This indicates the variation of magnesium content in the low magnesium calcite phase in sample G. In addition, high magnesium calcite was detected in point 4 of the micro-area, the Mg

content in this spot is slightly higher than typical for the low Mg calcite phase. The elevated contents of Si and Al in some points of the micro-area indicate the presence of silicates and aluminosilicates in this rock, probably quartz, chalcedony and clay minerals. According to the measurement results, the tested rock could be classified as limestone. In sample of Gogolin limestone (G), SEM-EDS analysis showed the dominance of stoichiometric calcite (1.82–6.94% MgO), and small amounts of stoichiometric magnesium calcite (10.11% MgO) (see Table 4).

PSK sample – Tarnowice Dolomite from Piekary Śląskie City

Sample PSK is characterized by the predominance of proto-dolomite (Text-figs 6 and 7). It is a carbonate-dolomite phase with reduced Mg content (Table 5) compared to the stoichiometric value for dolomite – 13.18%, but lower than high-Mg calcite. In addition, high-Mg calcite was identified there. It was found that Mg in this phase has a higher content compared to low-Mg calcite. In proto-dolomite, on the other hand, the amount of magnesium is lower. In BSE images, the color of the proto-dolomite phases changes from grey to dark grey and the high-Mg calcite phases are light grey. However, two types of high magnesium calcite were identified in sample PSK. The first one (Text-fig. 6 – point 4) is characterized by lower Mg content and the second one (Text-fig. 6 – point 5) presents higher Mg content, slightly lower than that of proto-dolomite. According to the results, the tested rock could be classified as a dolomite composed of proto-dolomite (20.73–21.22% MgO) and high-Mg calcite phases (13.43–18.74%).

PSZ sample – Tarnowice Dolomite from Piekary Śląskie City

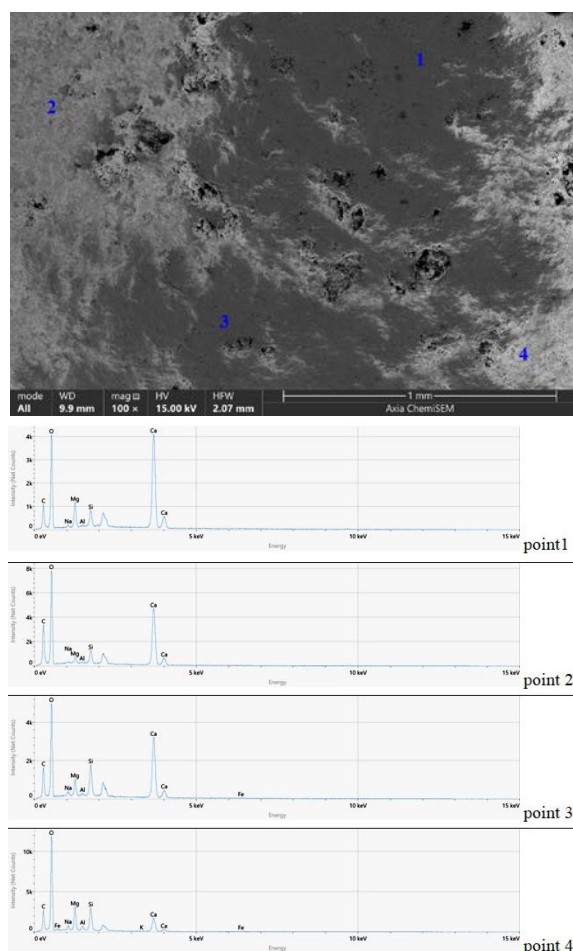
The PSZ sample is composed of four carbonate phases: proto-dolomite, ordered dolomite, high-Mg calcite as also huntite (Text-figs 7 and 8 and Tables 6, 7). In BSE images the colour of high Mg calcite is light grey, while dolomite and huntite are grey. The high magnesium calcite of PSZ sample is characterised by a higher Mg content than the low Mg calcite, but lower

Point number / Mineral chemical formula	Content [%wt]									Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Fe	Na	K		
1/calcite/ $\text{Ca}_{0.84}\text{Mg}_{0.16}\text{CO}_3$	8.8	62.7	4.2	21.4	0.1	2.2	–	0.6	–	100.00	6.94
2/calcite/ $\text{Ca}_{0.93}\text{Mg}_{0.07}\text{CO}_3$	16.8	64.6	1.1	14.9	0.1	2.1	–	0.4	–	100.00	1.82
3/calcite/ $\text{Ca}_{0.84}\text{Mg}_{0.16}\text{CO}_3$	14.4	61.6	2.8	15.1	0.2	4.7	0.2	1.0	–	100.00	4.64
4/magnesium calcite/ $\text{Ca}_{0.71}\text{Mg}_{0.29}\text{CO}_3$	18.0	52.7	6.1	15.1	1.0	5.4	0.2	1.4	0.1	100.00	10.11

Table 4. Chemical composition in micro-area of sample G.

Point number / Mineral chemical formula	Content [%wt]										Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Na	Cl	Rb	Nb		
1/proto-dolomite/ $\text{Ca}_{0.54}\text{Mg}_{0.46}(\text{CO}_3)_2$	14.6	58.8	12.8	12.9	–	–	–	–	0.9	–	100.00	21.22
2 /proto-dolomite/ $\text{Ca}_{0.53}\text{Mg}_{0.47}(\text{CO}_3)_2$	13.6	58.9	12.5	13.5	0.1	1.4	–	–	–	–	100.00	20.73
3/proto-dolomite/ $\text{Ca}_{0.52}\text{Mg}_{0.48}(\text{CO}_3)_2$	13.5	57.8	12.6	13.4	0.0	2.2	0.5	–	–	–	100.00	20.89
4/magnesium calcite/ $\text{Ca}_{0.56}\text{Mg}_{0.44}(\text{CO}_3)_2$	25.5	50.0	8.1	10.1	0.3	4.1	1.0	0.9	–	–	100.00	13.43
5/magnesium calcite/ $\text{Ca}_{0.60}\text{Mg}_{0.40}(\text{CO}_3)_2$	10.6	53.1	11.3	17.1	0.1	1.7	–	–	–	6.1	100.00	18.74

Table 5. Chemical composition in micro-area of sample PSK.



Text-fig. 5. Microphotography of the G sample with points of analysis, BSE and EDS spectrums.

than typical for proto-dolomite. The Mg content of proto-dolomite is lower than the stoichiometric value for dolomite (13.18% of Mg), but ordered dolomite is characterised by a Mg content slightly higher than the stoichiometric value for dolomite. The amount of magnesium in huntite is significantly lower than the stoichiometric value for this carbonate phase (20.62% of Mg). Therefore there is probably a de-huntite carbonate phase in sample PSZ. In point 2 of the first micro-area of sample PSZ increased contents of Cr and Pb were measured and in point 1 of the second micro-area – 0.1% of Na was determined. Cr, Pb and Na could probably be related to non-carbonate minerals. To sum up, in the tested sample from Tarnowice, SEM-EDS analysis showed the dominance of stoichiometric dolomite (22.55% MgO), as also: stoichiometric de-huntite (24.37–25.37% MgO) and magnesium calcite (16.08–19.56% MgO (see Tables 6 and 7).

Rd sample – Tarnowice Limestone from Radzionków City

The results are confirmed by the elemental spectrum taken at point 6 of the Rd sample (Text-fig. 9). Similar to the Gogolin Unit samples and the P sample, a high Ca content was also measured in the micro-area of this sample, indicating the presence of low-magnesium calcite. Only in point 6 the Mg content was 1.2%. The measurement results indicate the purity of the calcium carbonate mineral phase (Table 8). Fe was measured at three points. Elevated Si and Al contents at points 1, 3, 4 and 6 and low Na addition indicate the presence of silicate and aluminosilicate admixtures. The results are confirmed by the elemental spectrum taken at point 6 of the micro-area (Text-fig. 9). According to the measure-

Point number / Mineral chemical formula	Content [%wt]										Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Fe	Rb	Cr	Pb		
1/dolomite/ $\text{CaMg}(\text{CO}_3)_2$	14.2	54.4	13.6	17.3	—	—	—	0.5	—	—	100.00	22.55
2/magnesium calcite/ $\text{Ca}_{0.60}\text{Mg}_{0.40}(\text{CO}_3)_2$	18.9	49.1	9.7	14.4	0.2	0.6	1.5	0.0	1.5	4.1	100.00	16.08
3/magnesium calcite/ $\text{Ca}_{0.58}\text{Mg}_{0.42}(\text{CO}_3)_2$	21.3	50.4	11.8	16.1	—	0.4	—	—	—	—	100.00	19.56

Table 6. The results of measurements in first micro-area of sample PSZ.

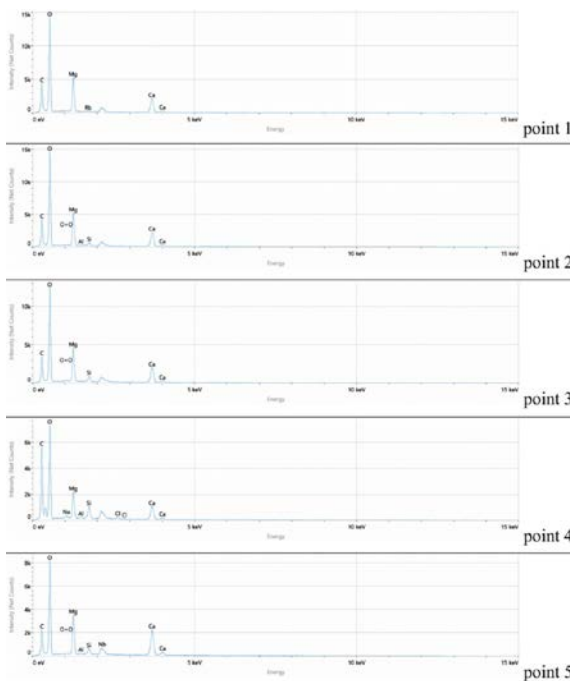
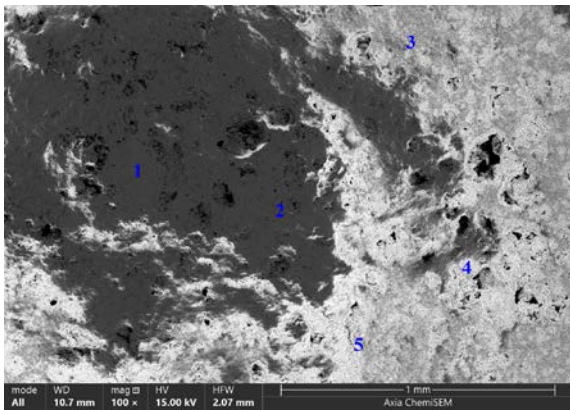
Point number / Mineral chemical formula	Content [%wt]							Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Na		
1/de-huntite/Ca _{1.86} Mg _{2.14} (CO ₃) ₂	11.5	53.8	14.7	19.7	—	0.2	0.1	100.00	24.37
2/de-huntite/Ca _{1.85} Mg _{2.15} (CO ₃) ₂	15.5	50.7	14.8	19.0	—	—	—	100.00	24.54
3/de-huntite/Ca _{1.77} Mg _{2.23} (CO ₃) ₂	10.0	52.8	15.3	21.9	0.0	—	—	100.00	25.37

Table 7. Chemical composition in second micro-area of sample PSZ.

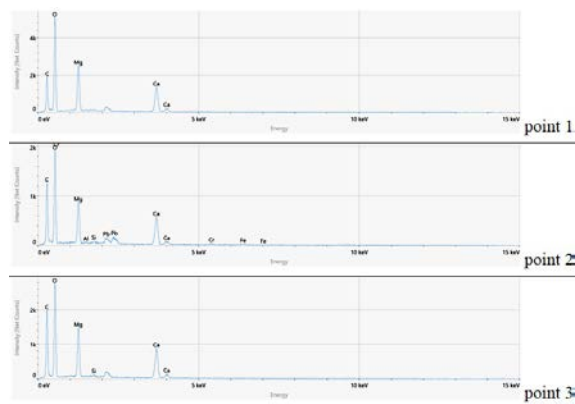
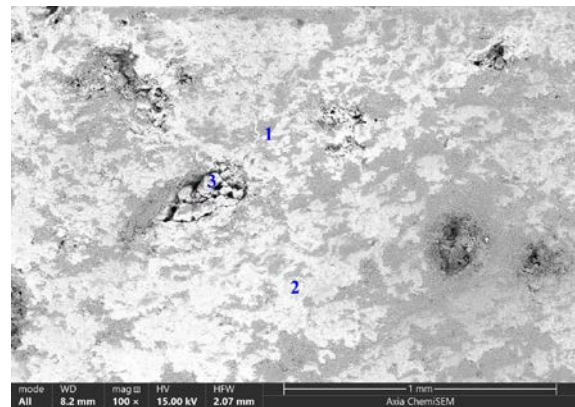
ment results, the tested rock could be classified as a limestone, with calcite (0.50–1.99%) dominance and low admixtures of non-carbonate minerals.

TGO sample – Boruszowice Limestone from Tarnowskie Góry City

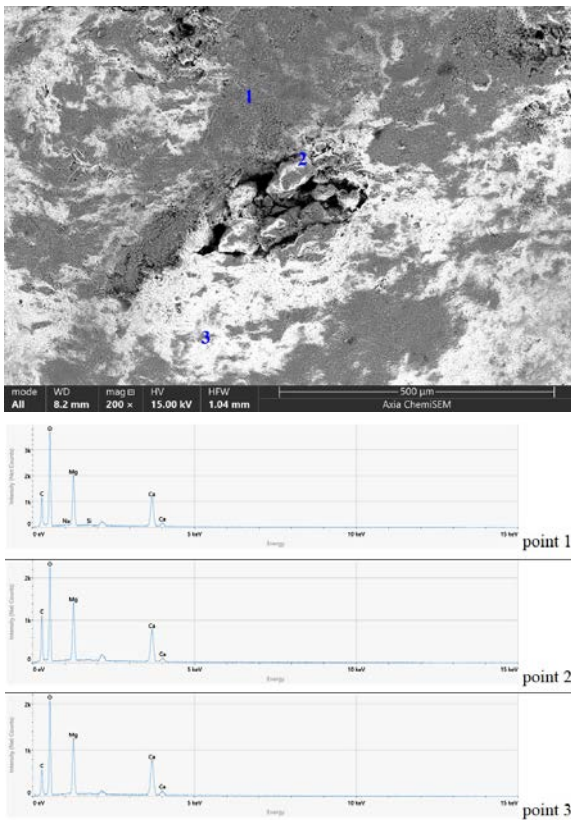
A high Ca content was also found in this sample, indicating the presence of low magnesium calcite (Text-fig. 10 and Table 9). Only at point 5 the Mg con-



Text-fig. 6. Microphotography of the PSK sample with points of analysis, BSE and EDS spectra.



Text-fig. 7. Microphotography (1) of the PSZ sample with points of analysis, BSE and EDS spectra.



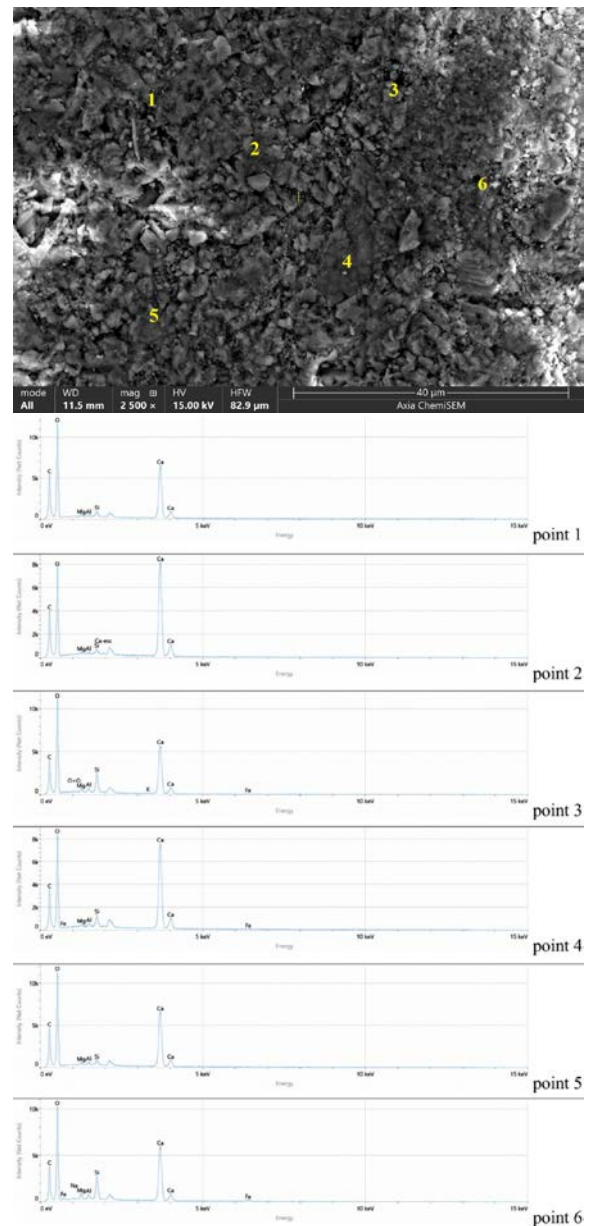
Text-fig. 8. Microphotography (2) of the PSZ sample with points of analysis, BSE and EDS spectra.

tent was 1%. The measurement results for this sample also indicate the purity of the calcium carbonate phase, Fe being only measured at one point. Elevated Si and Al contents at points 2 and 5 and the presence of K at point 2 indicate the presence of silicate and aluminosilicate admixtures. In addition, 2.3% Nb was measured at point 3 of the micro-area. Niobium is a common impurity in minerals rich in Ti and Zn, and also occurs in manganese concretions. The results confirm the elemental spectrum carried out at point 5 of the TGO microsite sample. According to the results of the measurements, this rock, similar to the sample from the Gogolin Unit – G and the Rd sample from Tarnowice Unit, can be classified as limestone (main mineral calcite – 0.17–1.66% MgO) with a low content of non-carbonate minerals.

DISCUSSION

The results presented in this work and the results of previous projects (Stanienda, 2011, 2013a, b, 2014,

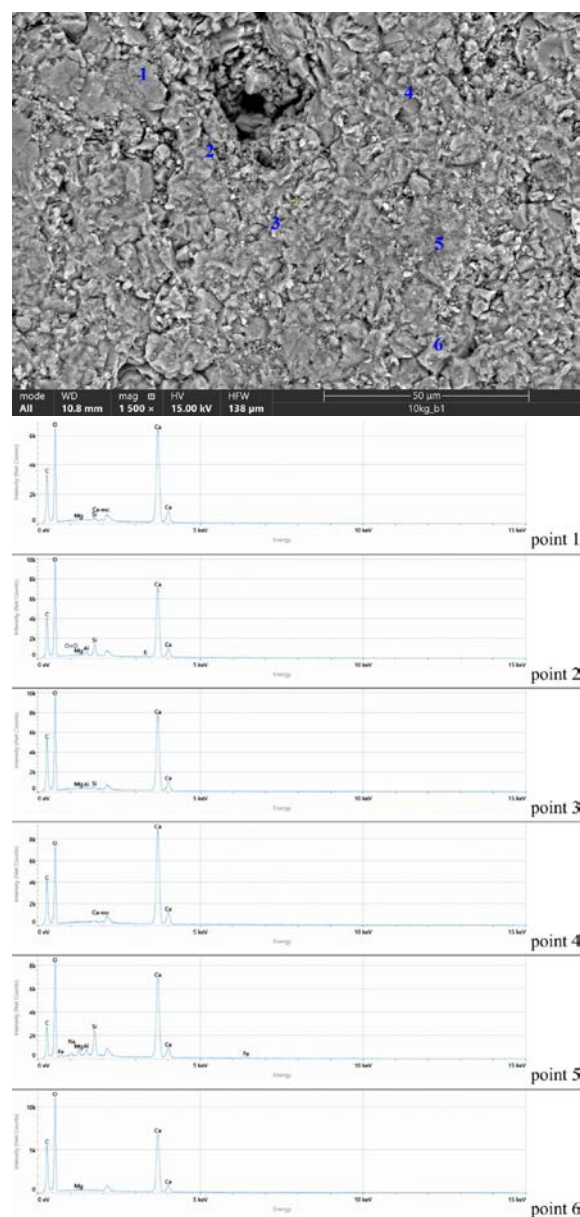
2016a, b; Stanienda-Pilecki, 2017, 2018, 2021, 2023), allow the determination of the chemical formulae of the studied carbonate phases with magnesium. Based on the results of the research, as well as on the basis of literature data, it can be stated that in a high-Mg calcite monocrystalline cell, 11 ions are Ca, while Mg is 3 ions (Stanienda 2011, 2013a, b, 2014, 2023). F. Zhang *et al.* (2010) found that the values of cell parameters – a_0 (Å) and c_0 (Å) decrease with increasing $MgCO_3$ content in high-Mg calcite. The analysis of the data obtained by F. Zhang and others (2010) shows the pos-



Text-fig. 9. Microphotography of the Rd sample with points of analysis, BSE and EDS spectra.

Point number / Mineral chemical formula	Content [%wt]								Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Fe	Na		
1/calcite/Ca _{0.99} Mg _{0.01} CO ₃	10.90	55.79	0.30	31.30	0.30	1.40	—	0.01	100.00	0.50
2/calcite/Ca _{0.99} Mg _{0.01} CO ₃	8.40	48.20	0.30	42.10	0.20	0.80	—	—	100.00	0.50
3/calcite/Ca _{0.98} Mg _{0.02} CO ₃	10.10	54.00	0.60	28.90	0.90	4.60	0.90	—	100.00	0.99
4/calcite/Ca _{0.99} Mg _{0.01} CO ₃	8.20	49.50	0.40	38.80	0.40	2.10	0.60	—	100.00	0.66
5/calcite/Ca _{0.99} Mg _{0.01} CO ₃	9.70	55.40	0.50	32.60	0.60	1.20	—	—	100.00	0.83
6/calcite/Ca _{0.90} Mg _{0.10} CO ₃	10.10	50.60	1.20	29.60	1.00	5.20	1.90	0.40	100.00	1.99

Table 8. Chemical composition in micro-area of sample Rd.



Text-fig. 10. Microphotography of the TGO sample with points of analysis, BSE and EDS spectra.

sibilities of determining the cell parameters based on the MgCO_3 content. When the amount of MgCO_3 is 22.7%, the parameters of the high-magnesium calcite cell are as follows: $a_0 = 4.91 \text{ \AA}$, $c_0 = 16.65 \text{ \AA}$. When the amount of MgCO_3 is 36.71%, the cell parameters are as follows: $a_0 = 4.88 \text{ \AA}$, $c_0 = 16.45 \text{ \AA}$ (Zahng and Dave 2000; Zhang *et al.* 2010). The chemical formula of the proto-dolomite of the Tarnowice Dolomites is as follows $\text{Ca}_{0.52-0.54}\text{Mg}_{0.48-0.46}\text{CO}_3$. This means that the Mg content is lower than the stoichiometric value for protodolomite. They indicate the reduced Mg content according to the stoichiometric value for huntite. The reduction of Mg in this carbonate phase is an effect of diagenetic processes – dehuntization (Stanienda 2011, 2014). Based on the presented research, the chemical formula of the magnesite of Precambrian deposits can be shown as follows: $\text{Mg}_{1-0.88}\text{Ca}_{0.00-0.22}(\text{CO}_3)$ (see Table 10 and Text-fig. 11).

The research results have shown that the Triassic carbonate rocks of the Polish part of the Central-European Basin contain a phase that could be a huntite $\text{CaMg}_3[\text{CO}_3]_4$. The Mg content in the huntite phase chemical formula can be shown as follows $\text{Ca}_{0.25}\text{Mg}_{0.75}\text{CO}_3$. It was found that the studied huntite is characterized by a lower MgCO_3 content (50.20% to 57.98%) than the amount typical for this phase: 69.30 to 72.28% MgCO_3 . The lower Mg content in this mineral is probably related to diagenetic processes, perhaps it is dehuntization or calcitization (Stanienda 2011, 2013a, 2014; Stanienda-Pilecki 2023).

SEM observations have allowed us to obtain data on the formation of the analyzed carbonate rocks and diagenesis processes that formed the mineral composition of these rocks. It can be assumed that low-Mg calcite and high-Mg calcite were formed in the epicontinental Central-European Basin (Szulc 1990, 2000) during direct crystallization from sea-water, at the same time as the aragonite and dolomite phases. Dolomites were formed in the mixing zone of phreatic zone waters and salty sea waters in the early period of constructive diagenesis during dolomitization processes. In such an environment, two different phases of dolomite could have formed: pro-

Point number / Mineral chemical formula	Content [%wt]									Total [%wt]	MgO [%wt]
	C	O	Mg	Ca	Al	Si	Fe	K	Nb		
1/calcite/Ca _{0.99} Mg _{0.01} CO ₃	8.80	49.50	0.20	41.10		0.40	–	–	–	100.00	0.33
2/calcite/Ca _{0.99} Mg _{0.01} CO ₃	9.00	52.30	0.30	35.00	0.70	2.40	–	0.30	–	100.00	0.50
3/calcite/Ca _{0.99} Mg _{0.01} CO ₃	10.10	50.90	0.20	35.40	0.00	0.40	–	–	3.00	100.00	0.33
4/calcite/CaCO ₃	8.10	47.10	0.10	44.70	0.00	0.00	–	–	–	100.00	0.17
5/calcite/Ca _{0.94} Mg _{0.06} CO ₃	7.50	48.40	1.00	35.90	1.10	4.80	1.30	–	–	100.00	1.66
6/calcite/Ca _{0.99} Mg _{0.01} CO ₃	10.70	55.90	0.20	33.20	–	–	–	–	–	100.00	0.33

Table 9. Chemical composition in micro-area of sample TGO.

Carbonate phase name	Chemical formula	Cell parameters	Space group
Low-Mg calcite (Text-fig. 11a)	Gogolin limestones (Ca _{1.00-0.71} Mg _{0.00-0.29})CO ₃ Tarnowice limestones (Ca _{0.99-0.90} Mg _{0.01-0.10})CO ₃ Boraszowice limestones (Ca _{1.00-0.94} Mg _{0.00-0.06})CO ₃	a _o = 4.989 Å c _o = 17.062 Å	Scalenohehedral-R3c
High-Mg calcite (Text-fig. 11b)	Gogolin limestones (Ca _{0.71} Mg _{0.29} CO ₃) Tarnowice dolomites (Ca _{0.76-0.63} Mg _{0.24-0.37})CO ₃	a _o = 4.941 Å c _o = 16.854 Å	Rhombohedral-R3c
Proto-dolomite (Text-fig. 11c)	Tarnowice dolomites [Ca _{0.52-0.54} Mg _{0.48-0.46} CO ₃]	a _o = 4.842 Å	Rhombohedral-proto-dolomite-R3c
Ordered dolomite (Text-fig. 11d)	Precambrian magnesites [Ca _{0.5} Mg _{0.5} CO ₃]	c _o = 15.95 Å	Rhombohedral-ordered dolomite-R3
De-huntite (Text-fig. 11e)	Tarnowice dolomites [Ca _{1.77-1.86} Mg _{2.23-2.14} (CO ₃) ₂]	a _o = 9.5027 Å	Trapezohedral-R32
Huntite (Text-fig. 11f)	Precambrian magnesites [CaMg ₃ CO ₃]	c _o = 7.8212 Å	
Magnesite (Text-fig. 11g)	Precambrian magnesites [Mg _{1-0.88} Ca _{0.00-0.22} (CO ₃) ₂]	a _o = 4.6632 Å c _o = 15.015 Å	Rhombohedral-R3c

Table 10. Structures of crystal cell and chemical formulas of carbonate phases with magnesium.

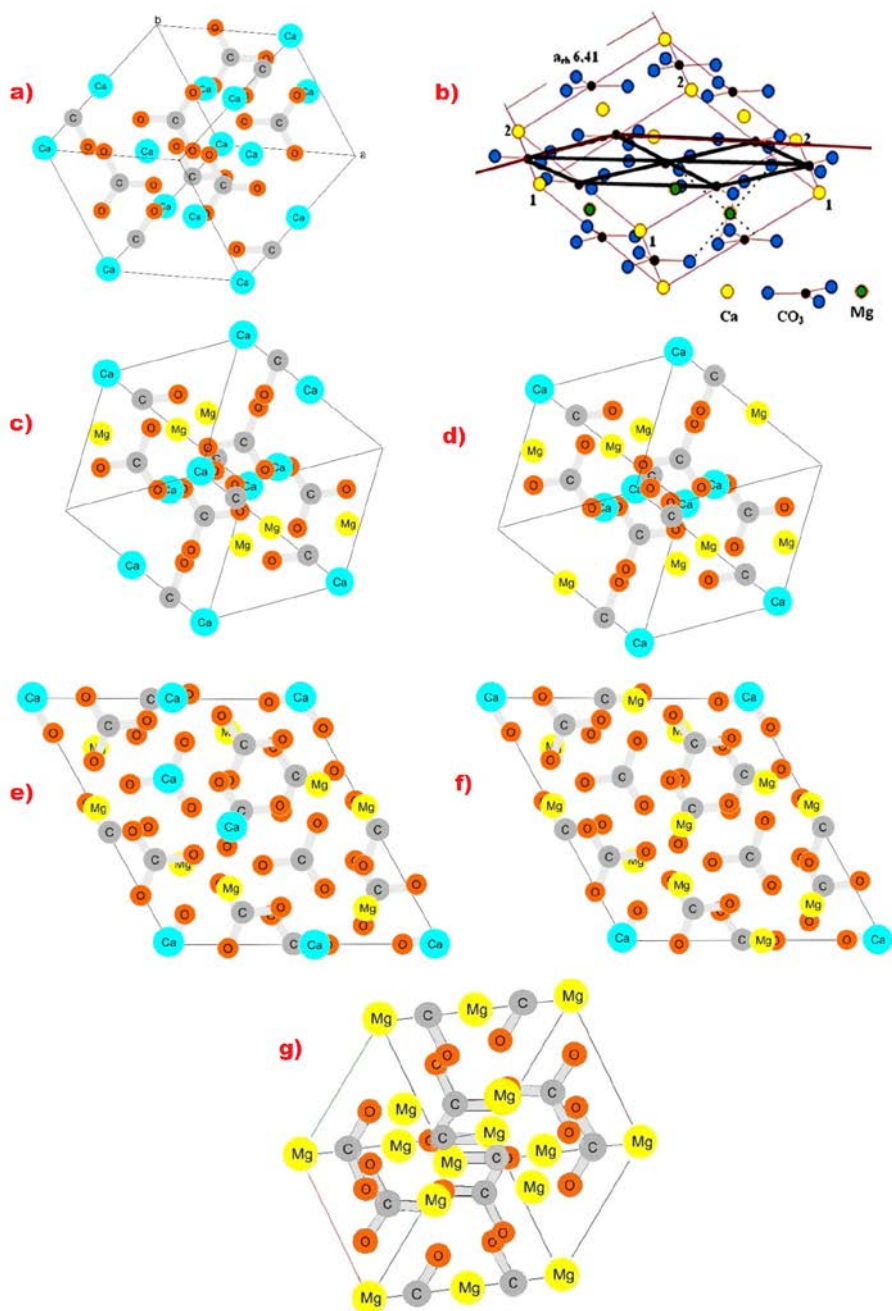
to-dolomite and ordered dolomite. Moreover, due to the waters with a high content of dissolved mineral components, the process of fixation of the high-Mg calcite unstable carbonate phase, originally formed in the environment of the seabed, took place. Huntite is a specific phase with a higher Mg content than dolomite, which occurs in igneous, sedimentary and metamorphic rocks of different geological periods. Its formation is most often associated with hydrothermal processes, weathering of dolomite or transformation of magnesium calcite under high temperature conditions. In sedimentary rocks it occurs in the sediments of the aeration zone (Szulc 1990, 2000; Stanienda 2011, 2013a, 2014; Stanienda-Pilecki 2023). In Triassic carbonate rocks, de-huntite was probably formed in areas of the Central-European Basin where diagenetic processes took place with the contribution of water from the vadose zone. The environment in which it was formed and the process of dehuntization could be the reasons for the reduced magnesium content of this mineral. The formation of the magnesite that makes up Precambrian magnesite rocks was quite different. The magnesites were probably formed during the serpentinisation of the gabbro massif of Braszowice-Grochowa. In rocks with the composition of peridotite, magnesite is stable at high pressures and high temperatures. The sources of Mg are the Mg-rich minerals of ultramafic rocks, usually peridotite, undergoing serpentinization processes (Greco *et al.*

2023). Sources of CO₂ can be diverse, including organic, carbonate rocks, meteoric waters or hypogenic hydrothermal fluids (Greco *et al.* 2023). The magnesite from the Braszowice deposit is associated with serpentinites, which are diversely cut by a fine network of magnesite inclusions (Stefanicka *et al.* 2016). In some zones of the serpentinite rock, the magnesite veins vary from a few millimetres to 20 cm. These are mainly yellow (ferrous) and brown (non-ferrous) magnesite. Magnesite occurs mainly in serpentinite with varying degrees of weathering and occasionally in gabbro (Stefanicka *et al.* 2016). Analysing its genesis, it could be said that magnesite was formed during the metamorphosis of gabbro into serpentinite. It is likely that magnesium was released from Mg-rich olivines during this process. Some of the Mg ions were bound to serpentine minerals and the rest to magnesite.

CONCLUSIONS

The research presented here has allowed the following conclusions to be drawn:

- The results of scanning electron microscopy indicate the presence of the following minerals: low-Mg calcite, high-Mg calcite, proto-dolomite, ordered dolomite, de-huntite, huntite and magnesite. The carbonate phases are characterised by different magnesium contents.



Text-fig. 11. Structures of crystals: a) low-Mg calcite; b) high-Mg calcite; c) proto-dolomite; d) ordered dolomite; e) de-huntite, f) huntite, g) magnesite (Stanienda 2011; Stanienda-Pilecki 2023).

- The chemical formulae of calcite, dolomite, huntite phases and magnesite were calculated from the results. They are as follows: low-Mg calcite – $(\text{Ca}_{1.00-0.71}, \text{Mg}_{0.00-0.29})\text{CO}_3$, high-Mg calcite – $(\text{Ca}_{0.76-0.63}, \text{Mg}_{0.24-0.37})\text{CO}_3$, proto-dolomite – $\text{Ca}_{0.52-0.54}, \text{Mg}_{0.48-0.46}\text{CO}_3$, ordered dolomite – $\text{Ca}_{0.5}, \text{Mg}_{0.5}\text{CO}_3$, de-huntite – $\text{Ca}_{1.77-1.86}\text{Mg}_{2.23-}$

$2.14(\text{CO}_3)_2$, huntite – CaMg_3CO_3 , magnesite – $\text{Mg}_{1-0.88}\text{Ca}_{0.00-0.22}(\text{CO}_3)$.

- According to the results, the de-huntite of the studied limestones presents a lower value of MgCO_3 than typical for this carbonate phase. The reduction of Mg in this mineral may be an effect of diagenetic processes – dehuntization (calcitiza-

tion?). The Mg content in magnesite is typical of the stoichiometric value for this stable carbonate phase. The results of the research provided new data on the conditions of formation of the studied carbonate phases and the diagenetic processes that could influence their final chemical composition.

- It was also possible to explain the coexistence of carbonate phases with different magnesium contents and the conditions in the sea basin that allowed the preservation in Triassic limestones of some carbonate phases, such as high-Mg calcite, characteristic of younger sediments. It was also possible to formulate the theory of magnesite genesis.
- In conclusion, SEM observations make it possible to distinguish mineral phases with different amounts of a particular component.

Acknowledgements

The authors would like to thank the Reviewers for reviewing the manuscript and for their comments and suggestions.

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