

Trace Elements and REY in the Muschelkalk Limestones of the Opole Silesia in Poland

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Research Article

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Abstract

The results of researches of the selected trace elements: Ti, Sr, Ba, Zn, and also Cr, Ni, Cu, Zr, Mo, Pb, Rb, Mn, Na, K, P, Y and REE (REY) content were presented in this article. The elements were measured in the carbonate minerals of Muschelkalk (Middle Triassic) limestones of the Opole Silesia in Poland, using two methods: ICP MS spectrometry and X-ray fluorescence. These methods are characterized by very high precision and sensitivity of measurements. The results of researches show that the content of analyzed trace elements varies in from value below 1 ppm up to some hundreds ppm. However, the highest contents were measured for strontium and barium, elements characteristic for aragonite carbonate phase which is transformed such as high-Mg calcite into low magnesium calcite during diagenesis. So as Sr and Ba indicate the presence of aragonite in the primary carbonate material. The other trace elements probably form substitutions in clay or carbonate minerals. Some of trace elements such as Zn, Pb, Cu, Mo, Ni may also be associated with sulfide minerals and Ti, Cr, Mn, with oxides. Some measured REY elements- Ce, Nd, Sm, Gd, Dy, Er and Y are found in the rocks in very small quantities. So their content is really very low. It varies in from value below 1 ppm up to 6 ppm. REY usually substitute Ca ions in calcite.

1. Introduction

Limestones are one of the most important of all the sedimentary rocks used in different branches of industry. They are composed mostly of calcite mineral (CaCO_3 – low magnesium calcite). Sometimes includes other carbonate phases, like high-Mg calcite, protodolomite, ordered dolomite or huntite (Pozzi and Stanienda 2000; Stanienda 2006, 2011, 2013, 2016a and b; Stanienda-Pilecki 2018, 2019). They also may contain some non-carbonate impurities also some amounts of different trace elements and REY (Banner 1995; Barrat et al. 2000; Bouazza et al. 2016; Elzinga et al. 2002; Hua et al. 2013; Jiang et al. 2015; Mori 2007; Ostrom 1957; Stanienda 2013, 2016a; Tanaka et al. 2003; Tanaka and Kawabe 2006).

Usually elements occurring in minor amounts and trace elements including K, Na, Fe, Mn, B, P, V, Ti, Cr, Mo, Ni, V, Cu, Zn, Rb, Sr, Zr, Nb, Ba, Pb, also REY, (REE, Y) and Sc may be present in limestones (Mori 2007; Tanaka et al. 2003; Tanaka and Kawabe 2006). Strontium and barium are elements characteristic for aragonite. They substitute Ca in this carbonate phase. Aragonite is usually transformed such as high-Mg calcite into low magnesium calcite during diagenesis. So as Sr and Ba indicate the presence of aragonite in the primary carbonate material. The other trace elements could form substitutions in clay or carbonate minerals. Some trace elements such as Zn, Pb, Cu, Mo, Ni may also be associated with sulphide minerals and Ti, Cr, Mn, with oxides.

REY- Rare-Earth (REE) and Y (Yttrium) element patterns- have long been recognized as valuable indicators of provenance and alteration for minerals and rocks. Ca-bearing minerals are commonly enriched in REEs and Y relative to other phases, reflecting the ease with which REEs and Y substitute for Ca (Cherniak 1998; Elzinga et al. 2002; Tanaka et al. 2009). The REEs and Y usually occur as trivalent ions and show similar chemical behaviors owing to their electronic configurations. Carbonate minerals which are major constituents of sediments and sedimentary rocks incorporate a number of minor and trace elements,

including the REEs and Y, that provide invaluable information about the environment and processes that influence mineral formation and growth, as well as the circumstances characterizing subsequent alteration (Cherniak 1998; Elzinga et al. 2002; Tanaka et al. 2003; Tanaka et al. 2009). Carbonate Y and REE proxies have also been considered problematic, particularly with regard to perceived diagenetic alteration. However, even extant scleractinian corals have proven unsuitable because they have: very low initial Y and REE contents requiring laborious concentration techniques and high matrix to signal ratios, unpredictable differences in Y and REE fractionation between different taxa (Sholkovitz and Shen 1995), nonproportional incorporation of Y and REEs into the lattice (i.e., coral/ seawater partition coefficients vary systematically as a function of ionic radius (Sholkovitz and Shen 1995) and there are problems with reproducibility owing to the need for complicated, semiquantitative cleaning procedures (Sholkovitz and Shen 1995; Shaw and Wasserburg 1985).

The area of Opole Silesia is situated in the South-West part of Poland. There are numerous Triassic limestone deposits in this territory. Limestones from these deposits are used in various branches of the industry: in the lime industry, as a sorbent in the desulfurization process of flue gases in power plants, for cement production, in agriculture for the production of fertilizers and as an additive to animal feed and in other branches of the economy (Pozzi and Stanienda 2000; Stanienda 2006, 2011, 2013, 2016b).

The results of researches of the selected trace elements content, mainly: Ti, Cr, Mn, Na, K, Ni, Cu, Zn, Sr, Y, Zr, Mo, Ba, Pb, Rb, and selected REY, measured in the carbonate minerals of the Triassic limestones of the Opole Silesia in Poland were presented in this article.

The term of the research was to determine the content of trace elements and REY in Triassic limestones. It was very important for determining the purity of the tested limestone in the term of the possibility of their practical application. Moreover, the research results provided information on the amount of REY and the possibility of their recovery from limestone.

2. Experimental

2.1. Materials

The samples for laboratory tests of the selected trace elements content were collected in different places of the Opole Silesia: in Gogolin Quarry (samples G1, G6), Ligota Dolna Quarry (sample LD11), Wysoka Quarry (samples W1, W5), Szymiszów Quarry (sample S2), Strzelce Opolskie Quarry (samples SO1, SO14, SO17, SO20) and the area of Saint Anne Mountain (sample SA5, SA12). 12 samples were studied: 3 samples from Gogolin Beds (G1, G6, LD11), 3 – from Góraźdze Beds (W1, W5, SA5), 3 – from Terebratula (Dziewkowice) Beds (SA12, S2, SO1) and 3 – from Karchowice Beds (SO14, SO17, SO20) (Fig. 1).

2.2. Methods of measurement

Samples were tested using two following methods: ICP MS spectrometry and X-Ray fluorescence (XRF). These methods have been chosen because of their high precision in the determination of trace elements.

Moreover, the methods present the high detection limit, what is very important when determining the elements with low content. The ICP-MS analysis was carried out in the Institute of Non-Ferrous Metals in Gliwice. A semi-quantitative analysis was used. Measurements were carried out using the method of mass spectrometry with ionization in inductively coupled plasma (ICP-MS). X-ray fluorescence (XRF) was carried out using ZSX Primus II Rigaku spectrometer. The spectrometer, equipped with the 4 kW, 60 kV Rh anode and wavelength dispersion detection system, allowed for the analysis of the elements from Be to U. No external standards were necessary, only the internal standards coupled with the fundamental parameters method (the theoretical relationship between measured X-ray intensities and the concentrations of elements in the sample) were implemented.

Table 1 Results of ICP MS spectrometry of major elements in the samples G1, G6, LD11, W1, W5, SA5.

No.	Element	Sample numbers (element content in %mass)					
		G1	G6	LD11	W1	W5	SA5
1	Mg	1.40	0.70	0.77	0.85	0.98	0.00
2	K	0.85	0.31	0.81	0.17	0.23	0.04
3	Mn	0.01	0.01	0.07	0.01	0.01	0.01
4	Fe	0.54	0.42	0.47	0.36	0.43	0.41

3. Results Of Study

3.1. ICP MS Spectrometry

The results of researches of the following trace elements content: K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr,

Nb, Mo, Cd, Ba, Hf and Pb were presented in Tables 1 to 4.

Table 2

No.	Element	Sample numbers (element content in %mass)					
		G1	G6	LD11	W1	W5	SA5
1	Mg	1.40	0.70	0.77	0.85	0.98	0.00
2	K	0.85	0.31	0.81	0.17	0.23	0.04
3	Mn	0.01	0.01	0.07	0.01	0.01	0.01
4	Fe	0.54	0.42	0.47	0.36	0.43	0.41

Results of ICP MS spectrometry of trace elements in the samples G1, G6, LD11, W1, W5, SA5.

Table 3

No.	Element	Sample numbers (element content in ppm)					
		G1	G6	LD11	W1	W5	SA5
1	Ti	250	100	330	90	110	100
2	V	< 1400	< 1300	< 700	< 1000	< 1700	< 500
3	Cr	320	260	200	260	460	210
4	Ni	350	340	330	380	750	340
5	Cu	< 10	< 10	290	< 10	30	< 10
6	Zn	20	110	30	50	70	110
7	Rb	< 10	< 10	< 10	< 10	< 10	< 10
8	Sr	260	120	450	240	370	240
9	Zr	20	10	10	10	20	< 1
10	Nb	40	< 10	< 10	< 10	< 10	< 1
11	Mo	120	120	120	130	210	140
12	Cd	< 1	< 1	1	1	1	< 1
13	Ba	24	15	29	10	20	16
14	Hf	2	< 1	< 1	2	2	1
15	Pb	25	9	79	24	39	20

Results of ICP MS spectrometry of major elements in the samples SA12, S2, S01, S014, S017, S020.

Table 4

No.	Element	Sample numbers (element content %mass)					
		SA12	S2	S01	S014	S017	S020
1	Mg	1.10	-	-	-	-	-
2	K	0.47	to 0.05	0.14	0.13	0.37	0.23
3	Mn	0.08	0.02	0.01	0.01	0.03	0.05
4	Fe	0.43	0.48	0.39	0.68	0.90	0.87

Results of ICP MS spectrometry of trace elements in the samples SA12, S2, S01, S014, S017, S020.

The results of researches show that the contents of trace elements change in the following ranges: in the case of K – from 0.04 to 8500 %, in the case of Fe – from 0.36 to 0.90 %, for Mn – from 0,01 to 0.08 %, in

the case of Ti – from 90 to 1700 ppm (Fig. 2a), for V – from value below 200 ppm to below 1700 ppm, for Cr – from 200 to 94000 ppm, in the case of Ni – from 310 to 180000 ppm, for Cu – from value below 10 ppm to 290 ppm, for Zn – from 20 to 240 ppm (Fig. 2b), for Rb – the content is always below 10 ppm, in the case of Sr – from 32 to 540 ppm (Fig. 2c), in the case of Zr – from value below 1 ppm to 30 ppm, for Nb – from value below 1 ppm to 40 ppm, for Mo – from 120 to 90000 ppm, for Cd – from value below 1 ppm to 120 ppm, for Ba – from 10 to 260 ppm (Fig. 2d), in the case of Hf – from value below 1 ppm to 2 ppm, in the case of Pb – from 9 to 79 ppm and in the case of Y – from value below 1 ppm to 3 ppm (Fig. 2e).

The data indicate the increased content of K in limestones of Gogolin Beds, Ti (Fig. 2a), Nb and Pb – in limestones of Gogolin Beds and the ones of Karchowice Beds, Ba (Fig. 2d) and Y (Fig. 2e) – in Terebratula limestones and Karchowice limestones, Cr, Ni, Mo, Cd – in limestones of Karchowice Beds and Hf – in Gogolin and Górażdże limestones. Therefore, the highest contents of analyzed trace elements concentrate usually in limestones of Gogolin Beds and the ones of Karchowice Beds and lower – in Terebratula limestones. The lowest values of trace elements were determined in limestones of Górażdże Beds.

The results of researches show a very small content of REE. The amount of the most of these elements is below 1ppm. Only Ce, Nd and Sm were determined in analyzed rocks (Figs. 2f, 2g, 2h). Moreover their contents are very low (Table 5).

Table 5

No.	Element	Sample numbers (element content in ppm)					
		SA12	S2	S01	S014	S017	S020
1	Ti	270	100	110	190	380	1700
2	V	< 700	< 200	< 200	< 300	< 500	< 400
3	Cr	1200	1300	260	210	220	94000
6	Ni	310	1600	400	350	360	180000
7	Cu	10	10	to 10	30	60	60
8	Zn	30	70	20	40	50	240
9	Rb	< 10	< 10	< 10	< 10	< 10	< 10
10	Sr	32	230	360	210	540	160
11	Zr	10	30	< 10	< 10	20	10
12	Nb	10	10	10	10	10	40
13	Mo	120	1100	220	170	160	90000
14	Cd	< 1	2	< 1	< 1	< 1	120
15	Ba	28	260	20	20	34	35
16	Hf	< 1	1	< 1	< 1	1	< 1
17	Pb	27	22	10	20	20	62
Results of ICP MS spectrometry of REY in analyzed samples.							

3.2. X-Ray Fluorescence (XRF)

The results of researches of the following trace elements content: Na, Al, Si, P, S, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Mo and Pb were presented in Tables 6 to 9.

Table 6

element	Sample numbers (element content in ppm)											
	G1	G6	LD11	W1	W5	SA5	SA12	S2	S01	S014	S017	S020
Ce	6	4	7	1	2	<1	5	1	3	3	5	3
Nd	4	2	4	1	1	<1	3	<1	2	2	3	1
Pm	-	-	-	-	-	-	-	-	-	-	-	-
Sm	2	1	2	1	1	<1	2	<1	<1	<1	2	<1
Dy	1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1
∑ REE	~ 14	~ 7	~14	~3	~4	<1	~10	~ 1	~5	~5	~10	~4
Y	2	2	2	1	1	<1	2	1	3	3	3	2
Results of XRF fluorescence of major elements in the samples G1, G6, LD11, W1, W5, SA5.												

Table 7

No.	Element	Element content in %mass					
		G1	G6	LD11	W1	W5	SA5
1	C	10.60	11.09	10.13	10.58	11.41	11.11
2	O	47.89	48.06	47.81	47.97	47.64	47.14
3	Na	0.30	0.17	0.32	0.31	0.13	0.23
4	Mg	0.31	0.20	0.36	0.29	0.16	0.18
5	Al	2566	1448	4165	1191	1244	600
6	Si	1.35	0.69	2.00	0.91	0.55	0.65
7	K	0.10	0.04	0.14	0.02	0.02	0.01
8	Ca	38.73	39.28	38.35	39.51	39.62	40.11
9	Mn	0.02	0.02	0.01	0.002	0.02	0.01
10	Fe	0.31	0.23	0.29	0.17	0.22	0.35
Results of XRF fluorescence of trace elements and Er in the samples G1, G6, LD11, W1, W5, SA5.							

Table 8

No.	Element	Element content in ppm					
		G1	G6	LD11	W1	W5	SA5
1	P	48	41	73	39	56	38
2	S	473	235	462	221	179	436
3	Ti	114	25	235	31	60	24
4	V	0	0	0	0	0	0
5	Cr	1	0	10	0	11	14
6	Ni	20	17	17	22	20	23
7	Cu	23	21	20	23	19	17
8	Zn	16	15	25	44	50	90
9	Rb	4	0	7	0	0	0
10	Sr	436	185	676	395	517	471
11	Y	5	4	2	3	3	1
12	Zr	0	3	0	5	5	0
13	Nb	0	0	0	0	0	0
14	Pb	0	0	58	0	33	22
15	Mo	0	0	0	0	0	0
16	Er	0	0	13	0	0	0

Results of XRF fluorescence of major elements in the samples SA12, S2, S01, S014, S017, S020.

Table 9

No.	Element	Element content in %mass					
		SA12	S2	S01	S014	S017	S020
1	C	10.28	11.25	10.88	11.49	11.44	10.37
2	O	47.64	47.71	47.42	7.38	51.24	47.41
3	Na	0.39	0.22	0.26	0.41	0.16	0.41
4	Mg	0.38	0.21	0.27	6.16	6.16	0.36
5	Al	0.33	0.12	0.11	0.28	0.53	0.15
6	Si	1.87	0.78	0.75	1.54	1.71	1.55
7	K	0.09	0.02	0.02	0.06	0.09	0.03
8	Ca	38.64	39.17	39.94	40.89	27.34	38.95
9	Mn	0.01	0.04	0.01	0.71	0.04	0.05
10	Fe	0.24	0.38	0.19	20.13	1.05	0.62

Results of XRF fluorescence of trace elements and Er in the samples SA12, S2, S01, S014, S017, S020.

The results of XRF show that the contents of trace elements change in the following ranges: in the case of Na – from 1264 to 4117 ppm, in the case of Al – from 1114 to 5278 ppm, for Si – from 5502 to 20027 ppm, for P – from 38 to 331 ppm, for S – from 179 to 1854 ppm, in the case of K – from 118 to 1364 ppm, in the case of Ti – from 24 to 293 ppm (Fig. 3a), for V – the value determined in one sample of Karchowice limestones is 331 ppm, for Cr – from 0 to 90759 ppm, for Mn – from 18 to 7129 ppm, in the case of Fe – from 1730 to 201335 ppm, in the case of Ni – from 17 to 13035 ppm, for Cu – from 17 to 731 ppm, for Zn – from 15 to 90 ppm (Fig. 3b), for Rb – from 0 to 7 ppm, in the case of Sr – from 185 to 676 ppm (Fig. 3c), in the case of Y – from 1 to 9 ppm (Fig. 3d), in the case of Zr – from 0 to 5 ppm, for Nb – the value determined in one sample of Karchowice limestones is 13 ppm, in the case of Pb – from 0 to 58 ppm and for Mo – similar to V and Nb the content of Mo was determined only in one sample of Karchowice limestones and it is 343 ppm. Therefore, the data indicate that the highest contents of analyzed trace elements concentrate usually in limestones of Gogolin Beds and the ones of Karchowice Beds. It confirms the results of ICP MS spectrometry.

The XRF fluorescence allowed to determine among REE only erbium and only in three samples (Tables 8 and 9). Moreover, its contents are very low.

4. Discussion

The results of researches of the selected trace elements content: Ti, Cr, Mn, Na, K, Ni, Cu, Zn, Sr, Y, Zr, Mo, Ba, Pb, Rb and selected REY content, measured in the carbonate minerals of Triassic limestones of the Opole Silesia in Poland were presented in this article.

The results of researches show the increased content of some of the trace elements in analyzed limestones. Higher amounts of Fe, Na, K, Al, Si, S and P were determined. Moreover, in some samples also increased content of Sr, Ba, Cr, Ni, Mo and Mn were measured. Definitely lower contents were determined for Pb, Zn and Cu and the lowest for Nb, Cd, Zr, V, Y, Hf and Rb. The data indicate the increased content of trace elements in limestones of Gogolin Beds and the ones of Karchowice Beds, therefore in the rocks that were formed during marine regression. Lower amounts of trace elements were determined in rocks of Górażdże Beds and the ones of Terebratula Beds.

Some trace elements probably form substitutions in clay or carbonate minerals the others such as Zn, Pb, Cu, Mo, Ni may be associated with sulphide minerals and Ti, Cr, Mn, with oxides. Fe could substitute Mg in carbonates. It can also form pyrite or occur in clay minerals. Na is usually connected with salt minerals or Na plagioclases. K, Al and Si form aluminosilicates – feldspars or clay minerals. Sulfur is a component of sulfides (Fe, Zn, Pb, Cu) or sulfates and P is connected with organic matter. Organic acids and carbonic acids are produced during decomposition of organic substances in anaerobic conditions. Then the dissolution of the phosphates goes. If limestone coexisted, both phosphate and limestone could compete as receptors of hydrogen ions. They affect the dissolution of phosphate (Kim and Park 2008). Mn usually substitute Ca in carbonate minerals. Sometimes this element occurs in form of manganese oxides which create in some limestones characteristic manganese dendrites, sometimes creates manganese concretions on the bottoms of the oceans. Sr and Ba occur in carbonate mineral phases. According to the literature data Sr is present in skeletons of marine organisms (Boggs 2010; Mackenzie and Andersson 2013; Morse and Mackenzie 1990; Morse et al. 2006; Stanienda 2013a and 2014). Its presence in aragonite is connected with its bigger ionic radius from the Ca radius, therefore, it easier enters into the aragonite structure analogous to that of the strontianite structure than to the calcite structure. Therefore the material built of aragonite contain higher amount of Sr than the one built of calcite (Boggs 2010; Stanienda 2014). But aragonite is unstable carbonate phase similar to high magnesium calcite and during diagenesis these phases are transformed into low magnesium calcite. Only the presence of strontium indicate that primary calcium carbonate phase was aragonite. Ba, like strontium occurs in the skeletons of marine organisms. Ba has the similar ionic radius to the strontium one (Boggs 2010; Morse and Mackenzie 1990; Morse et al. 2006; Stanienda 2014). Therefore it easier enter into aragonite structure than the calcite one. Then its presence now in low magnesium calcite indicates that the primary calcium carbonate phase was aragonite. Ni during the sedimentation processes is included in clay minerals. It could also form sulphides and arsenic minerals. Cd is usually a component of Zn sulphides. It could also occur together with Fe, Mn and Co in smitsonite. Zr comes usually from seawater. Hf is usually associated with Zr. In all geochemical environments it is accompanied by Zr as a dispersed element. V is sometimes found in marine organisms. Nb forms often admixtures in minerals of Ti, Zr, Sn and W. Some Nb amounts also occurs in manganese concretions situated on the bottoms of the oceans. Cr dispersed in rock-forming minerals is released from them during weathering. However, it is quickly bound by

products of weathering, often into clay minerals. Mo is usually connected with clay minerals. Mo contents up to 0.1% may contain deep-sea manganese concretions. Rb is associated with K. It coexists with K in feldspar and carnalite. Only small amounts of Rb could occur in sea water.

Yttrium and lanthanides (REE) could occur in limestones. These elements substitute Ca usually in calcite sometimes in dolomite. In general, the content of yttrium varies in carbonate phases from 1 to 9 ppm. It is very low content. Yttrium occurred in carbonates which build skeleton remains of marine organisms. It could be also delivered to carbonate mud and preserved by warm fluids mixing followed by early lithification in shallow burial marine environment during early diagenesis. ICP MS spectrometry and XRF fluorescence allowed to determine only Ce, Nd and Sm (lanthanides of LREE group) (identified by ICP MS) and Er (lanthanides of HREE group) (identified by XRF) in investigated limestones. Moreover, the results indicate very low content of REE.

The results of researches show a low content of analyzed trace elements. This indicates the high purity of the tested limestones. However, there are also very low contents of identified REY elements: Ce, Nd, Sm and Er. Therefore, there is not possible to recover them from limestones.

It should be noted that all identified trace elements occur in very small amounts. Therefore, their presence has no harmful effect on the natural environment. It also does not affect the use of limestone in various branches of the industry, as well as products creating during limestone processing.

5. Conclusions

One of the most important results to come from the investigation the Triassic (Muschelkalk) limestones of the area of Opole Silesia in Poland is the identification of some trace elements and some of REY elements. The principal results can be summarized as follows:

1. The following trace elements: Ti, Cr, Mn, Na, K, Ni, Cu, Zn, Sr, Y, Zr, Mo, Ba, Pb, Rb and Y, Ce, Nd, Sm and Er were identified in studied limestones.
2. The results of study show the increased content of some of the analyzed elements.
3. Higher amounts of Fe, Na, K, Al, Si, S and P were determined.
4. In some samples increased content of Sr, Ba, Cr, Ni, Mo and Mn were measured.
5. Lower contents were determined for Pb, Zn and Cu and the lowest for Nb, Cd, Zr, V, Y, Hf and Rb.
6. The increased content of trace elements were determined in limestones of Gogolin Beds and the ones of Karchowice Beds and lower amounts of trace elements were determined in rocks of Góraźdże Beds and the ones of Terebratula Beds.
7. Trace elements like Zn, Pb, Cu, Mo, Ni are probably associated with sulphide minerals, Ti, Cr, Mn, with oxides and Fe could substitute Mg in carbonates. It can also form pyrite or occur in clay minerals.
8. Na forms salt minerals or Na plagioclases. K, Al and Si form aluminosilicates, feldspars or clay minerals.
9. Sulfur is a component of sulfides (Fe, Zn, Pb, Cu) or sulfates. P is a component of organic matter.
10. Mn substitute Ca in carbonate minerals sometimes form manganese oxides.

11. Sr and Ba occur in carbonate mineral phases. The presence of Sr and Ba indicate that primary calcium carbonate phase was aragonite.
12. Ni is included in clay minerals or forms sulphides and arsenic minerals. Cd could be a component of Zn sulphides or occur together with Fe, Mn and Co in smitsonite. Zr comes usually from seawater. Hf is usually associated with Zr.
13. Nb forms admixtures in minerals of Ti, Zr, Sn and W. It could also occur in Mn concretions. Cr is dispersed in rock-forming minerals.
14. Mo occurs in clay minerals. It could also occur in contents up to 0.1% in deep-sea manganese concretions.
15. Rb coexists with K in feldspar and carnalite. Small amounts could occur in sea water.
16. REY substitute Ca usually in calcite sometimes in dolomite. The researches allowed to determine only Y, Ce, Nd, Sm and Er.
17. Very low contents of identified REY elements: Ce, Nd, Sm and Er indicate that is not possible to recover them from limestones.
18. Because trace elements occur in very small amounts, their presence has no harmful effect on the natural environment. Moreover it does not affect the use of limestone and products forming during limestone processing.

Declarations

Author contribution

I am the only author of this article. All published results are the results of my own research. The interpretation and analysis of the results of the research were done by myself.

Ethical statements

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Figures

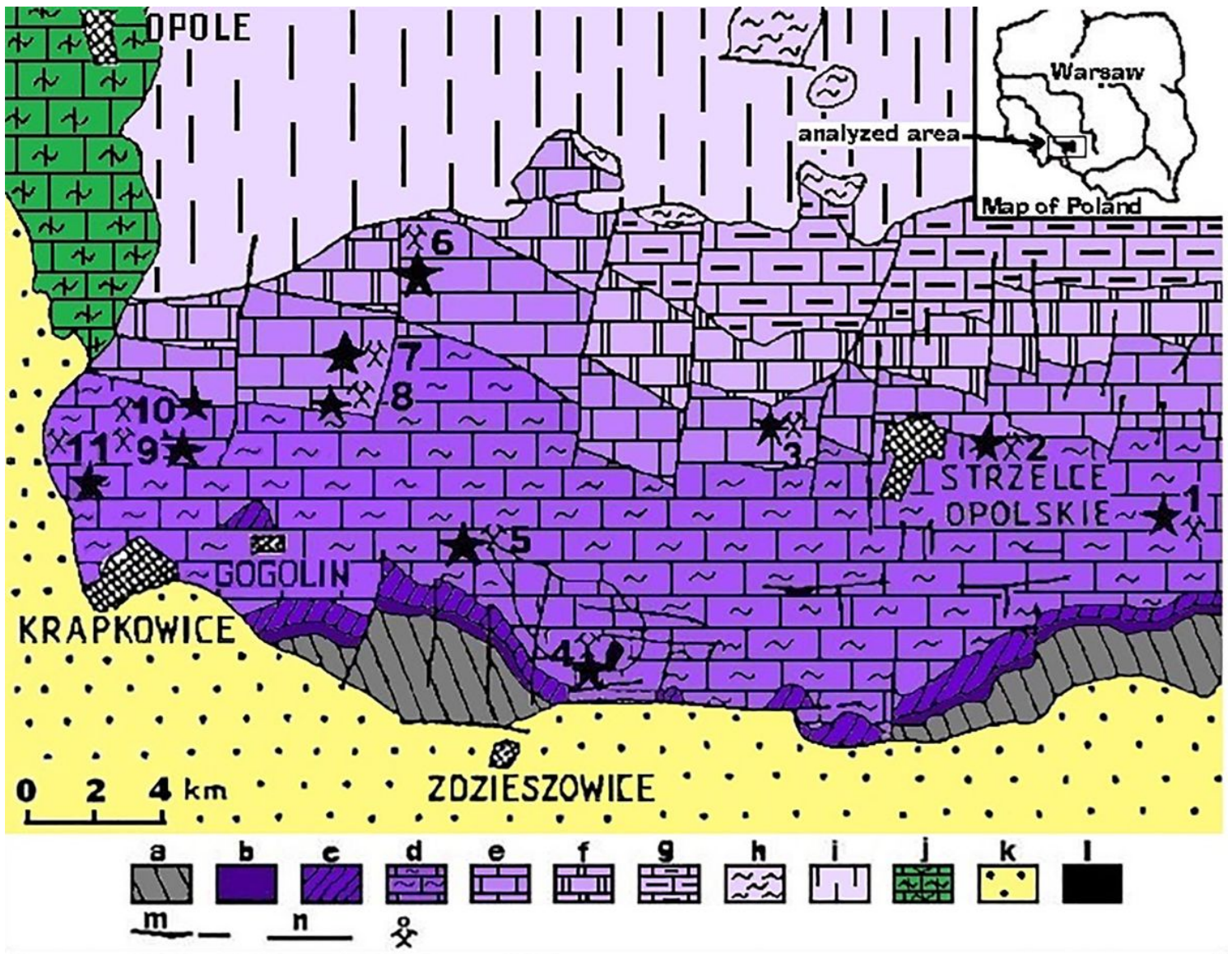


Figure 1

Geological map of the central part of Opole Silesia, according to Niedźwiedzki (Niedźwiedzki 2000), modified by Stanienda (Stanienda 2013). a- greywackes of Lower Carboniferous; b- sandstones and mudstones of Middle Buntsandstein; c- limestones, dolomites and marls of Upper Buntstandstein (Roethian); d- limestones and marls of Gogolin Beds; e- limestones of Górażdże Beds, Terebratula Beds and Karchowice Beds; f- dolomites of Jemielnice Beds; g- limestones and dolomites of Rybna beds and Borszowice Beds; h- claystones, mudstones and sandstones of Keuper; i- claystones of Rhaetian; j- sandstones, marls and limestones of Upper Cretaceous; k- sandstones, clays and gravels of Neogene; l- Tertiary basalts; m- faults; n- stratigraphic boundaries; o- important quarries: 1- 11- quarries and outcrops: 1- Błotnica Strzelecka; 2- Dziekwowice; 3- Szymiszów; 4- Góra Św. Anny and Wysoka; 5- Ligota Dolna and Kamienna; 6- Tarnów Opolski; 7- Kamień Śląski; 8- Górażdże and Kamionek; 9- Malnia; 10- Chorula; 11- Rogów Opolski *areas of sampling

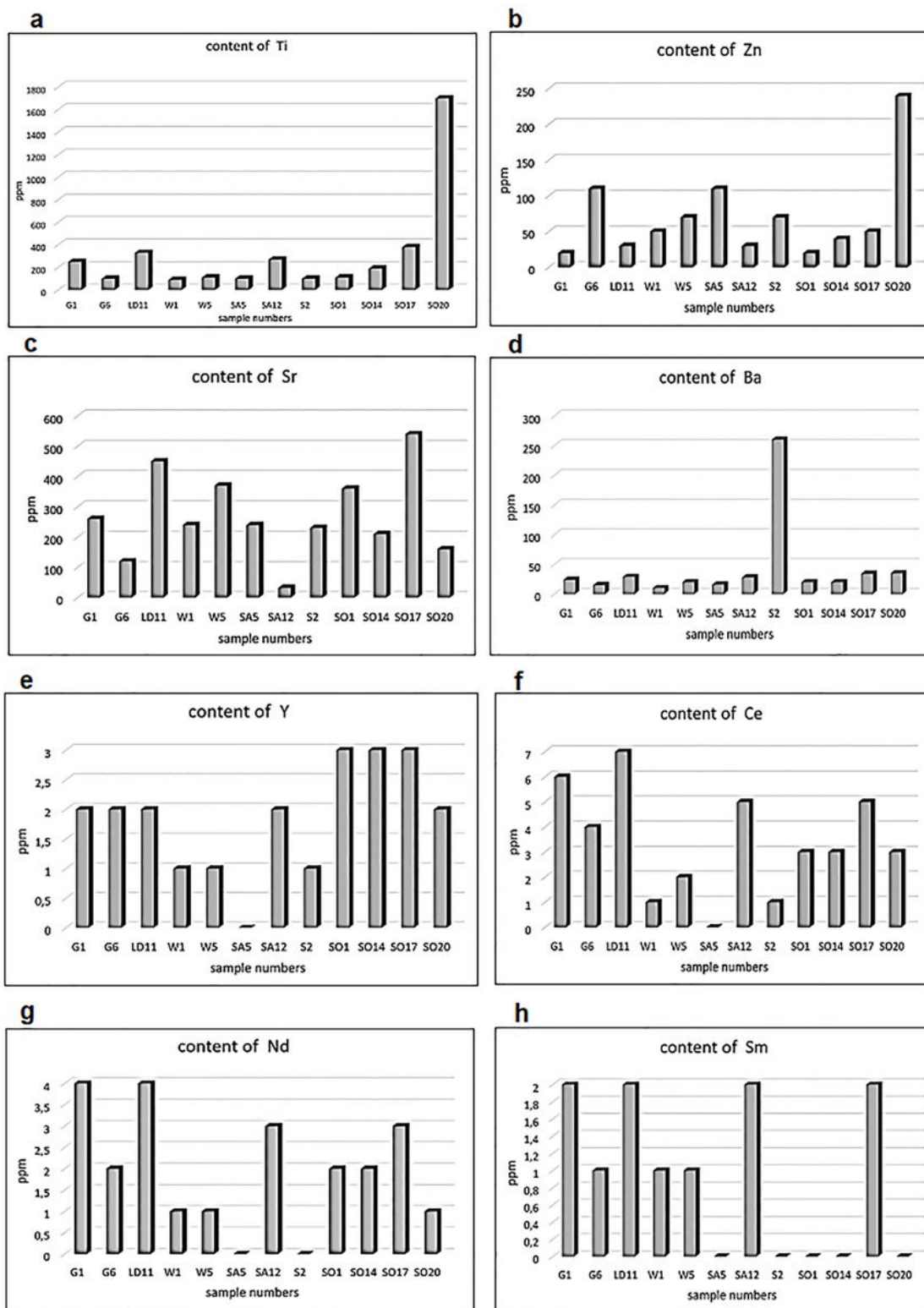


Figure 2

Variability of selected elements content in studied limestone samples, based on ICP MS Spectrometry. a- variability of Ti content, b- variability of Zn content, c- variability of Sr content, d- variability of Ba content, e- variability of Y content, f- variability of Ce content, g- variability of Nd content, h- variability of Sm content.

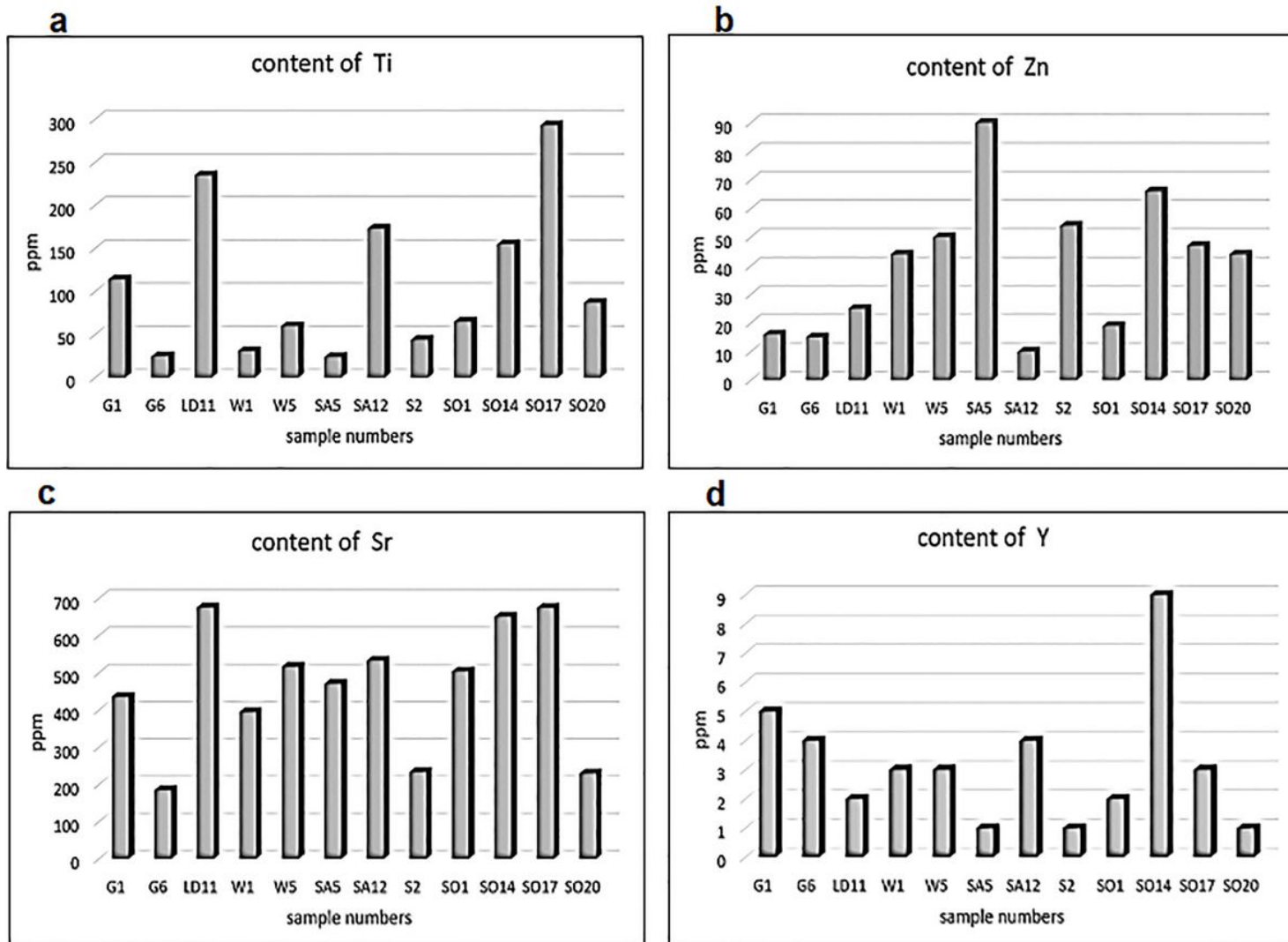


Figure 3

Variability of selected elements content in studied limestone samples, based on X-Ray Fluorescence (XRF). a- variability of Ti content, b- variability of Zn content, c- variability of Sr content, d- variability of Y content.