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Major and minor elemental trends of gypsum-ghost limestones of the Osiek–Baranów Sandomierski native sulphur deposit (northern Carpathian Foredeep, Poland): implications for limestones genesis

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The Middle Miocene (middle Badenian) "gypsum-ghost" limestones composed of calcite and/or sulphur pseudomorphs after selenitic gypsum, are a salient feature of the Polish sulphur deposits from the northern Carpathian Foredeep (S. Poland). Sulphurous rocks (including the gypsum-ghost limestones) are present within the evaporite unit, the so-called "Chemical Series", and are commonly believed to be lithological equivalents of synchronous gypsum deposits, resulting from regionally extensive, wholesale replacement of the selenite lithofacies by limestones and limestone + native sulphur. However, detailed geochemical examination of regional major and minor element compositions in these unusual carbonates suggests considerable internal differences. Distinct variations in chemical distribution along the main development of the Osiek–Baranów Sandomierski native sulphur deposit, together with the associated barren limestone areas, are clearly recognized. The pattern of the geochemical parameters of these gypsum-ghost limestones is inconsistent with an epigenetic model of formation of the Polish sulphur deposits (wholesale replacement of sulphate deposits by carbonates + native sulphur) and argues for their formation within a sedimentary-early diagenetic regime.

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INTRODUCTION

Limestones containing evident pseudomorphs of original selenitic gypsum crystals, preserved as calcite and/or calcite + sulphur after gypsum crystals or as mouldic voids, are relatively common in Middle Miocene (Badenian) sulphur-bearing limestones of northern part of the Carpathian Foredeep (CF) of the Southern Poland (Gąsiewicz, 1994*a*, 2000*b*; Fig. 1). They make up the so-called gypsum-ghost limestones (termed after van de Poel, 1991), which constitute a characteristic lithofacies of the carbonate member of the evaporite sequence. Carbonate bodies with such structures, both sulphur-bearing and barren, are volumetrically secondary and their regional distribution in native sulphur deposits is usually interpreted as being a result of wholesale large-scale post-burial, transformation of primary gypsum rocks into sulphurous or barren limestones due to molecular replacement in a closed system (e.g., Pawłowski *et al*., 1965, 1979, 1985, 1987; Osmólski, 1972; Pawlikowski, 1982; Kubica, 1992, 1994, 1997; Nieć, 1992).

However, based on geometrical, sedimentological, petrographic, and overall geochemical features of these limestones as well as on extensive comparisons with associated selenite gypsum facies and mass balance – the preservation of such selenite gypsum precursors within the limestones – (both sulphur-bearing and barren) their lithological incompatibility has been demonstrated (Gąsiewicz, 1994*a*, *b*; 2000*a*, *b*). Instead it has been proposed that the gypsum-ghost limestones reflect a unique setting of simultaneous formation of carbonate and selenites in a sedimentary, transitional millieu between the carbonate and gypsum domains, where bottom calcium carbonate deposition was locally accompanied by hypersaline episodes with the growth of selenite crystals followed by diagenetic alteration in a meteoric regime (*op. cit.*).

The preservation of original selenite fabrics in the gypsum-ghost limestones is of special importance mainly for association with high sulphur mineralization as well as for their spectacular nature, and serve as one of the cardinal arguments for the bioepigenetic (*sensu* Ruckmik *et al*., 1979) formation of the Polish native sulphur deposits. The origin of the epigenetic native sulphur deposits must be viewed in terms of regional

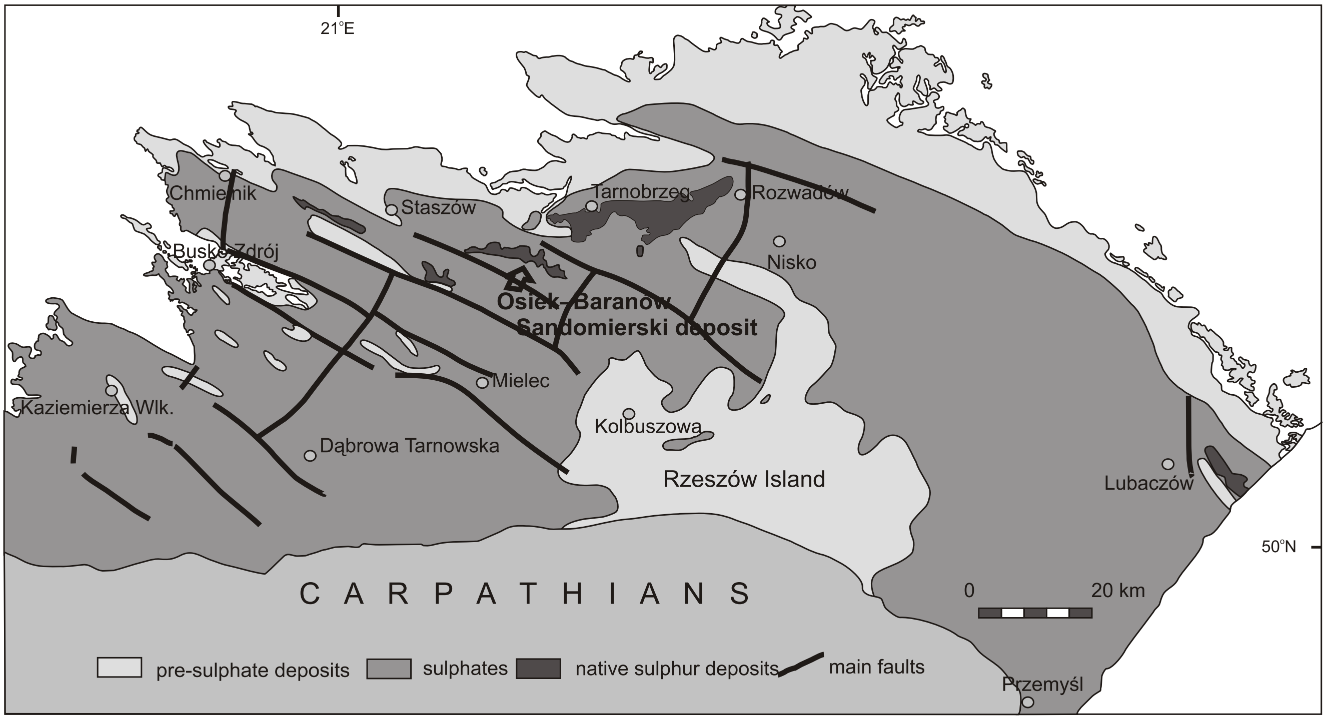

Fig. 1. Location of native sulphur deposits in the northern Carpathian Foredeep

processes where pervasive flow forms a geochemical exchange front as a consequence of infiltration, alteration of solid sulphates and mass balance transfer. The limestones with their apparently entire suite of sedimentary to (epi)diagenetic signatures provides a unique possibility to reconstruct the original processes that formed the gypsum-ghost limestones and allow evaluation of the current model for the orgin of the Polish native sulphur deposits.

Thus, one may expect that, whether the limestones were epigenetic or syngenetic, their original features should be retained, at least to some extent, in the final product. Because of different patterns of geochemical features recorded in these two settings, generally directional or systematic and irregular respectively, the examination of geochemical characteristics preserved in these rock units could potentially test these contrasting views. Therefore, the purpose of this study is to recognize major and minor elemental distribution along the Osiek–Baranów Sandomierski (O–BS) native sulphur deposit of Southern Poland and thus provide further understanding of the origin of native sulphur mineralization in the CF. The distribution of oxygen and carbon isotopes in these limestones will be published separately.

REGIONAL SETTING

The Miocene succession of the northern part of the Carpathian Foredeep (Fig. 2) is composed of thick (locally exceeding 3.5 km), mainly clastics deposits intercalated with a thin (up to about 60 m thick) evaporite unit (e.g., Ney *et al.*, 1974; Pawłowski *et al.*, 1979, 1985). Sands, sandstones, sandy limestones and coralline algal limestones, characterized by variable thickness (up to about 150 m), underlie the evaporites. These deposits, called the Baranów Beds and belonging to the lower Badenian, are the basal Miocene deposits in the northern foredeep.

The evaporite unit belonging to the middle Badenian is lithologically inhomogenous. Sulphates (mainly gypsum) are the most widespread evaporites within the CF (Fig. 1). The gypsum unit, composed of various lithofacies (Kubica, 1992; Kasprzyk; 1993; Bąbel, 1999), and well-preserved in the peripheral part of the basin, was transformed diagenetically into anhydrite during burial, especially towards the basin centre (Kubica, 1992; Kasprzyk, 1995, 2005; Gąsiewicz and Czapowski, 1998; Jasionowski and Peryt, 2010). In front of the Carpathians a narrow and elongate belt of halite deposits developed during that time (e.g., Garlicki, 1979).

Larger areas of sulphurous and/or barren limestones occur irregularly in the marginal part of the CF within the sulphate unit (Fig. 1). The carbonate succession is generally thinner (maximally about 45 m thick) compared to the sulphurous rocks which may exceed 60 m in thickness. The sulphur-bearing succession is dominated by massive, bedded and unbedded barren or sulphurous, commonly marly limestones which include the following main lithofacies: gypsum-ghost limestones, massive, bedded, and pelitic mudstones; rudstones; marls; claystones-siltstones; and gypsum lenses and intercalations. The sulphurous lithofacies contain up to 7% of clay (Pawłowski *et al.*, 1985) and show usually 2–12% (10% at average) porosity (Rybicki, 1973). The gypsum-ghost limestones considered in this paper are much more porous than the other sulphurous rocks. They often show empty post-selenite voids and small caverns and the porosity is usually 10–20% and occasionally up to 40% (Gąsiewicz, 2000*b*).

The native sulphur content of minable deposits ranges from about 25 to 35% (Pawłowski *et al*., 1987). The extent of the sulphur-bearing outcrop is irregular, especially close to the gypsum deposits, where limestones commonly interfinger with sulphate deposits in a complex fashion.

Both the sulphur-bearing limestones and gypsum deposits constitute an evaporitic unit, the so-called "Chemical Series" (Pawłowski *et al*., 1979). The overburden of the Chemical Series unit in this area of the CF consists of marine, monotonous, mainly pelitic, relatively thick clastic (marls and siltstones) rocks of late Badenian–Sarmatian age (e.g., Pawłowski *et al*., 1979, 1985; Gąsiewicz *et al*., 2004).

METHODS

A total of 128 samples representing both the sulphur-bearing and barren gypsum-ghost limestones of 27 boreholes were collected for bulk sample analyses of the mineralogy, major and trace element contents of the O–BS sulphur deposit.

The gypsum-ghost mineralogy was determined by X-ray diffraction (XRD) using a *Phillips PW 1729* diffractometer at the Polish Geological Institute (Warsaw). Because the samples come from different stratigraphic levels, as the limestones bodies are dispersed irregularly throughout the sulphur-bearing, succession the samples analysed (N = 1–17) from particular gypsum-ghost bodies found in boreholes were averaged. Analyses were performed at the Central Chemical Laboratory of the Polish Geological Institute by a combined method of ASA and ICP (spectrometer *JY 70 PLUS Jobin Yvon*). The precision of the major and trace element measurements was 1.0–1.5 and 5%, respectively.

Because of the irregular spatial distribution of the gypsum-ghost limestones the geochemical measurements in this study were conventionally arranged roughly according to elongation of the O–BS sulphur deposit, i.e. generally from west to east in a series of boreholes through the deposit and outside, at varying distances from the sulphur orebody. For the purpose of this paper, i.e. to minimize local or occasional influences, the data have been averaged and the location of the samples is shown in Figure 3.

GYPSUM-GHOST LIMESTONES OF THE OSIEK–BARANÓW SANDOMIERSKI NATIVE SULPHUR DEPOSIT

THE SULPHUR DEPOSIT

The native sulphur deposit that occurs on the Staszów–Baranów Sandomierski tectonic block is bounded by generally parallel and laterally normal faults having a north-west-southeast trend and stepping and dipping towards the SW (Pawłowski *et al*., 1976). The sulphur deposit is distinctly elongated (up to 18 km) in a generally NW–SE direction and its width changes from several hundreds of metres to about 2 km (Fig. 1). It occurs in the marginal, NE part of the elongated and wider carbonate zone, generally close to the irregular boundary with extensive outcrops of gypsum lithofacies surrounding the depositional area. Towards the SW, the sulphurous zone irregularly passes into the less mineralized and finally barren (and larger) limestone area. In the NW part of the area, the sulphur-bearing strata are commonly intercalated with gypsum layers.

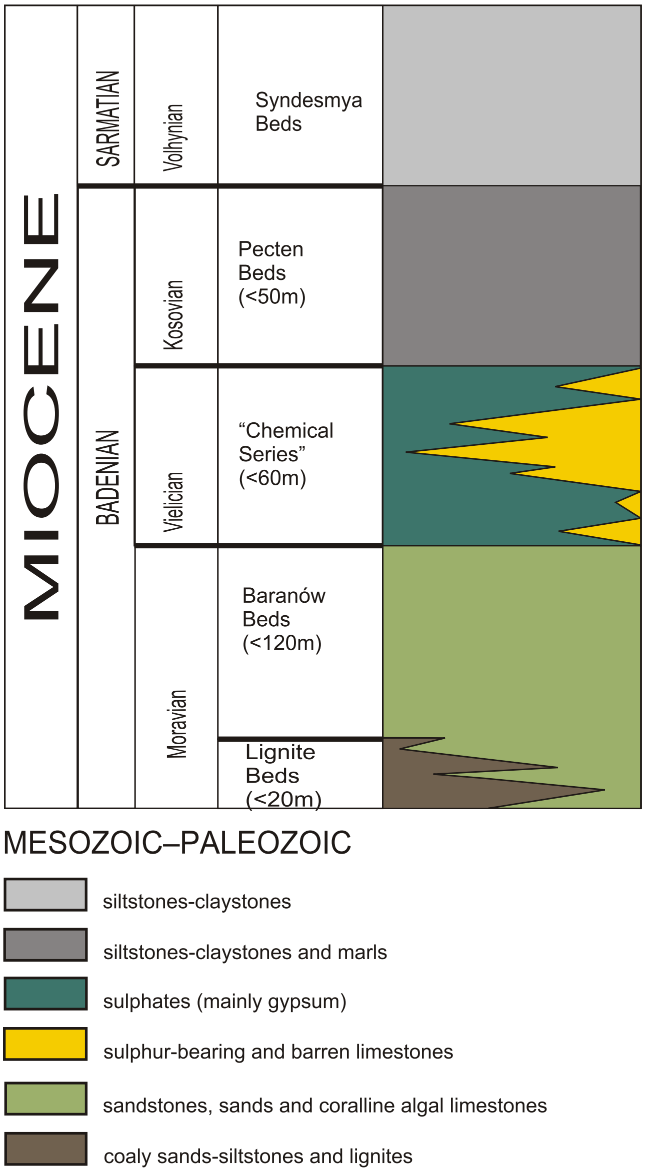

Fig. 2. Lithostratigraphic framework of the Miocene of northern Carpathian Foredeep

The thickness of the sulphur-bearing succession is up to about 45 m and generally becomes distinctly thinner towards the NW. The deposit progressively dips into towards the SE. The concentration of native sulphur is highly irregular and ranges from 10–42% (Pawłowski *et al*., 1987). The sulphur mineralization generally decreases towards SW.

In general the unit consist of limestones (commonly marly limestones) with a minor admixture of clay and gypsum interbeds. Comprehensive lithological descriptions of the gypsum-ghost limestones were first made by Gąsiewicz (1994*a*, *b*, 2000*b*). The latter, more recent and exhaustive sedimentological study combined field observations (Machów

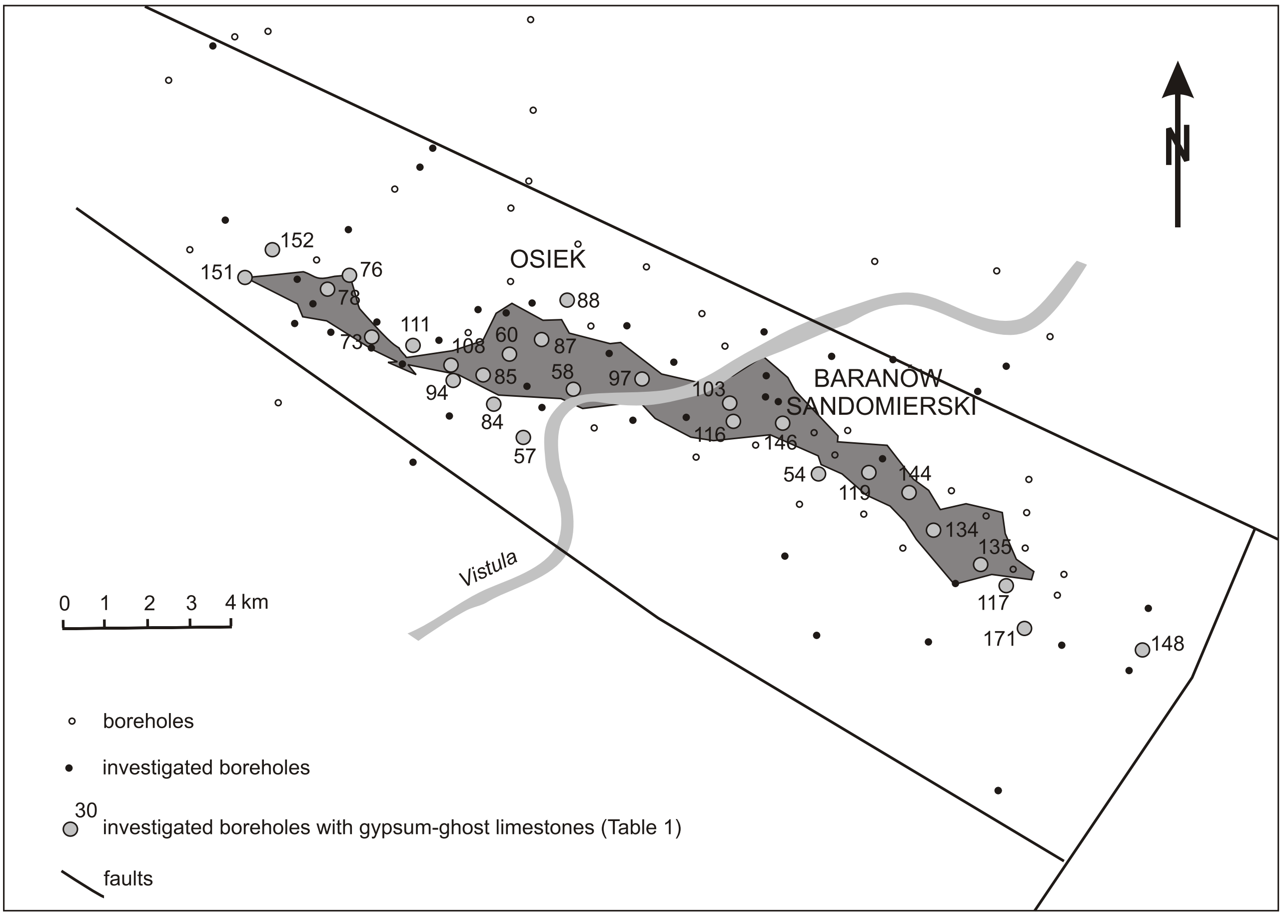

Fig. 3. Distribution of boreholes investigated with gypsum-ghost limestones in the Osiek–Baranów Sandomierski area

open-pit mine) with extensive core studies of carbonate petrography, mineralogy and geochemistry (including stable-isotope analyses) with an evaluation of the origin of the gypsum-ghost limestone in the context of formation of the Polish native sulphur deposits.

Varying concentrations of relics after original selenite crystals occur in the prevailing calcite groundmass and appear as the main textural component of the limestones. The structures are empty, or partly or fully infilled with calcite or calcite + native sulphur entombed in a generally micritic groundmass. The limestones are pale, grey to dark grey and may be barren or sulphur-bearing. The transition of the limestones into the surrounding variously bedded or unbedded limestones is usually rapid and indistinct, commonly accompanied by relative enrichment or impoverishment in native sulphur content.

GYPSUM-GHOST LIMESTONES

GEOMETRY

The gypsum-ghost facies of the O–BS sulphur deposit and associated area occurs locally and irregularly as more or less laterally elongated lenticular bodies in both sulphur-bearing and barren limestones, that are locally stacked (Gąsiewicz, 1994*b*, 2000*b*). The limestones do not show any correlation with the surrounding selenite gypsum lithofacies. A total of 119 interbeds have been found in 50 boreholes (of 66 investigated). The number of gypsum-ghost beds varies from 1 to 6 bodies per borehole and they cannot be correlated over a distance of about 300 m. The limestone bodies are from 5 cm to 8.2 m thick (mostly less than 1 to 1.5 m on average). The total thickness of the gypsum-ghost interbeds in the deposit area comprises 14.3% of the sulphurous depositional succession in the boreholes where the limestones occur (Gąsiewicz, 2000*b*).

The gypsum-ghost beds are relatively less common and thinner in the NW part of the Osiek–Baranów Sandomierski sulphur deposit compared to SE part. In the same direction there is an increase in the average total thickness of the beds, from 1.36 m in the Niekrasów sulphur field to almost 5 m in the Skopanie. Consequently, the average total thickness of the limestone bodies comprise about 12% of the sulphurous section in both Niekrasów and Osiek sulphur fields and 19.6% in the Skopanie one. The smallest average thickness of the interbeds occurs in Niekrasów (0.64 m), and the thickest one in the Osiek sulphur field (1.72 m). Generally both the number and total thickness of the gypsum-ghost limestone interbeds decreases perpendicularly to the elongation of the sulphur deposit, i.e. towards the SW.

MINERALOGICAL COMPOSITION

Petrographic analyses (Gąsiewicz, 1994*a*, 2000*b*) indicate that the gypsum-ghost limestones are mainly composed of low-Mg calcite. In the sulphur-bearing areas these limestones contain various amount of native sulphur. Calcite is mainly present as micritic matrix sometimes with aragonite and dedolomite relics and commonly forms distinct drusy cements. The inhomogeneous matrix, locally contains locally common limy clasts and peloids as well as irregular patches of microsparite and often coarse sparite. Calcite usually form distinct low-Fe and not uncommon high-Mg cement-filling voids after selenite crystals. Native sulphur fills or encrusts gypsum-ghost structures, and occurs in the matrix as usually dispersed fine grains and aggregates, locally forming fine laminae or streaks with a small admixture of clay matter. There is no correlation between the gypsum-ghost limestone thickness and their native sulphur content.

The two main mineral phases are accompanied by clay minerals (usually less than 1%), celestite (up to 8%), and volumetrically insignificant pyrite (framboids and rarely euhedras). Clay minerals (kaolinite, illite and chlorite) are irregularly dispersed or form short and wavy streaks and laminae. They are locally accompanied by relatively higher concentrations of fine (up to 0.2 mm) irregular, anhedral quartz grains as well as by occasional grains of mica, plagioclases, fine bioclasts, amorphic and coalified plant organic matter. Gypsum fragments (mainly close to larger sulphate beds), strontianite (up to do 10%), barite (up to 7%) and silica (lutecite) appear very locally. There are trace amounts of witherite, glauconite, dolomite and fine aggregates of dispersed organic matter and bitumen inclusions.

CHEMICAL COMPOSITION

The average major element composition of the gypsum-ghost limestones varies throughout the sulphur deposit (shown in Table 1). The most remarkable features along the deposit are the high content and highly variable concentrations of two predominant elements i.e. calcium and native sulphur. These two components are accompanied by subordinate contents (usually up to a few percent) of SiO_2 (clastic fraction, mainly clay) and sulphate (mainly celestites and rarely gypsum and barite). The content of other of components, although var-

Table 1

Average major and minor elements contents of the gypsum-ghost limestones of the O–BS native sulphur deposit

Borehole no.	General orientation of sulphur deposit	Borehole symbol	N	TOC [%]	CaO [%]	SiO_2 [%]	Al_2O_3 [%]	Fe_2O_{3T} * [%]	MnO [%]	MgO [%]	Na_2O [%]	K_2O [%]	SrO [%]	TiO_2 [%]	SO_4 [%]	S^0 [%]
1	NW	M. 151	3	0.15	49.09	5.57	1.86	0.63	0.06	0.47	0.04	0.27	0.08	0.07	0.93	0.67
2	↕	M. 152	2	0.11	50.30	2.45	0.60	0.27	0.05	0.49	0.03	0.11	0.05	0.03	0.52	0.00
3		M. 78	1	0.14	51.30	2.20	1.06	0.37	0.16	0.47	0.04	0.17	0.08	0.04	0.60	0.00
4		P. 76	1	0.11	47.05	3.70	0.81	1.07	0.12	0.42	0.04	0.13	0.06	0.03	0.96	6.00
5		N. 73	2	0.10	41.45	4.10	1.20	0.51	0.09	0.34	0.05	0.21	0.23	0.02	2.89	8.00
6		P. 111	1	0.09	49.70	1.40	0.47	0.19	0.03	0.45	0.04	0.07	0.06	0.02	1.35	0.00
7		P. 108	8	0.16	44.51	4.83	0.71	0.29	0.21	0.45	0.06	0.29	0.44	0.02	12.97	2.31
8		T. 94	8	0.16	50.34	3.98	1.28	0.53	0.10	0.59	0.06	0.25	0.12	0.03	0.70	0.25
9		N. 57	5	0.13	49.48	2.58	0.72	0.35	0.03	0.50	0.06	0.12	0.04	0.03	0.40	0.00
10		M. 84	5	0.14	47.03	1.48	0.49	0.21	0.08	0.40	0.04	0.09	0.12	0.02	0.52	0.20
11		M. 85	4	0.09	40.05	0.60	0.23	0.10	0.01	0.27	0.03	0.04	1.20	0.01	1.58	26.50
12		M. 60	1	0.10	31.80	1.24	0.25	0.10	0.08	0.25	0.02	0.04	0.05	0.01	0.51	40.00
13		O. 88	1	0.10	47.70	1.70	0.50	0.23	0.45	0.65	0.04	0.09	0.04	0.04		1.00
14		O. 87	2	0.08	34.10	2.90	0.75	0.29	0.03	0.27	0.03	0.16	3.52	0.02	3.86	21.50
15		Ł. 58	7	0.08	39.38	1.23	0.29	0.11	0.01	0.24	0.02	0.06	0.67	0.01	0.87	32.43
16		L. 97	2	0.05	29.50	0.85	0.30	0.12	0.04	0.15	0.04	0.05	0.51	0.02	0.96	43.00
17		K. 103	2	0.06	35.80	3.72	0.16	0.08	0.13	0.19	0.09	0.03	3.88	0.01	0.67	27.50
18		D. 116	1	0.06	49.70	1.10	0.18	0.07	0.12	0.34	0.05	0.03	0.18	0.01	0.45	0.00
19		M. 146	16	0.12	31.66	2.49	0.58	0.25	0.02	0.16	0.06	0.11	1.15	0.02	1.49	38.44
20		B. 54	4	0.13	49.30	2.53	0.59	0.39	0.01	0.22	0.14	0.14	0.06	0.06	1.00	0.00
21		M. 119	17	0.07	31.47	1.62	0.88	0.16	0.02	0.17	0.04	0.09	1.94	0.02	2.87	29.59
22		S. 144	3	0.08	32.67	1.10	0.30	0.14	0.01	0.14	0.02	0.05	0.78	0.01	1.53	38.67
23		M. 134	4	0.14	30.14	2.13	0.72	0.30	0.02	0.16	0.09	0.15	1.81	0.02	5.48	30.00
24		H .135	4	0.07	33.00	2.45	0.58	0.29	0.04	0.28	0.04	0.12	2.42	0.02	4.71	21.50
25		G. 117	10	0.10	44.92	2.42	0.75	0.34	0.06	0.37	0.10	0.14	0.11	0.37	0.70	0.00
26		M. 171	6	0.12	52.15	2.83	0.73	0.32	0.02	0.32	0.07	0.13	0.06	0.03	0.37	0.83
27	SE	J. 148	8	0.13	47.10	11.15	1.02	0.64	0.02	0.43	0.08	0.21	0.08	0.04	0.49	0.63

* – total iron content; N – number of analysed samples

Table 2

Main statistical parameters of major and minor element contents (in percent) for all the gypsum-ghost limestones samples of the O–BS native sulphur deposit

	TOC	CaO	SiO_2	Al_2O_3	Fe_2O_{3T}	MnO	MgO	Na_2O	K_2O	SrO	TiO_2	SO_4	S^0
Average	0.11	40.72	3.03	0.72	0.30	0.05	0.31	0.06	0.13	0.82	0.05	2.25	16.04
S.E.	0.00	0.89	0.54	0.07	0.02	0.01	0.01	0.00	0.01	0.12	0.01	0.57	1.63
S.D.	0.05	10.03	6.13	0.82	0.25	0.09	0.17	0.04	0.14	1.31	0.13	6.38	18.41
Range	0.42	45.99	66.10	7.90	1.73	0.69	0.79	0.20	1.24	7.64	0.89	52.85	62.00
Minimum	0.04	13.92	0.20	0.10	0.03	0.00	0.05	0.02	0.02	0.01	0.01	0.18	0.00
Maximum	0.46	59.91	66.30	8.00	1.76	0.69	0.84	0.22	1.26	7.65	0.89	53.03	62.00
Count	128	128	128	128	128	128	128	128	128	128	128	127	128
95% c.i.	0.01	1.75	1.07	0.14	0.04	0.02	0.03	0.01	0.02	0.23	0.02	1.12	3.22

S.E. – standard eror, S.D. – standard deviation, c.i. – confidence interval

ied, is below 1% (Table 1). The content SiO_2, Al_2O_3, SrO, and SO_4^{2-} is very variable (Table 2). Based on the high average content of CaO (about 53% $CaCO_3$) the limestones appear as the purest lithofacies of the sulphur-bearing carbonates.

The relationships among the elements analysed (Table 3) indicate three main groups of elements:

1. CaO, S^0, SrO and MgO. The correlation pattern within this group is complex. CaO is strongly negatively correlated with native sulphur (r = –0.77) and poorly with SrO (r = –0.43), and positively with MgO (r = 0.64). S^0 is moderately negatively correlated with MgO (r = –0.64) and poorly with SrO (r = 0.41) and Fe_2O_{3T}. The correlation between SrO and MgO is poor and negative (r = –0.42). These elements are included in different mineral phases, i.e. in native sulphur and calcite (Ca and Mg) as well as commonly in celestite (Sr) (Gąsiewicz, 2000*b*).

2. SiO_2, Al_2O_3, Fe_2O_{3T}, K_2O, Na_2O and MnO exhibit also highly variable contents but are linked more closely to each other than to elements of any other group. They display moderate positive correlation each other (r = 0.40–0.63) and also poor correlation with MgO (r = 0.33–0.53) as well as between both MnO and Na_2O and the elements of this group (r = 0.33–0.60). The elements are typical components of the clastic fraction and in the case of gypsum-ghost limestones represent mainly clay material.

3. The group composed of TiO_2 and SO_4^{2-} displays a specific behaviour which shows a lack of correlation. Because of the very low content of Ti its mineralogical phase(s) could not be identified while SO_4^{2-} is mostly included in celestite. This group includes also TOC, which shows a complex or mixed pattern of correlation. Its average values exhibit moderate to distinct positive correlations with the elements of the second group and MnO and MgO (r = 0.36–0.79) as well as a poor negative correlation with S^0 (r = –0.30).

DISTRIBUTION OF MAJOR ELEMENTS ALONG THE DEPOSIT

The analysis was carried out to test the relationships between the major element geochemistry and the geological position of the samples analysed related to the strongly elongated sulphur deposit area (Fig. 3 and Table 1). For this reason the av-

Table 3

Correlation matrices of major and minor element contents for all the gypsum-ghost limestones samples of the O–BS native sulphur deposit

	TOC	CaO	SiO_2	Al_2O_3	Fe_2O_{3T}	MnO	MgO	Na_2O	K_2O	SrO	TiO_2	SO_4	S^0
TOC	1												
CaO	0.1226	1											
SiO_2	0.3756	–0.2258	1										
Al_2O_3	0.2299	–0.0452	0.1589	1									
Fe_2O_{3T}	0.4526	0.1226	0.6311	0.4432	1								
MnO	0.3857	0.1498	0.1510	0.1063	0.1570	1							
MgO	0.3639	0.6403	0.1235	0.3025	0.5272	0.4601	1						
Na_2O	0.5151	0.0740	0.3270	0.1992	0.4045	0.1964	0.1734	1					
K_2O	0.7876	–0.0320	0.5556	0.2958	0.5590	0.4650	0.3391	0.5998	1				
SrO	–0.2168	–0.4262	–0.0531	–0.1759	–0.2925	–0.0911	–0.4196	–0.1427	–0.1338	1			
TiO_2	–0.0391	0.0966	0.0179	0.0091	0.0551	–0.0218	0.0709	0.1192	–0.0042	–0.1555	1		
SO_4	–0.2047	–0.0997	–0.0530	–0.0652	–0.0894	–0.0726	–0.0992	–0.0884	–0.0696	0.1541	–0.0711	1	
S^0	–0.2950	–0.7733	–0.1659	–0.0390	–0.3495	–0.2661	–0.6413	–0.2745	–0.2800	0.2791	–0.2396	–0.0511	1

erage geochemical values for particular boreholes shown in Table 1 were arranged according to a generally west-east direction. Thus the distribution of the elements throughout the sulphur area may be an indication of the existence of trends in the variables considered.

When comparing the elemental average values with their position on the map (Table 1 and Fig. 3), it can be seen from west to east that the samples show two distinct trends:

- an increase in the Na_2O, SrO and S^0 contents;
- a decrease in the contents of TOC, CaO, Al_2O_3, Fe_2O_{3T}, MnO, MgO, and K_2O.

Moreover, the average contents of TiO_2, SiO_2 and SO_4^{2-} are in general even, but in the case of Ti only one borehole (G. 117) is exceedingly enriched in this element. Note also, if one sample strongly enriched in clayey matter in borehole J. 148 and two samples distinctly enriched in gypsum in borehole P. 108 are omitted, then SiO_2 displays a distinctly decreasing and SO_4^{2-} a distinctly increasing trend respectively. Thus the first group of components may be completed by SO_4^{2-} and the second one by SiO_2.

From the above survey a grouping of the average values of samples analysed according to their location is observed. There is a clear difference between the western and the eastern parts of the sulphur deposit reflected by different trends in the elemental distribution. The distribution of most elements analysed indicates a progressive eastwards decrease in the averaged contents. Only some components show an opposite trend. In summary, it may be concluded that according to the element variability, the western part of the deposit is relatively enriched in calcium carbonate and in siliciclastic material, while the eastern part is enriched in native sulphur and strontium minerals (also in sulphate bodies). The geochemical trends observed in the distribution of the components show a distinctly progressive change without any sharp boundary between the sulphur deposit fields.

INTERPRETATION

EPIGENETIC VIEW

The data presented above clearly indicate an elemental differentiation of the O–BS sulphurous and associate deposits and is highlighted by very irregular native sulphur distribution throughout the deposit (Kowalik *et al*., 1979, 1980, 1982). As far as one may expect it is linked to the lithological composition of the sulphurous rock succession. The evident lithological difference between gypsum and sulphur-bearing sections is commonly referred to the enigmatic processes of (metasomatic) gypsum alteration into limestones + native sulphur or local differences in gypsum lithology (e.g., Pawłowski *et al*., 1979, 1985, 1986; Nieć, 1982, 1992; Pawlikowski, 1982; Kubica, 1992, 1997), although their lithological stability is well-recognized elsewhere around the sulphur deposits and throughout the marginal part of the Carpathian Foredeep (e.g., Pawłowski *et al*., 1985; Kubica, 1992; Kasprzyk, 1994*a*; Bąbel, 1999). Also, Nieć (1983, 1993) has assumed that lithological zonation of the Tarnobrzeg native sulphur deposit depends on the depth of the deposits and thus the chemistry of the transforming fluids (during the alteration reactions) and suggested the primary differentiation of the gypsum succession as the cause. This, however, contradicts the commonly observed chemical homogeneity of the sulphate succession throughout the CF. Based on chemical analyses gathered for larger regions of sulphate and sulphur-bearing associated areas, Pawłowski *et al*. (1985, 1987) and Kubica (1992) indicated highly equalized quantitative chemical compositions of both lithologies. They considered that the sulphate deposits are very pure and originated in very uniform depositional environments throughout the CF while metasomatic groundwater epigenetically infiltrating and alterating the solid sulphate framework were responsible for the chemical differentiation of the sulphur-bearing and barren limestones. In this context irregularly anomalous concentrations of native sulphur are realized as areas of optimal conditions for unusual accumulations of the epigenetic reaction by-product, governed by secondary structural elevations of the basement and susceptibility to molecular replacement. According to this hypothesis the process must have involved high permeability and throughflow in the sandstones and marls below (and possibly mudstones-siltstones above) allowing the replacement of precursor sedimentary sulphates. In this replacement model hydrocarbons expelled along the nearby fault(s) bounding the deposit outside (within sulphate areas) and groundwater (+ bacteria) must have moved laterally parallel to and throughout the impermeable solid evaporitic strata (the thick clayey overburden is impermeable) for a distance of up to about 20 km. The hydrocarbons advanced to the place of gypsum transformation from below, across lithologically various strata. The epigenetic alteration of solid sulphates into calcium carbonate may proceed on local as on regional scale. This process must have involved total permeation and effective conduits for fluid flow in the host rocks allowing the replacement of previous solid sulphates via fluid(s) of unknown origin and constant composition. Because the fluid migrates within the host rock in a particular direction, reaction and subsequent changes in chemical and physical properties must have taken place along the flows, path which should lead to the precipitation of native sulphur and associated complex paragenetic sequence in succession (zonation). Because of the isolated nature of the gypsum-ghost bodies, embedded usually in marly and compacted carbonates of much lower porosity, they could not serve as eventual conduits for the epigenetic fluids.

However, these properties of the epigenetic model do not explain either the elemental patterns of distribution documented above or the high differentiation of native sulphur concentrations within the deposit. Moreover, both the spatial and petrographic comparisons of the gypsum-ghost limestones and selenite gypsum indicate no analogous between the lithofacies (Gąsiewicz, 1994*a*, *b*). The gypsum-ghost limestones are isolated limestones bodies and occur at different stratigraphic positions within the sulphurous rock succession. There is no known epigenetic mechanism explaining such a pattern of their distribution: why the post-selenite facies often occur in the uppermost part of the succession while gypsum selenites are essentially present in the lower part of the evaporite unit and why the limestone bodies are isolated while the gypsum selenite units are horizontally continuous. Also mass balance calculations for the gypsum-ghost limestones clearly indicate imbalance with regards to calcium sulphur and other elements (Gąsiewicz, 2000*a*, *b*).

Moreover, using a reference frame in which Si, Al, K or Ti are immobile during diagenesis, the elemental average values show far more complex patterns and trends in the data distribution (Figs. 4–11) that could be expected from one-way alteration of regionally stable (mineralogically and geochemically) gypsum selenite facies in a closed system. This mechanism should produce a relatively uniform suit of diagenetic features. This is not the case, detailed petrographic studies (microprobe and isotopic analyses) of the limestones indicating morphological and chemical varieties of calcite cements and strong stable isotopic (C and O) differentiation (Gąsiewicz, 2000*b*). These features suggest that they evolved in local and separate sub-settings. We do not know a regionally constrained mechanism for such a segregation of the chemical compounds (as described above) during pervasive molecular replacement of the gypsum host rock and thus successive mineral occlusions ensuring the development of the typical textures found in the sulphurous rocks. The replacement process is related to close relationships between dissolution and re-precipitation processes (Morse and Mackenzie, 1990, 1993), large fluid troughputs (e.g., Bathurst, 1975; Enos and Sawatsky, 1981; Morse and Mackenzie, 1993) and variable interplay between the entering and final fluids, rock properties, and mechanical conditions. Thus, such process is not likely to effectively transform gypsum into limestones + S^0.

MAJOR AND MINOR ELEMENTS

The results presented in this paper show a change in the chemical composition of the gypsum-ghost limestones associated with the sulphur deposit. A slight grouping according to the sample location in the deposit marks two groups of variables consistent with their degree of variability. The groups seem to represent two zones of the deposit indistinctly separated one from the other: north-west (or west in general) and south-east (or east) characterized by different sets of geochemical features. In general the elemental distribution along the deposit shows a trend towards relative enrichment in average content of TOC, CaO, Al_2O_3, Fe_2O_{3T}, MnO, MgO, K_2O and SiO_2 in the western part of the deposit and in Na_2O, SrO, S^0, and SO_4^{2-} in the eastern one. The average TiO_2 contents show a relatively constant distribution along the deposit.

Most of these elements are inert during bacterial sulphate reduction and their enrichment or depletion in the gypsum-ghost limestones should be ascribed to unknown factors operating during the epigenetic alteration of solid sulphates. Also the predominat calcite composition of the limestones with preserved rare relics of high Mg-calcite and aragonite (Gąsiewicz, 2000*b*) indicate that during the early diagenetic transformation (mineral stabilization) there was not a substantial release of trace elements into the carbonate framework.

The covariance between (Fe, Mg, Al, K, and Si as well as partially Mg and Na) within the limestones typically indicate that they are part of the elements making up the clastic fraction. If the differences relate to relatively constant (epigenetic precursor) selenite gypsum composition, as mentioned above, and not to a variable influx of detrital impurities into the sedimentary limestone environment, then the regional enrichment or depletion of certain elements in the gypsum-ghost limestones should be ascribed to unknown kinetic factors operating during the epigenetic alteration of solid sulphates into rapidly precipitated calcite + native sulphur. Mg, Al, K, Na, and Si as well as partially Mg are approximately immobile in such reactions and would not be affected by changes in the oxygen content of such brines. Distribution of Fe_2O_{3T}/MgO ratio, in which a weak trend of the element distribution, increasing slightly eastwards, can be seen along the deposit (Fig. 4). Considerable variation of the Fe/Mg ratio seen in the western part of the area is most likely related to a variable contribution of Fe-enriched clays, rather than being related to metasomatic segregation. Thus, the possibility that redox conditions were a factor in the depletion of Fe and other elements in the thicker bodies of the limestones is unlikely. This again indicates that most Fe was a part of the clastic component. A moderate correlation between Fe and Mg average contents ($r = 0.53$) means that Mg partially is included in other mineral phases.

The average contents of Fe_2O_{3T}, MgO and MnO recorded in the gypsum-ghost limestones (Table 1) are distinctly lower than those found for marine carbonates (Veizer, 1983; Morse and Mackenzie, 1990) and their ranges correspond to the composition of brackish carbonates (Friedman, 1969). The MgO moderately correlates with MnO (Table 3). The concentrations of these compounds and their consistent eastwards decrease suggests higher freshwater input(s) in this part of the area.

A primary sedimentary origin of such an elemental pattern in the area of the deposit is confirmed by an eastwards decrease in the K_2O/Na_2O ratio (Fig. 5). This seems to reflect a regionally changing pattern in clay mineral composition, indicating a pattern of more potassium in the western part and of more sodium in the eastern part (Fig. 5). This pattern of clastic distribution may indirectly be supported by the average TOC contents, which reflect the same pattern of distribution (Table 1) and moderate to distinct positive correlations with the clastic major elements (Table 3). Alternatively it cannot be excluded that the increase in average Na contents eastwards reflects a relative increase in evaporation in this area. This may be supported indirectly by higher concentrations of SO_4^{2-} and Sr in this part of the sulphur deposit.

The TOC distribution in the area discussed suggests that part of the organic matter was transported along with clastics into the sulphur deposit area. This contribution was higher in the western part of the area despite dilution by the sulphate input. Moreover, degradation of organic matter, whether allo- or autochthonous, could have been coupled to oxidation of ferrous iron in a anoxic metabolic cycle. This seem to be supported by a moderately positive correlation between TOC (reduced carbon) and Fe and a poor negative correlation with S^0 contents (Table 3).

The average CaO contents reflect exactly the same pattern of distribution as do the clastic-fraction chemical components, i.e. an eastwards decreasing trend in its average contents. This may result from either relative enrichment of the area in calcium sulphate (reflected by gypsum intercalations in the sulphur-bearing succession in this area) or relatively lower native sulphur contents or both. Average CaO contents normalized to

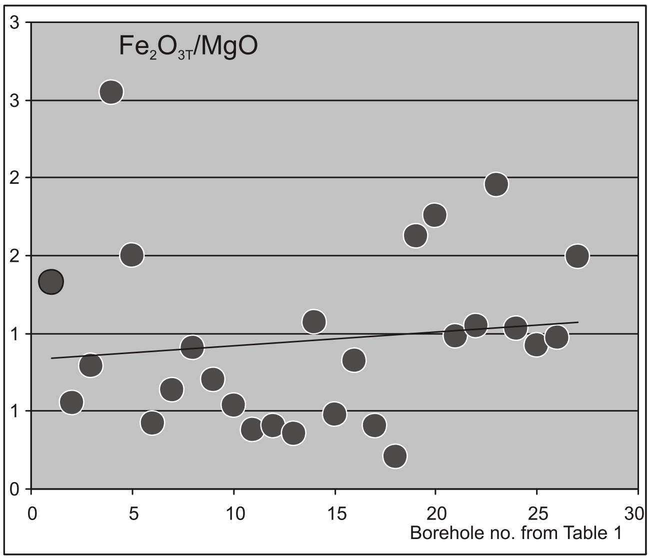

Fig. 4. Distribution of the average values of Fe_2O_{3T} /MgO ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

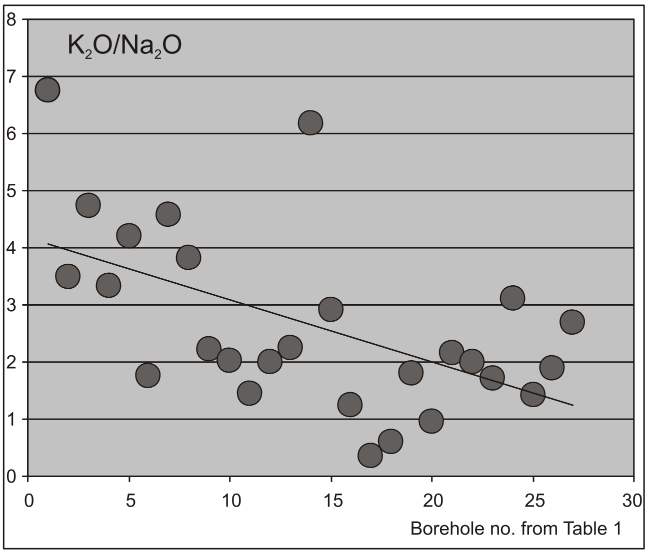

Fig. 5. Distribution of the average values of K_2O/Na_2O ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

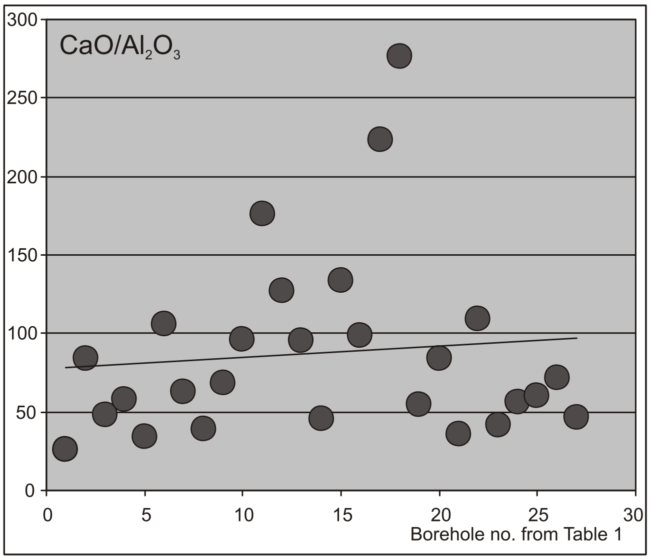

Fig. 6. Distribution of the average values of CaO/Al_2O_3 ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

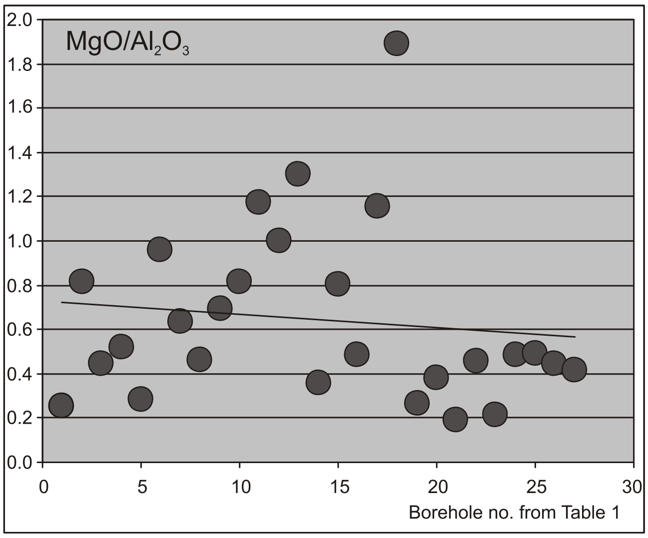

Fig. 7. Distribution of the average values of MgO/Al_2O_3 ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

TiO_2 or Al_2O_3 (Fig. 6) exhibit distinct changes along the deposit, with strong variation in the central part of the deposit and a tighter cluster of the ratio values in the eastern part of the area. The MgO/Al_2O_3 ratio shows a similar distribution (Fig. 7). There is no systematic change in the element distribution and this clearly does not fit the epigenetic model. Instead, the efficiency of bacterial reduction of dissolved sulphate ion present in the sedimentary regime is locally variable and depends on various kinetic factors. This process may lead to local enrichment in calcium.

The variation in Mg content between cores may be interpreted as being partially the result of diagenetic processes. Part of the Mg could be released during early diagenetic transformation of a high Mg-calcite into a low Mg-calcite. Relics of high-Mg calcites and rarely aragonite are found in the limestones (Gąsiewicz, 2000*b*). The low Mg-calcite distinctly dominates the mineralogical composition of the limestones. A plot of Ca *vs*. Mg shows that the range in values from the two parts of the deposit overlap (Fig. 8). A distinct correlation between the CaO and MgO contents of the limestones investigated indicates that at least part of the Mg co-precipitated with calcite. A higher Mg admixture in calcite is supported by petrographic analyses (Gąsiewicz, 2000*b*). Because Mg/Ca in diagenetic calcite depends on Mg^{2+}/Ca^{2+} in interstitial water (Morse and Mackenzie, 1990), it suggests an enrichment of pore waters in magnesium.

A plot of CaO/MgO along the deposit (Fig. 9) clearly shows no systematic change in the average ratio, arguing for a

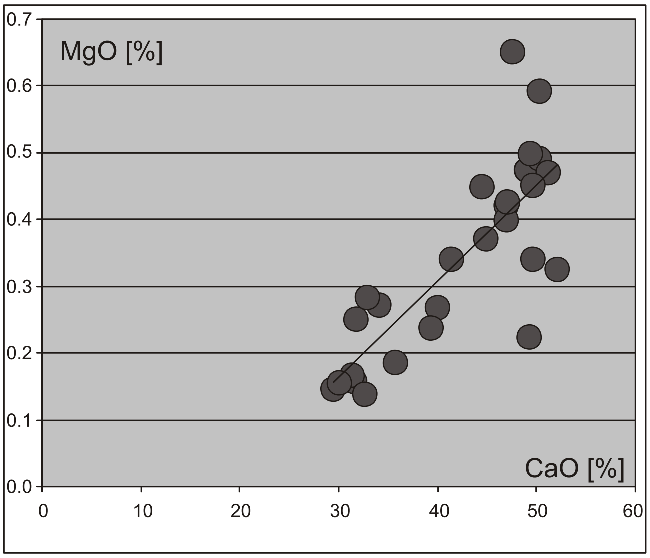

Fig. 8. Bivariate diagram showing variation of MgO and CaO for the gypsum-ghost limestones of the O–BS native sulphur deposit

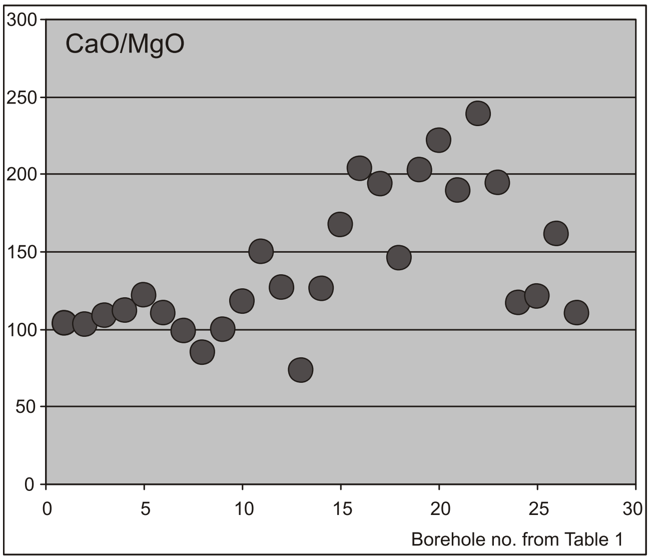

Fig. 9. Distribution of the average values of CaO/MgO ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

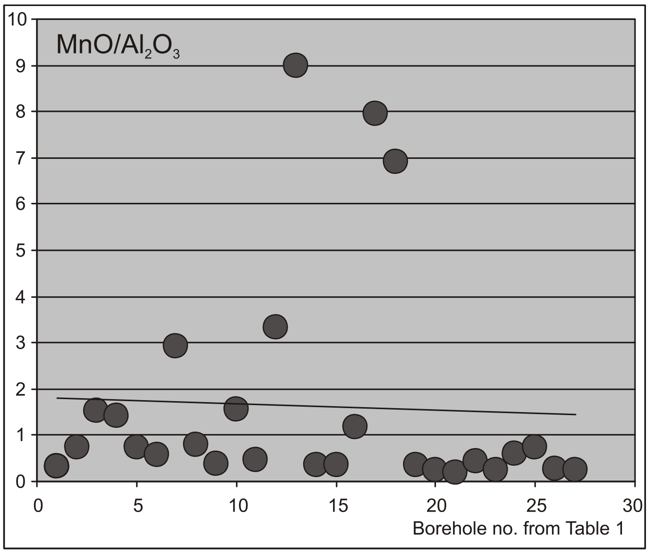

Fig. 10. Distribution of the average values of MnO/Al_2O_3 ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

distinct variations in the Ca/Mg ratio in diagenetic waters. The ratio is distinctly higher in the central part of the deposit indicating there a relative depletion in Mg and an excess of Ca. A lack of linearity in the CaO/MgO distribution along the deposit suggests that this Ca/Mg trend is not a product of water/rock reactions but supports a mixing of chemically different waters that controlled the elemental composition of the limestones and/or reflect the efficiency of bacterial sulphate reduction. The mixing of chemically different waters may simply reflects an influence of more saline water (higher Mg content in calcite) and inputs of freshwater (lower-Mg calcite) in this part of the deposit (Fig. 9). The low Mg/Ca ratios and salinities of most meteoric waters favor the precipitation of calcite (e.g., Moore, 1989, with references).

The average amounts of MnO normalized to Al_2O_3 show distinct variation and higher values in most of the deposit (western part) and a tight cluster of the data in the eastern part (Fig. 10). A moderate correlation between Ca/Al *vs.* Mn/Al for all samples (r = 0.64) confirms that Mn could be potentially fixed in the carbonate phase during diagenesis. The Mn content is mainly dependent on the Eh conditions during sediment diagenesis. Its pattern of distribution along the deposit seems to reflect more unstable diagenetic conditions in the western part of the deposit compared to its eastern part. Moreover, this differentiation reflects also a zonation of the limestone subenvironments of formation.

A poor correlation between Na_2O and both TiO_2 and SiO_2 suggests that Na is partly a clay mineral component and partly it may reflect an admixture of halite, suggested earlier for gypsum sequences (Bąbel, 1991). The higher Na contents in the eastern part of the deposit than in the west one reflect a change in clay mineral composition but also may partially reflect a local salinization of water occurring at some point in this area due to evaporation. It suggests that the origin of Na in this sector may be basically marine similar to those areas evaporitic where marine influence predominates (i.e. sulphates). The presence of selenite gypsum moulds in the limestones confirms saline episodes during their formation.

Distinctly higher average elemental sulphur contents occur in the central-eastern part of the area studied (Table 1). This agrees with the distribution of S^0 measured for the whole deposit, where generally higher contents occur irregularly in the central and eastern parts of the sulphur body (Kowalik *et al.*, 1979, 1980, 1982). Native sulphur is the result of bacterial reduction of dissolved sulphate. Anomalously high contents, a strong variation in the elemental sulphur distribution along the deposit and the relationships among the elements determined suggest not only variable efficiency of the bacterial process but also various mechanisms responsible for the mineral accumulation, and point to unique sources for S^0. With the epigenetic model there is no known mechanism explaining the observed sulphur distribution within the sulphur deposit.

The sulphur shows negative distinct correlations with Ca and Mg and weak with $\delta^{13}C$ values, Fe and TOC. This pattern suggests independent mechanisms of formation of calcite (Ca, Mg) and native sulphur.

Higher SrO, and SO_4^{2-} contents accord with the mineralogical composition of the gypsum-ghost samples, i.e. the presence of celestite as well as barite, which may contain trace amounts of Sr (Parafiniuk, 1987). The elemental concentrations reflect distinctly higher contents of celestite in the eastern part of the deposit where it usually is below 1%, and barite occurs in the limestones in insignificant amounts. Strontium may be incorporated in calcite of both the matrix and cements (Gąsiewicz, 2000*b*) and may commonly occur as later diagenetic celestite replacement of the limestone framework and as encrustation of vugs. The later diagenetic origin of Sr minerals is confirmed by poor negative correlations between SrO and both CaO and MgO contents for all samples (r = from –0.42 to –0.43) and moderate ones for average data (r = –0.61 and –0.53 respectively) as well as by an essential lack of correlation between Sr and S^0 ($r = 0.28$). The relatively highest variation in Sr/Ca ratio, shown in Figure 11, is related to the more eastern part of the area indicating again an independent, later diagenetic mechanism of strontium distribution. The Sr/Mg ratio shows the same behavior.

The features of Sr distribution simply point to the more normal diagenetic evolution of the sedimentary succession than to the epigenetic stages of Sr enrichment. The Sr content of carbonate is a function of the pore water and mineral compositions, stabilization processes and the degree of diagenesis (Veizer, 1983). The distribution of Sr in the gypsum-ghost limestones indicates that the diagenetic calcite precipitated from waters containing a variable Sr/Ca ratio already at the sedimentary stage. This is supported by commonly observed sequestration of some of the Sr ions in calcite (Parafiniuk, 1987) and in both the matrix and calcite cements (Gąsiewicz, 2000*b*). Also the sulphurous rocks of the O–BS sulphur deposit and the associated area contain 2–3 times more Sr than gypsum (Gąsiewicz, unpubl. data). This indicates that higher Sr concentrations have already existed during the sedimentary stage and after, during a later diagenetic stage. Further (diagenetic) evolution of interstitial waters relying on carbonate diagenetic stabilization of $CaCO_3$ minerals (dissolution-precipitation processes) has released a part of the Sr into solution. The strontium released into diagenetic waters would combine with the relict dissolved SO_4^{2-} operating in the carbonate framework and lead to local replacement of the limestone, and have precipitated late generations of celestite and other Sr-containing minerals.

An eventual release of Sr during the rehydration of anhydrite to secondary gypsum may be excluded because according to e.g., Pawłowski *et al.* (1985), Kubica (1992), and Kasprzyk (1993) there is no secondary gypsum in this area.

Taking into account a comparatively low Sr content in gypsum (Kasprzyk, 1994*b*; Gąsiewicz, 2000*b*) and much higher contents in the sulphurous sequence of the sulphur deposit area (including the gypsum-ghost limestones; Table 2) the source of Sr in the epigenetic model remains a puzzle. Also diagenetic the paths and causes of such locally significantly elevated levels of celestite remain unknown.

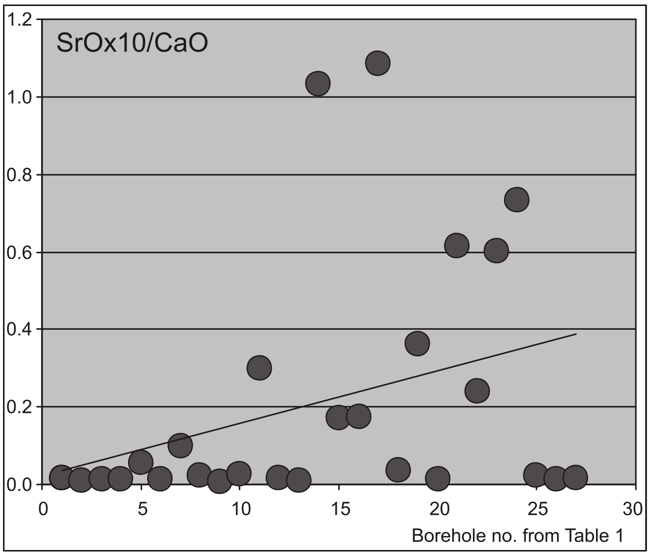

Fig. 11. Distribution of the average values of SrO/CaO ratios of gypsum-ghost limestone samples along the region of the O–BS native sulphur deposit

SUMMARY AND CONCLUSIONS

The gypsum-ghost limestones of the O–BS native sulphur deposit occur within a sulphur-bearing or barren succession essentially lacking evaporite structures (i.e. structures of gypsum precursors) and having otherwise similar chemical and isotopic characteristics (Parafiniuk *et al*., 1994; Gąsiewicz, 2000*b* and own unpubl. data). Because of the local occurrence of the limestones within the area discussed, the present dataset is not large and may not fully define the primary elemental variations. Thus, the geochemical variations identified in this study cannot be used as definitive indicators of sedimentary environment or water chemistry during deposition of the gypsum-ghost limestones, but there are several indicators within the data set that throw some light on the problem.

Numerous gypsum molds in the gypsum-ghost limestones are indicative of a hypersaline environment. Local occurrence of the limestones, usually far from the gypsum succession, indicate also that saline conditions occurred locally and led to precipitation of gypsum selenite crystals together with carbonate phases at the same time. The local occurrence of the gypsum-ghost limestones within the sulphurous succession and the lack of a simple structural relationship between specific natural products, i.e. the gypsum-ghost limestones (with their geometrical, structural, petrographic, mineralogical and geochemical incompatibility) and selenite gypsum lithofacies (the epigenetic precursors) has led the author to suggest that the distribution of the geochemical markers investigated reflects a normal sedimentary-diagenetic regime (Gąsiewicz, 2000*a*, *b*). From this study it is clear that the variations are related to primary sedimentary features linked to original depositional composition and diagenetic evolution within a sedimentary framework.

The geochemical data indicate that the carbonate environment of formation received a low detrital sediment supply. This is generally supported by the consistently low content of siliciclastic elements (MgO, SiO_2, Al_2O_3, Fe_2O_{3T}, K_2O MnO, Na_2O, and TiO_2). The CaO, S^0, SrO and SO_4^{2-} contents of the facies suggest that complex diagenetic processes operated at the sedimentary-diagenetic stages and may have supplied mineralized waters into the depositional system. The average contents of Fe_2O_{3T}, MgO and MnO recorded in the gypsum-ghost limestones are distinctly lower than those found for marine carbonates and their ranges correspond to the composition of brackish carbonates.

The first and most basic result of this study is that the major and minor elemental contents are laterally variable across the deposit. The distinct variation of the average major and minor elemental values in the gypsum-ghost limestones is observed along the field of the O–BS native sulphur deposit and surrounding area, over a distance of approximately 20 km. The regional variations in major and minor element composition of the second (“clastic”) group of elements + Ti and TOC as well as a part of Mg and Na, appear to be independent of significant variations in salinity and are simply linked to a variable input of detrital materials into the basin. A local variation in brine chemistry may be responsible for local and regional changes in Ca, SO_4^{2-} and Mn as well as a part of the Mg and Na contents. The elemental content variations indicate changing sedimentary-diagenetic conditions.

The variations in chemistry mark more or less distinct trends in their distribution along the deposit. In general the western zone of the deposit is enriched in most of the compounds (TOC, CaO, Al_2O_3, Fe_2O_{3T}, MnO, MgO and K_2O) compared with the eastern one (enriched in Na_2O, SrO and S^0). The transition between the various zones of the deposit is poorly delineated. Such a pattern may suggest either high mobility or irregular sedimentary distribution of the components. The trends in average chemical composition sampled over the sulphur deposit and the associated area suggest that there were changes in brine chemistry during the limestone formation. These trends suggest also that on a larger scale, a part of the elemental composition of the limestones within the area was controlled by the sedimentary regime and chemical composition (cation concentration) of the brine.

The variations of the elemental distribution patterns argue for a hydrologically open system for the limestone formation. The weight of evidence (variations of elemental contents and the trends of distribution along the deposit indicates a general lack of shallow burial epigenetic sorting constraint. There is also no evident source for a regional epigenetic enrichment in Ca, Mg, and likely other elements (Sr, Mn) as well as for their variations in the gypsum-ghost limestone compared to the selenite facies (Gąsiewicz, 2000*a*, *b*) except for a primary sedimentary contribution. In this context, the elemental relationships more likely represent a unique contribution into the sedimentary pool (to the area of carbonate + carbonate-sulphate domain) than being the result of subsurface regional alteration of a solid sulphate framework and mass transfer in a closed system.

The results gained from the geochemical features of the gypsum-ghost limestones do not pretend to fully resolve the question of whether mineralizing processes were syngenetic or epigenetic, but they did indicate that the processes operated in a relatively normal sedimentary-diagenetic regime.

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