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S AND O ISOTOPE COMPOSITION OF THE BADENIAN (MIDDLE MIOCENE) SULPHATES IN THE CARPATHIAN FOREDEEP

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Abstract: A study of 333 samples from eight sulphate sections of the Badenian (Middle Miocene) from the marginal part of the Carpathian Foredeep basin and one section from its central part proved that the isotopic compositions of both oxygen and sulphur show a similar trend of evolution throughout the sections. In some cases, in the lower part of gypsum sections a gradual decrease of δ^{34}S and δ^{18}O is observed. In turn, the upper part of the section shows fluctuations of quite high amplitude, but within a clearly defined interval. The variation of δ^{18}O values in the whole area is similar to that of δ^{34}S values although in particular facies the variation ranges are different. Clastic gypsum shows the greatest spread of δ^{34}S and δ^{18}O values. 39 % of all δ^{34}S values and 46.5 % of all δ^{18}O values are higher than those characteristic for the marine sulphate values, and these higher values are mostly characteristic for clastic gypsum. Selenitic gypsum shows relatively narrow ranges of δ^{34}S and δ^{18}O values and hence is especially useful for analyses of depositional conditions. The isotopic composition of Badenian sulphates reflects the marine origin of brines. The recorded great spread of δ^{34}S and δ^{18}O values in the Badenian sulphates is related to the recycling of previously formed evaporites already during gypsum precipitation in the Carpathian Foredeep basin.

Key words: Carpathian Foredeep, Badenian, sulphates, isotopic composition, facies.

Introduction

δ^{34}S and δ^{18}O are very helpful tools to investigate the origin of sulphate deposits for a number of reasons (Pierre 1989). One of them is that the δ^{34}S and δ^{18}O values are very insensitive to nonmarine contribution. On the other hand, redox processes of sulphur species during gypsum deposition have great impact on the sulphate δ^{34}S and δ^{18}O (Lu & Meyers 1997).

Our preliminary study of one section (Borków quarry — Halas et al. 1996) from the Badenian (Middle Miocene) evaporite basin of Carpathian Foredeep suggested that there is a lithological control on the δ^{34}S and δ^{18}O values. However, this was questioned by the results of study of another section (Wiązownica 1 — Kasprzyk 1997). Therefore, it was decided to gather a larger set of new data, which should help in the evaluation of the importance of lithological variation (being the reflection of sedimentary conditions) on changes of the δ^{34}S and δ^{18}O values.

The depositional environments of the Badenian sulphate deposits have been the subject of detailed research (e.g. Bąbel 1999; Kasprzyk 1999; Kasprzyk & Orti 1998; Peryt 1996, 2000, 2001). These studies have shown that although the gypsum originated mainly from marine water, nonmarine water and mixtures of both marine and nonmarine water could be important in some areas and times of gypsum deposition. This was additionally supported by geochemical evidence based on study of roughly coeval halite deposits: the chemical composition of major solutes trapped in the halite, the Br content in halite and the modelling of the brine evolution (Cendón et al. 1999). The aim of this paper is to ascertain the origin of the parent brines and the depositional conditions of the Badenian gypsum on the basis provided by δ^{34}S and δ^{18}O data.

Geological setting

The Carpathian Foredeep basin is a typical peripheral foredeep basin filled with Miocene synorogenic molasse sediments (Fig. 1). Evaporites are related mostly to the Badenian and they form an excellent correlation marker. The nannoplankton study showed that the Badenian gypsum corresponds to the lower part of NN6 Zone (cf. D. Peryt 1997, 1999).

Badenian evaporites show a regular spatial pattern of evaporite facies. Primary gypsum forming a wide (20–60 km) sulphate platform (with gypsum sections a few tens of meters thick) occurs in the most marginal, northern part of the Carpathian Foredeep (Fig. 1). The sedimentological studies of the Badenian gypsum (e.g. Bąbel 1999; Kasprzyk 1999; Peryt 1996, 2001; see also the review of earlier studies there) have shown that autochthonous gypsum facies (crystalline gypsum,

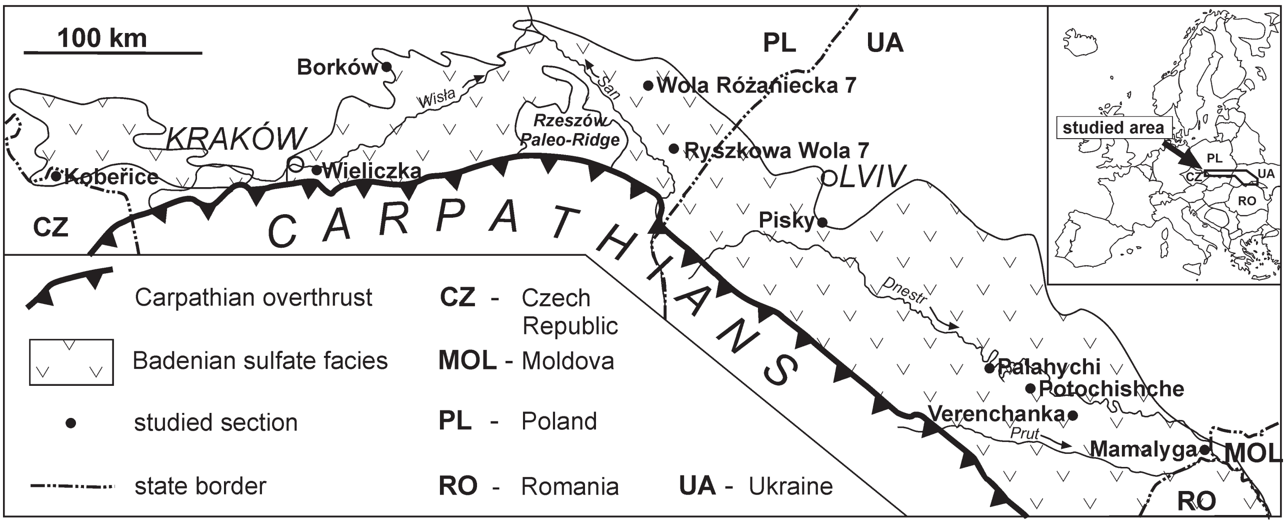

Fig. 1. Location map.

stromatolitic gypsum and massive alabastrine gypsum) were deposited in a vast brine pan, in extremely shallow-water to subaerial environments on broad, very low relief areas of negligible brine depth. Giant gypsum intergrowths originated by continual precipitation from a brine body. Allochthonous sulphate (encompassing clastic gypsum and gypsum breccias) originated in generally deeper environments. In more buried areas the sulphate platform sections are built of anhydrite, but in most cases it is possible to relate the anhydrite textures to the primary gypsum ones.

In the basinward part of the Badenian evaporite basin, anhydrite usually 10–30 m thick occurs in a zone 20–60 km wide (Fig. 1). The sulphates are laminated with sulphate breccia, nodular sulphate and siltstone intercalations. The petrographic study showed that those anhydrite deposits were originally composed of detrital gypsum (Kasprzyk & Orti 1998). A great deal of redeposition within the basin centre of the Badenian evaporite basin combined with the in situ brecciation suggests that the triggering mechanism for redeposition could be earthquakes (Peryt 2000). They generated mass flows and eventually turbidites, so that earlier deposited grains could be redeposited.

In the southern part of the sedimentary basin, in the narrow axial part of the basin, halite deposits (up to 110 m thick) occur in local salt basins.

Material and methods

Our data set comprises 333 samples (compared to 70 analyses done by other authors: Claypool et al. 1980; Parafiniuk et al. 1994; Bukowski & Szaran 1997; Kasprzyk 1997; Parafiniuk & Halas 1997; Rosell et al. 1998) coming from 9 sections. Five outcrop gypsum sections are located in the marginal part of the basin in Ukraine (Mamalyga, Potochishche and Verenchanka — Peryt 2001), Poland (Borków — Halas et al. 1996) and the Czech Republic (Kobeřice — Peryt et al. 1997). From the same, marginal part comes one anhydrite section (Wola Różaniecka 7 borehole in Poland). One anhydrite section (Ryszkowa Wola 7 borehole in Poland — Peryt et al. 1998) is from the central part of basin. In addition, 25 samples from two gypsum exposures (Pisky and Palahychi in Ukraine) have been taken from a part of the gypsum section where earlier a distinctive isotopic anomaly was recorded in the Borków gypsum section in southern Poland (Halas et al. 1996). When sampling the crystalline sulphate types, the pieces for analyses were taken from crystals.

Each sample was first powdered and dissolved in distilled water, then the solution was filtrated and acidified with HCl, to pH = 1, and then a 10% solution of $BaCl_2$ was added to precipitate $BaSO_4$. The precipitate was washed with water to eliminate Cl^- ions, centrifuged, and dried at 110 °C. Barium sulphate was then treated with different analytical procedures to study sulphur and oxygen isotopes. SO_2 was produced by the reduction of barium sulphate by $NaPO_3$ in a Cu-boat at 700 °C (Halas & Szaran 1999). CO_2 was produced using the method of Mizutani (1971) in a separate vacuum line, where $BaSO_4$ was quantitatively reduced by spectrally pure graphite in a thin platinum boat at 1000 °C to BaS and CO, which was subsequently converted to CO_2 by glow discharge between platinum electrodes. The SO_2 and CO_2 gases were collected into glass ampoules and analysed on a dual inlet and triple collector mass spectrometer (reconstructed MI 1305) with a precision of 0.05 to 0.08 ‰. The reproducibility of δ^{18}O and δ^{34}S measurement was 0.08 ‰.

Results

δ^{18}O and δ^{34}S changes with stratigraphic location are shown in Figs. 2–4, and plots of δ^{34}S versus δ^{18}O of gypsum in the studied sections are shown in Fig. 5A. All results are summarized in Tables 1 and 2. In Fig. 5, the box indicates the range of values for Miocene gypsum deposited from normal marine brines (δ^{34}S = 21.65‰±0.5‰, δ^{18}O = 12.5‰±0.5‰; Zak et al. 1980; Paytan et al. 1998).

In general, the isotopic compositions of both oxygen and sulphur show a similar trend of evolution throughout the sections. In a few cases (Borków — Fig. 2; Mamalyga and Verenchanka — Fig. 3), in the lower part of the sections a gradual

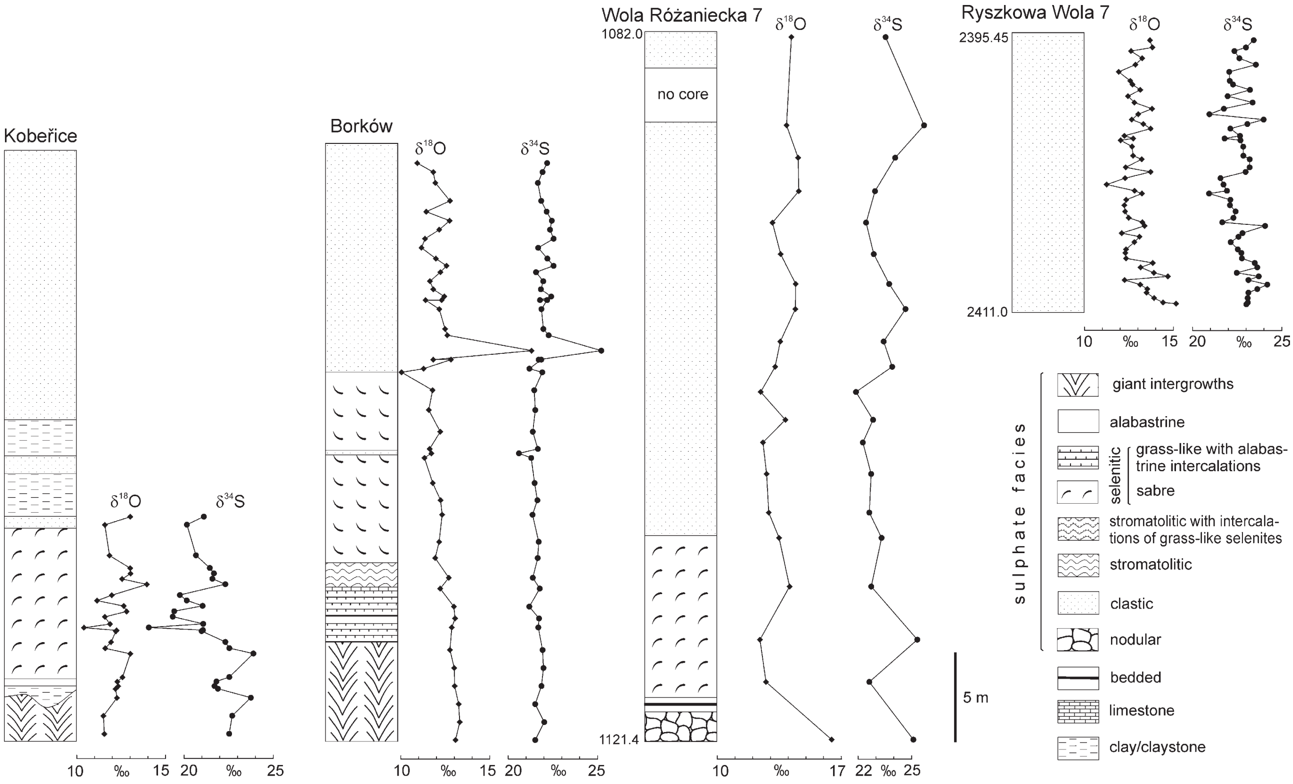

Fig. 2. Studied sulphate sections in the Czech Republic (Kobeřice — gypsum; composite isotope section after Peryt et al. 1997) and Poland (Borków — gypsum, after Halas et al. 1997, Wola Różaniecka 7 — anhydrite, and Ryszkowa Wola 7 — anhydrite, after Peryt et al. 1998) and the $\delta^{18}O$ and $\delta^{34}S$ values of sulphates.

Table 1: Isotopic composition ($\delta^{18}O$ [SMOW], $\delta^{34}S$ [CDT]) of undifferentiated sulphate facies in studied Badenian (Middle Miocene) sections of the Carpathian Foredeep. X — mean: $\overline{X}$ — median; X_M — maximum; X_m — minimum; σ_{n-1} — standard deviation; n — number of samples.

	n	$\delta^{18}O$					$\delta^{34}S$				
		X	$\overline{X}$	X_M	X_m	σ_{n-1}	X	$\overline{X}$	X_M	X_m	σ_{n-1}
whole area	333	12.95	12.92	17.67	10.08	1.00	22.13	21.96	25.70	18.04	0.94
Kobeřice	50	12.27	12.23	14.01	10.39	0.71	21.77	21.92	23.90	18.04	1.12
Borków	65	12.49	12.19	17.67	10.08	1.44	22.00	21.77	25.67	20.46	1.01
Wola Różaniecka 7	20	13.68	13.58	16.45	12.43	0.97	23.44	23.14	25.70	21.88	1.07
Ryszkowa Wola 7	51	12.98	12.82	15.15	11.26	0.75	22.68	22.73	24.18	20.92	0.75
Pisky	11	12.91	13.02	13.40	12.14	0.40	21.77	21.76	22.20	21.15	0.33
Palahychi	14	13.22	13.30	13.67	12.65	0.32	21.61	21.59	22.15	21.01	0.38
Potochishche	28	12.87	12.89	14.30	12.01	0.45	22.06	22.08	22.65	21.29	0.30
Verenchanka	46	13.53	13.29	15.83	11.93	0.84	22.08	21.90	24.79	20.83	0.89
Mamalyga	48	13.34	13.47	14.19	11.75	0.59	21.90	21.79	23.42	21.16	0.51

decrease of $\delta^{34}S$ and $\delta^{18}O$ is observed. In turn, in the lower part of other sections as well as in the upper part of the sections, fluctuations of quite high amplitude, but within a clearly defined interval are recorded (Figs. 2, 3). The exceptions from this general trend are: a rapid change of the $\delta^{34}S$ and $\delta^{18}O$ values in the middle part of the Borków section (Figs. 2, 4) and a rapid, regular decrease of $\delta^{18}O$ values and a concurrent slight increase of $\delta^{34}S$ values in the lowermost part of the Ryszkowa Wola 7 section (Fig. 2).

The variation of $\delta^{18}O$ in the whole area is similar to that of $\delta^{34}S$ (Fig. 5A), although in particular facies the variation ranges are different (Fig. 5B–F).

In the giant intergrowth facies, the isotopic composition shows values close to those characteristic for precipitates from normal marine brines (Fig. 5C). Fig. 5C also shows the $\delta^{34}S$ and $\delta^{18}O$ values of the nodular anhydrite from the Wola Różaniecka 7 borehole, which is regarded as pseudomorphing giant gypsum intergrowths. This anhydrite shows a major excursion from the marine values (Fig. 5C).

In the selenitic facies, total variation of $\delta^{18}O$ (4.94 ‰) is almost twice as large as that of $\delta^{34}S$ (2.89 ‰) (Fig. 5D). 70 % of the values are outside the marine field. Within this field, some selenites from Borków, Kobeřice, Palahychi, Potochishche, and Verenchanka are located. Other selenites from Borków

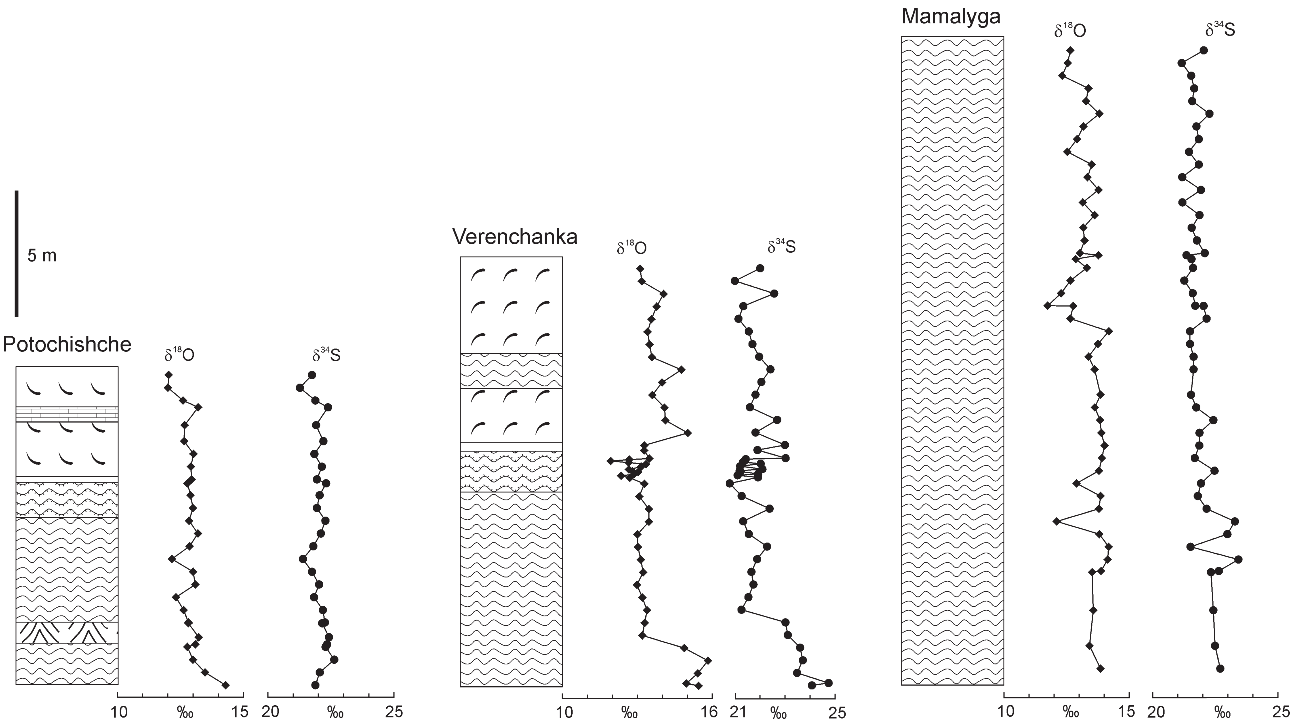

Fig. 3. Studied gypsum sections in Ukraine (Mamalyga, Verenchanka, and Potochishche) and $\delta^{18}O$ and $\delta^{34}S$ values of gypsum (after Peryt 2001). Lithology as explained in Fig. 2.

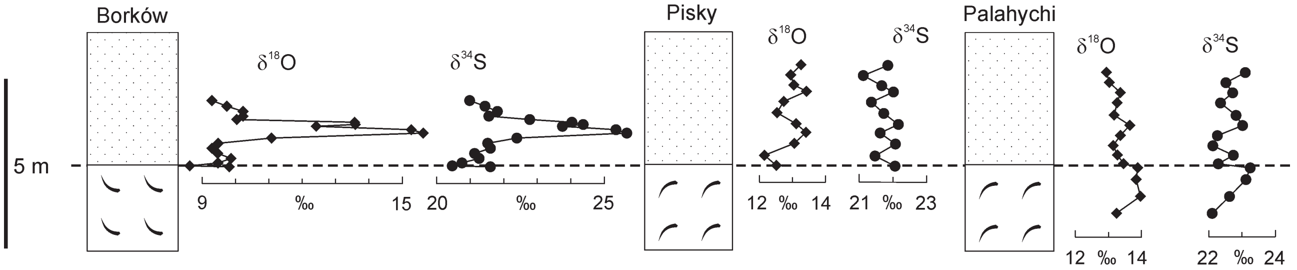

Fig. 4. $\delta^{18}O$ and $\delta^{34}S$ values of gypsum near the autochthonous gypsum-allochthonous gypsum boundary in Borków and in two sections in Ukraine (Pisky and Palahychi). Lithology as explained in Fig. 2.

and Kobeřice are slightly lighter in O. Selenites from Verenchanka show higher $\delta^{18}O$ (by 1–2‰) and sometimes $\delta^{34}S$; similar higher values have been found in the Wola Różaniecka 7 borehole.

In the stromatolite facies, the total variation of $\delta^{18}O$ is similar to that of $\delta^{34}S$ and only 30 % of the values are located within marine field (Fig. 5F). Results for some samples from Potochishche, Mamalyga, Verenchanka and Borków fall into the marine field. However, stromatolites from Verenchanka show values lying mostly outside the field that are up to 3‰ heavier in O and S. Stromatolitic facies of the Wola Różaniecka 7 borehole is heavier in S (1–4‰).

In the alabastrine facies, less than half the values are located within the marine field, and others are very slightly higher in O and/or slightly heavier in S (Fig. 5E).

In contrast to the autochthonous facies, the allochthonous facies show values that are mostly located outside the marine field (Fig. 5B). They also show the greatest range of values ($\delta^{18}O$ — 7.28‰; $\delta^{34}S$ — 7.66‰). Only values recorded in Pisky are located within the marine field or very close to it.

Interpretation

54 % of the $\delta^{34}S$ values and 38.5 % of the $\delta^{18}O$ values are located within the marine box, whereas 7 % of the $\delta^{34}S$ values and 15 % of the $\delta^{18}O$ values are below the marine sulphate values. Lighter data are interpreted as reflecting the reservoir effect — the special case of isotopic evolution in small-sized reactant reservoirs which diminish continuously as the reaction proceeds (Pierre 1988) — in gypsum precipitation. The greater drop in the $\delta^{18}O$ values is related to almost twice greater oxygen fractionation when compared to that of sulphur during gypsum precipitation (3.6‰ and 1.65‰, respectively — Lloyd 1968; Thode & Monster 1965). The slightly regressive curves for O and S are due to progressive crystalli-

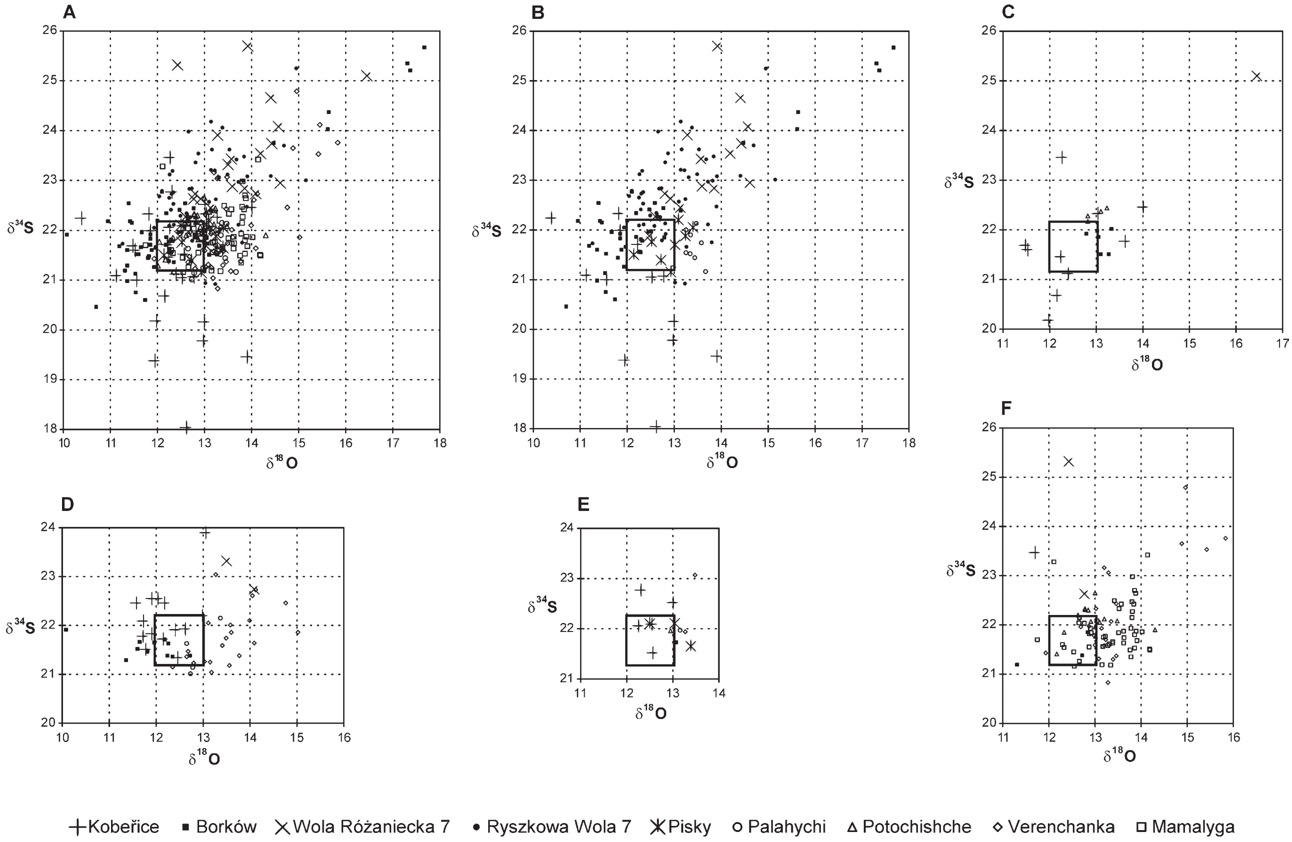

Fig. 5. Plot of δ^{18}O and δ^{34}S values in studied sulphate sections (A) and in the particular sulphate facies (B — allochthonous facies; C — giant intergrowth facies; D — selenitic facies; E — alabastrine facies; F — stromatolitic facies). The box shows the range of values for Miocene gypsum deposited from normal marine brines.

zation of gypsum. 39 % of the δ^{34}S values and 46.5 % of the δ^{18}O values are higher than those characteristic for marine sulphate values. Clearly higher δ^{34}S values could result from the bacterial reduction of a part of the sulphate ion or from the supply of heavier sulphate ion from dissolution of the earlier deposited Badenian gypsum or from the combination of both factors. The dissolution of previously precipitated sulphate leads to enrichment of sea-water sulphate in ^{34}S and ^{18}O. In contrast to the precipitation process, dissolution does not lead to isotope fractionation. Hence a repetitive precipitation of sulphates may lead to a double fractionation, that is to 3.3‰ in δ^{34}S and 7.2‰ in δ^{18}O. A major excursion from the marine values recorded in the anhydrite and interpreted as pseudomorphing giant gypsum intergrowths in the Wola Różaniecka 7 borehole is also interpreted as the result of a sulphate reprecipitation process.

A rapid change of the δ^{34}S and δ^{18}O values in the middle part of the Borków section (Figs. 2, 4) could be related to a considerable environmental change that occurred at the autochthonous-allochthonous gypsum boundary, but as no such change occurs in other sections in the same paleogeographical setting (Fig. 4), it could have resulted from repetitive precipitation of sulphate and/or bacterial reduction processes. The lowermost portion of the sulphate sequence in the Ryszkowa Wola 7 borehole showing also high δ^{34}S and δ^{18}O values is interpreted in the same way.

In Ryszkowa Wola 7, the δ^{18}O values range from 11.26 to 15.15‰, and the δ^{34}S values range from 20.92 to 24.18‰ (Fig. 5A). In the Wieliczka and Bochnia mines, the δ^{18}O values usually range from 11.7 to 13.2‰ while the δ^{34}S values range from 20.7 to 24.0‰ (Bukowski & Szaran 1997). Accordingly, the δ^{34}S values in anhydrite from the Ryszkowa Wola 7 well are very slightly higher when compared to those from the halite facies in Wieliczka and Bochnia mines and the δ^{18}O values are slightly higher when compared to those from the halite facies. This trend may reflect a reservoir effect, if halite precipitation post-dates sulphate crystallization.

Discussion

The modeling done by Lu & Meyers (1997) demonstrated that O isotopes can have larger variations than S because incorporation of water oxygen and dissolved free oxygen increases δ^{18}O of the reoxidized sulphate, while reoxidization of sulphide to sulphate decreases δ^{34}S. However, in the Badenian sulphates the O and S variations are similar (Table 2). The largest impact of bacterial oxidation-reduction of sulphur compounds on the variations of δ^{34}S and δ^{18}O values of sulphate is because microorganisms select preferentially light isotope species during metabolic activity (Pierre 1988). Redox between sulphur species during and/or before sulphate

Table 2: Isotopic composition ($\delta^{18}O$ [SMOW], $\delta^{34}S$ [CDT]) of particular sulphate facies in studied Badenian (Middle Miocene) sections of the Carpathian Foredeep.

	Facies									
	giant intergrowths		**stromatolitic**		**alabastrine**		**selenitic**		**clastic**	
	$\delta^{18}O$	**$\delta^{34}S$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{18}O$**	**$\delta^{34}S$**	**$\delta^{18}O$**	**$\delta^{34}S$**
mean	12.94	22.00	13.26	22.05	12.89	22.11	12.73	21.86	12.89	22.30
median	13.02	21.92	13.20	21.87	13.01	22.06	12.67	21.77	12.76	22.19
maximum	16.45	25.10	15.83	25.32	13.48	23.07	15.02	23.90	17.67	25.70
minimum	11.48	20.18	11.31	20.83	12.26	21.52	10.08	21.01	10.39	18.04
standard deviation	1.03	0.99	0.72	0.74	0.41	0.44	0.89	0.58	1.17	1.16
number of samples	**21**		**90**		**13**		**61**		**136**	

precipitation could result in significant variations of $\delta^{34}S$ and $\delta^{18}O$ values especially in deep-water basins (Lu & Meyers 1997), and this corresponds to large variations of $\delta^{34}S$ and $\delta^{18}O$ values as observed in the clastic facies (Fig. 5B, Table 2). Reducing conditions have been envisaged by Petrichenko et al. (1997) and Kasprzyk (1997) for the Badenian gypsum as it typically abounds in organic matter, bitumens and reduced iron species, and these conditions favoured anaerobic microbial activity and continuous production of H_2S during the sulphate-reduction reaction, and simultaneous ^{18}O and ^{34}S enrichments in residual sulphate.

The data on the isotopic composition of 70 samples of Badenian gypsum and anhydrite earlier published by other authors (Claypool et al. 1980; Parafiniuk et al. 1994; Bukowski & Szaran 1997; Kasprzyk 1997; Parafiniuk & Halas 1997; Rosell et al. 1998) fit our results, although our data set differs in its larger spread of δ values (especially $\delta^{34}S$ values) and different pattern of δ values (cf. Fig. 6A,B).

In general, the isotopic composition of sulphate reflects the marine origin of the brines as found in the marginal basins of the Messinian in SE Spain (Playà et al. 2000). The bromine content (e.g. Garlicki & Wiewiórka 1981; Galamay 1997) and the composition of primary fluid inclusions in Badenian halite (Kovalevich & Petrichenko 1997) suggest a marine origin for brines from which the Badenian evaporites have precipitated. However, Cendón et al. (1999) have deduced from the study of solute concentrations and the different evaporation scenarios modelled, that during halite precipitation in the Carpathian Foredeep basin, there was recycling of previously formed evaporites with an important input of water of continental origin.

The redeposition of Badenian evaporites is a common feature during both halite (e.g. Ślączka & Kolasa 1997) and gypsum deposition (e.g. Peryt 2000). Therefore, it is possible that, already during gypsum precipitation in the Carpathian Foredeep basin, the recycling of previously formed evaporites was of great importance. It is recorded in the great spread of $\delta^{34}S$ and $\delta^{18}O$ values as observed not only in the allochthonous gypsum unit (Fig. 5B), which could be expected taking into account the redeposited nature of that unit, but also in the most gypsum facies (Fig. 5A,C–F).

Relatively narrow ranges of $\delta^{34}S$ and $\delta^{18}O$ values are recorded in giant gypsum intergrowth, selenitic, and alabastrine gypsum facies. The selenitic facies also shows an important part of $\delta^{34}S$ and $\delta^{18}O$ values within the marine box (Fig. 5D), as well as the logical spatial occurrence of higher $\delta^{18}O$ values (sections Verenchanka and Potochishche from the facies zone II after Peryt 2001) and lower $\delta^{18}O$ values (sections: Palahychi, Borków and Kobeřice from the more basinward-located, facies zone III after Peryt 2001). Therefore, selenitic gypsum facies is especially useful for paleoenvironmental analyses.

The recorded great spread of $\delta^{34}S$ and $\delta^{18}O$ values in the Badenian sulphates is related to the recycling of previously

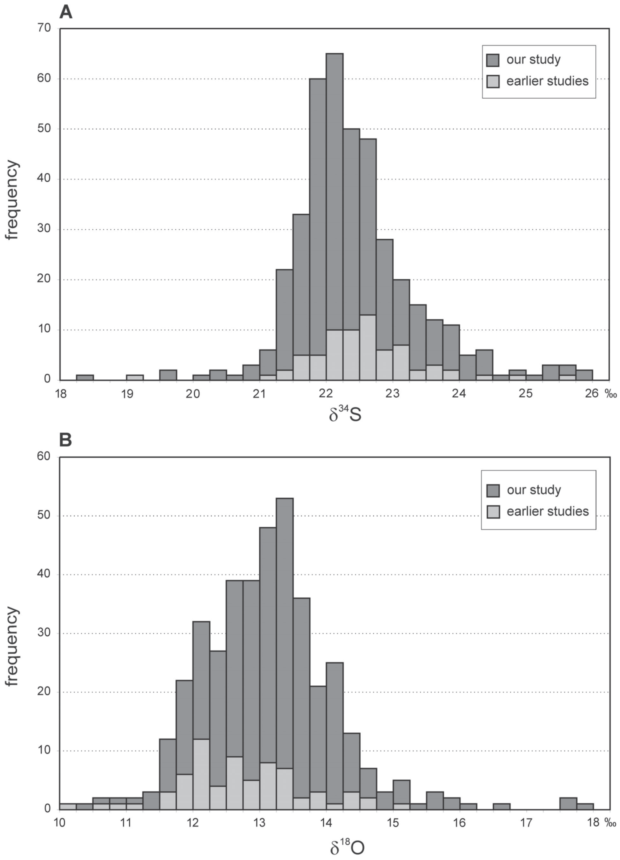

Fig. 6. Histogram of $\delta^{34}S$ values (A) and $\delta^{18}O$ values (B) of the Badenian sulphate rocks of the Carpathian Foredeep based on our study and the data of earlier workers (Claypool et al. 1980; Parafiniuk et al. 1994; Bukowski & Szaran 1997; Kasprzyk 1997; Parafiniuk & Halas 1997; Rosell et al. 1998).

formed evaporites already during gypsum precipitation in the Carpathian Foredeep basin. This recycling was earlier proved by Cendón et al. (1999) for the Badenian halite precipitation. As indicated by Taberner et al. (2000), the information provided by the isolated use of one geochemical marker (such as the isotopic composition of sulphates) should be used with caution; however, the interpretation of $\delta^{34}S$ and $\delta^{18}O$ values in the Badenian sulphates is supported by interpretation of their depositional environments.

Conclusions

1. The isotopic composition of Badenian sulphates reflects the marine origin of brines but the recycling of previously formed evaporites was of great importance. It is recorded in a great spread of $\delta^{34}S$ and $\delta^{18}O$ values as observed not only in the allochthonous gypsum unit but also in the most gypsum facies.

2. There is no essential isotopic difference between various depositional facies of sulphate rocks although they differ in respect of the mean $\delta^{34}S$ and $\delta^{18}O$ values as well as their standard deviation, and hence lithological variation (being the reflection of sedimentary conditions) influences changes in the $\delta^{34}S$ and $\delta^{18}O$ values.

3. Selenitic gypsum shows relatively narrow ranges of $\delta^{34}S$ and $\delta^{18}O$ values and hence it is especially useful for analyses of depositional conditions.

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