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Oxygen and sulphur isotope composition of Badenian (Middle Miocene) gypsum deposits in southern Poland: a preliminary study

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The isotopic studies of primary gypsum facies have been used as a tool for interpreting palaeoenvironments and the sedimentary evolution in the Badenian evaporite basin of southern Poland. The oxygen and sulphur isotope composition of gypsum is homogeneous throughout the section. The average d-values ($\delta^{18}O$ = 12.21‰ and $\delta^{34}S$ = 22.21‰) correspond very well to data found for the Messinian (Upper Miocene) primary gypsum in SE Spain, as well as to other Tertiary sulphate evaporites, and thus provide additional arguments for the marine origin of these deposits. For the Badenian gypsum, the relative depletion in $\delta^{18}O$ might reflect a distinct palaeogeographic control on sulphate sedimentation in the northernmost part of Central Paratethys. The results obtained, combined with other geochemical and sedimentological studies, reflect unstable sedimentary conditions in the peripheral part of the basin in the transition from the autochthonous to allochthonous gypsum members. The minor variations of isotope data are due to dissolution-precipitation and/or partial bacterial sulphate reduction.

INTRODUCTION

The oxygen and sulphur stable isotopes in sulphate minerals are good indicators of changing environmental conditions during sedimentation and early diagenesis, as evidenced by study of modern evaporitic settings (e.g., A. Longinelli, H. Craig, 1967; J. C. Fontes, C. Pierre, 1978; C. Pierre, J. C. Fontes, 1982; I. Zak *et al.*, 1980; C. Pierre, 1988, 1989). The isotope composition of marine aqueous sulphate have been roughly constant since the Tertiary; $\delta^{18}O$ and $\delta^{34}S$ values are respectively 9.5±0.5‰ *vs* SMOW (Standard Mean Ocean Water) and 20±0.5‰ *vs* CDT (Cañon Diablo Troilite) (H. G. Thode *et al.*, 1961; H. G. Thode, J. Monster, 1965; A. Longinelli, H. Craig, 1967; R. M. Lloyd, 1967, 1968; G. E. Claypool *et al.*, 1980). The constant δ-values reflect steady-state conditions in the oceanic environment, which are controlled either by the oxidation-reduction cycle of sulphur (R. M. Lloyd, 1967), or by mass balance between inputs and outputs of reduced and oxidized sulphur compounds (*cf.* W. T. Holser *et al.*, 1979; G. E. Claypool *et al.*, 1980; I. Zak *et al.*, 1980). Local variations of the oxygen and sulphur isotope composition are generally related to the crystallization of sulphate minerals and/or to biogeochemical processes.

For the Badenian (Middle Miocene) sulphate deposits of southern Poland the isotopic data are scarse and mainly related to gypsum occurrences in close vicinity of sulphur ores (S. Hałas, L. Mioduchowski, 1978; S. Hałas, 1982; S. Hałas, A. Kurpiewski, 1982; J. Parafiniuk *et al.*, 1994). Data of sulphur and oxygen isotope ratios, lastly summarized by J. Parafiniuk *et al.* (1994), are relatively homogeneous (the mean values are $\delta^{18}O \approx$ 13.3‰ and $\delta^{34}S \approx$ 22–23‰), and show no distinct differentiation in respect to three major lithofacies distinguished: coarse-crystalline selenite (*szklica* gypsum), *sabre-like* gypsum and fine-crystalline laminated gypsum, and to the location in the Carpathian Foredeep. A distinct isotopic anomaly in the middle gypsum section have been recently documented by S. Hałas *et al.* (1996). All these results are in good agreement with the oxygen and sulphur evolution curves of marine sulphates during Miocene (G. E. Claypool *et al.*, 1980). Apparently, however, till now no simple or direct relationships may be established between isotopic composition and the various parameters of sedimentologic and diagenetic interest for the Badenian gypsum.

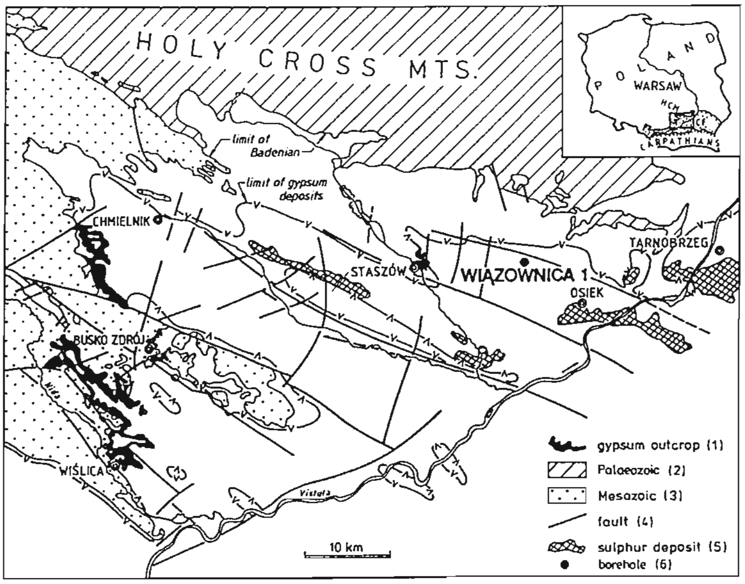

Fig. 1. Location of the Wiązownica 1 borehole in the peripheral part of the Carpathian Foredeep

Lokalizacja otworu wiertniczego Wiązownica 1 w peryferyjnej części zapadliska przedkarpackiego

1 — wychodnia gipsów, 2 — paleozoik, 3 — mezozoik, 4 — uskok, 5 — złoże siarki, 6 — otwór wiertniczy

The aim of this study is to contribute with new isotopic data of sulphur and oxygen to establish more detailed isotopic composition of different gypsum lithofacies throughout the Badenian section, which is important to know geochemical processes involved in deposition and diagenesis. For these purposes the gypsum section from the borehole Wiązownica 1, located in the northern peripheral part of the Carpathian Foredeep (Fig. 1), have been choosen to isotopic analyses. Furthermore, the available published data on isotopic composition of other primary gypsum deposits from the Messinian (Upper Miocene) of SE Spain are considered, as well, for comparison with the Badenian of southern Poland.

AREA AND FACIES

Badenian (Middle Miocene) evaporites occupy a large part of a narrow foreland basin which developed peripherically to the Carpathian orogen in the northernmost part of Central Paratethys. Evaporites are an interbed within marine formations and separate siliciclastic and organogenic carbonate deposits of the Lower Badenian (Skawina Formation) from a thick clay-marly complex of Badenian and Sarmatian age (Machów Formation) (A. Garlicki, 1994). In the northern part of the basin evaporites are 60 m thick and consist of sulphate deposits (gypsum and anhydrite) intercalated and/or laterally equivalent to carbonate and siliciclastic marginal facies. The sulphate deposits are the lateral equivalent to chloride facies of the deeper parts of the Carpathian Foredeep (A. Garlicki, 1979).

In the northern Carpathian Foredeep, in the area south of the Holy Cross Mts., gypsum deposits are well exposed or occur in shallow subsurface (Fig. 1). They form a laterally extended sequence of different lithofacies which comprise selenitic, massive (fine-grained) and clastic varieties; they may be roughly grouped into the lower (autochthonous) and upper (allochthonous) members (Fig. 2, Tab. 1). A brief description of these lithofacies was presented elsewhere (A. Kasprzyk, 1993*a*). In the lower part of the sequence (layers *a–i*) giant gypsum intergrowths (*szklica*) are overlain by bedded selenites with intercalations of alabastrine and stromatolitic gypsum; they are followed by *skeletal* and *sabre-like* gypsum. The upper member (layers *j–n*) is composed mainly of clastic gypsum facies: laminated gypsarenites and gypsorudites. Throughout the section, sulphates are accompanied by carbonates and siliciclastics which form intercalations and irregular bodies within the sulphate deposits. Locally gypsum is partly or completely replaced by sulphur-bearing limestones originated by bioepigenetic alterations of gypsum (B. Kubica, 1992) (Fig. 1). Gypsum sequence is incomplete over the large area along the present limit of sulphate deposits owing to the synsedimentary exposure and erosion.

The facies succession and lateral distribution of Badenian evaporites are an expression of distinct palaeoenvironmental conditions in the foreland basin, which was influenced by tectonic activity in the Carpathian area during the Miocene. As a result, a system of fault-controlled shallow-water basins (lagoons) formed in the peripheral part of the basin at the onset of evaporite deposition (A. Kasprzyk, 1993*b*).

SAMPLING AND ANALYTICAL PROCEDURES

Gypsum samples (total number 32) of different lithofacies and layers *a–n* from the borehole Wiązownica 1 were selected for stable isotope analyses, as representative for the Badenian gypsum section of the northern Carpathian Foredeep (A. Kasprzyk, 1993*a*, *b*) (Tab. 1). For selenitic facies, samples were taken mainly from gypsum crystals, but fine-grained gypsum matrix was sampled as well for the comparative study. All samples had been previously studied for petrographic and sedimentary description. The preparation of samples to analyses was made by the author in the Institut de

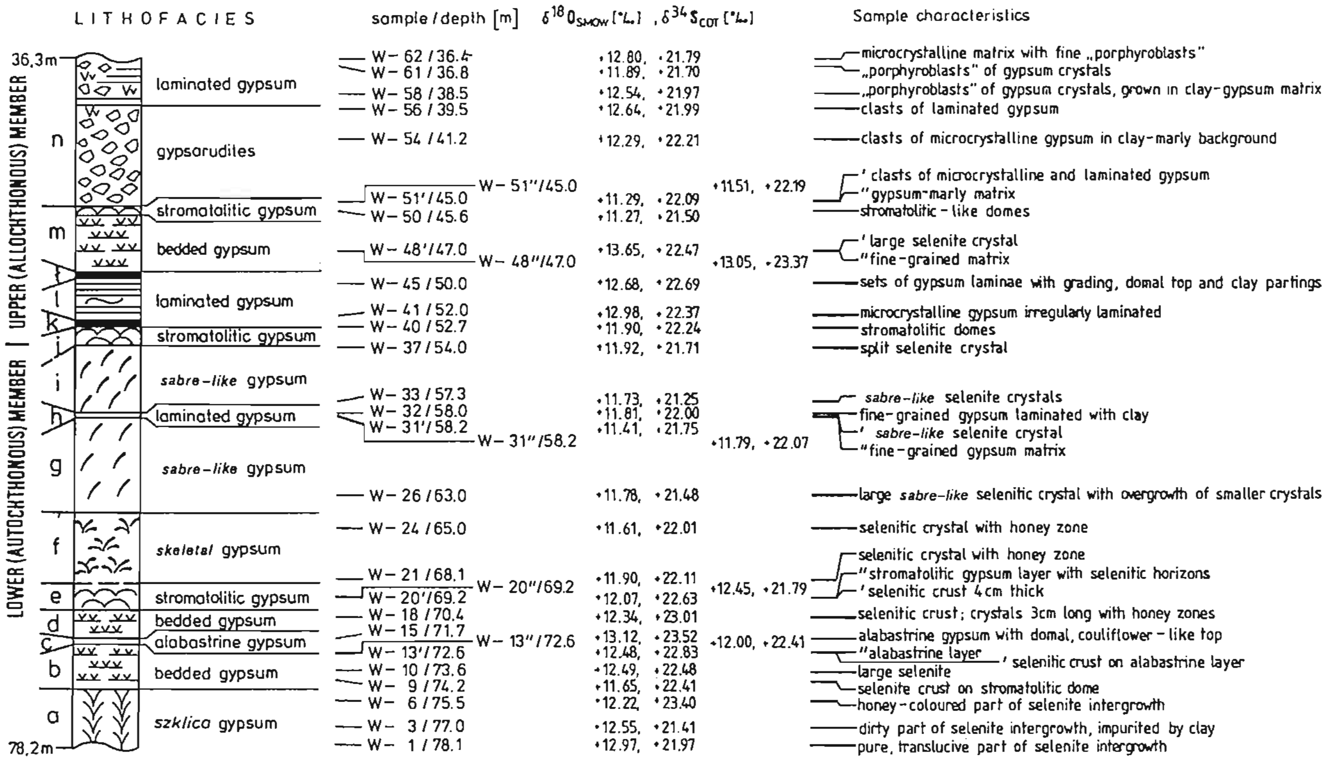

Fig. 2. Lithological profile of gypsum deposits in the Wiązownica 1 borehole with location of studied samples and isotopic data obtained

Profil litologiczny gipsów w otworze Wiązownica 1 z zaznaczeniem pobranych próbek i ich składem izotopowym

Ciències de la Terra (Jaume Almera) in Barcelona, and the isotopic studies were carried out in the Laboratoire d'Oceanographie Dynamique et de Climatologie at the Universite Pierre et Marie Curie in Paris.

Isotopic abundance measurements on oxygen and sulphur were carried out on chemically-stable gaseous species: CO_2 and SO_2, respectively. The sample preparation for stable isotope analyses followed the procedures described by A. Longinelli and H. Craig (1967) for oxygen and by A. Filly *et al.* (1975) for sulphur. Each gypsum sample was first dissolved in distilled water and precipitated as barium sulphate with a solution of $BaCl_2$ under the acid conditions to eliminate the contamination of calcium carbonates. Barium sulphate was then mixed with graphite and heated at about 1100°C to produce CO_2 for oxygen isotope analysis. The CO as another gaseous product of the reaction was transformed to additional CO_2 by electrical discharge. For sulphur isotope analysis, the residual barium sulphide was converted to silver sulphide in a solution of silver nitrate, and then burned in pure oxygen at ≈1200°C to produce SO_2. Gaseous products of the reaction were condensed first in liquid nitrogen ($T = -180$°C) and then in isopentane ($T = -135$°C) to avoid contamination of SO_2 by CO_2 and the remnant O_2.

Both CO_2 and SO_2 gaseous species were analysed in a triple collector mass spectrometer *Isogas*, type Sira 9, *Middlevich-Cheshire*, with an analytical precision (2σ) close to 0.03‰; the reproducibility was within the range 0.2‰ for ^{18}O and ^{34}S measurements. Reproducibility of $\delta^{18}O$ data was controlled by regular analysis of internal $BaSO_4$ reference prepared from the Messinian selenite gypsum of the Mediterranean region, with a mean $\delta^{18}O$ value 14.0‰ relative to SMOW. For sulphur measurements the interlaboratory reference of CdS was used. The $\delta^{18}O$ values have been converted from PDB scale to SMOW using the equation (I. Friedman, J. R. O'Neil, 1977): $\delta^{18}O_{SMOW} = 1.0412\ \delta^{18}O_{PBD} + 41.2$. The $\delta^{34}S$ values are expressed relative to CDT reference (N. Nakai, M. L. Jensen, 1964).

RESULTS AND DISCUSSION

ISOTOPIC COMPOSITION OF BADENIAN GYPSUM

All isotopic data obtained in the Badenian samples are presented in Figures 2 and 3. They show that the oxygen and sulphur isotope composition of gypsum are relatively homogeneous throughout the section; standard deviation values are 0.11 (oxygen) and 0.10 (sulphur) (Tab. 1). The δ-values vary within a narrow range: from 11.27 to 13.65‰ (mean = 12.21‰), and from 21.25 to 23.52‰ (mean = 22.21‰) for oxygen and sulphur, respectively. Overall, these δ-values fit

Table 1

Isotopic composition of gypsum lithofacies in Wiązownica 1 section

Lithofacies	Number of samples	$\delta^{18}O_{SMOW}$ [‰]	$\delta^{34}S_{CDT}$ [‰]
		mean value [‰]	mean value [‰]
Szklica gypsum	3	12.97	21.97
		12.55	21.41
		12.22	23.40
		12.58	22.26
Skeletal and *sabre-like* gypsum	7	11.90	22.11
		11.61	22.01
		11.78	21.48
		11.41	21.75
		11.73	21.25
		11.92	21.71
		11.79	22.07
		11.73	21.77
Bedded gypsum	6	11.65	22.41
		12.49	22.48
		12.48	22.83
		12.34	23.01
		13.65	22.47
		13.05	23.37
		12.61	22.76
Stromatolitic gypsum	4	12.07	22.63
		12.45	21.79
		11.90	22.24
		11.27	21.50
		11.92	22.04
Alabastrine gypsum	2	12.00	22.41
		13.12	23.52
		12.56	22.97
Laminated gypsum and laminated gypsarenites	6	11.81	22.00
		12.98	22.37
		12.68	22.69
		12.54	21.97
		11.89	21.70
		12.80	21.79
		12.45	22.09
Gypsorudites	4	11.29	22.09
		11.51	22.19
		12.29	22.21
		12.64	21.99
		11.93	22.12
All lithofacies	32	12.21	22.21
Standard deviation		0.11	0.10

well with the previous data reported for the Badenian gypsum of the Carpathian Foredeep (e.g., J. Parafiniuk *et al.*, 1994). Accordingly, new data on isotopic composition of gypsum fall into the ranges of variations of δ-values measured in the marine sulphates from the Miocene of the Carpathian Foredeep and of other areas (G. E. Claypool *et al.*, 1980).

Generally, the isotopic composition of both oxygen and sulphur show similar trend of evolution throughout the section, as presented in Figure 3. The anomalous isotopic values of some gypsum samples (nos. 6, 20", 26, 40, 45, 48', and 48") probably reflect variations in fractionation between isotope species, controlled by redox conditions in the basin. These variations seem to be mainly related to the kinetics of bacterial sulphate reduction, and to oxygen isotope exchange between water and the oxidized sulphur compounds (*cf.* C. Pierre, 1988).

The role of sulphur redox reactions in the oxygen and sulphur isotope transfers between sulphur compounds and the water has been documented in marine salt pans from the Mediterranean coast of France and of SE Spain (C. Pierre, 1982, 1985, 1988; C. Pierre *et al.*, 1984). In these recent evaporitic environments the isotopic variations are attributed to partial bacterial sulphate reduction in organic-rich sediments, followed by re-oxidation of reduced sulphur compounds in well-mixed water for which $\delta^{18}O$-values vary as a function of the evaporation — dilution mass balance (C. Pierre, 1989; C. Pierre, J. C. Fontes, 1982). Such an explanation may also be proposed for Badenian gypsum which typically abounds in organic matter, bitumens and reduced iron species (O. I. Petryczenko *et al.*, 1995), suggesting reducing conditions constituted within the organic-rich bottom sediments during the gypsum precipitation. 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, which was recorded in some studied samples (e.g. nos. 15, 48', 48", and 6 in Figures 2 and 3).

Considering the mean isotopic composition of different gypsum lithofacies, the lowest δ-values ($\delta^{18}O$ = 11.73‰; $\delta^{34}S$ = 21.77‰) were found in *skeletal* and *sabre-like* varieties (Tab. 1). The values for these lithofacies are homogeneous ($11.41 < \delta^{18}O‰ < 11.92$; $21.25 < \delta^{34}S‰ < 22.11$), whilst those from other lithofacies are relatively scattered (Tab. 1). It is thus inferred that there is no relationship between lithofacies and isotopic composition.

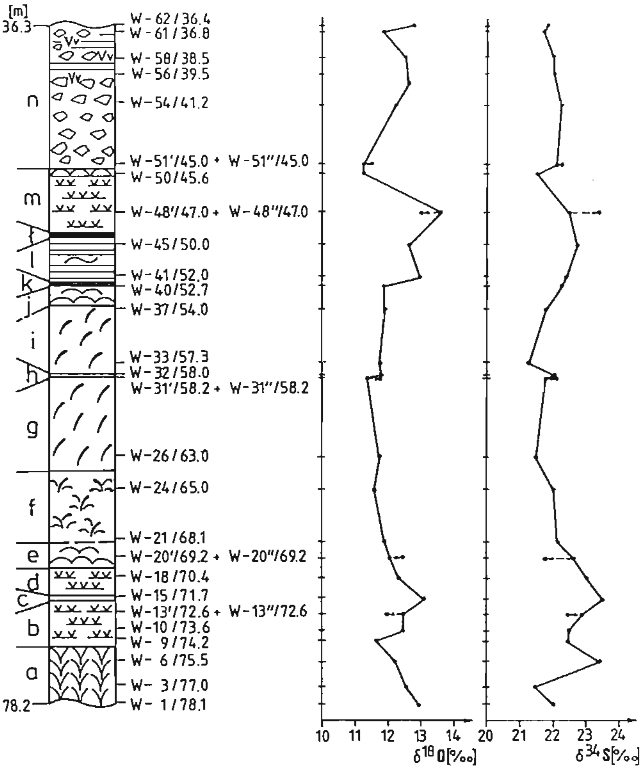

Fig. 3. Isotopic composition of gypsum plotted against depth in Wiązownica 1 section

Zmiany składu izotopowego gipsów wraz z głębokością

Layer	$\delta^{18}O$[‰]	$\delta^{34}S$[‰]
n	12.13	21.99
m	12.66	22.45
l	-	-
l	12.83	22.53
k	-	-
j	11.90	22.24
i	11.82	21.48
h	11.81	22.00
g	11.66	21.77
f	11.76	22.06
e	12.26	22.21
d	12.34	23.01
c	13.12	23.52
b	12.15	22.53
a	12.58	22.26
	$\bar{x}$ = 12.21	$\bar{x}$ = 22.21

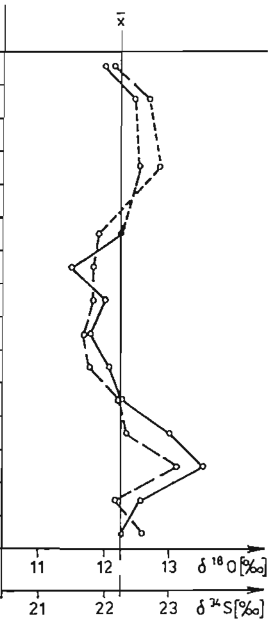

Fig. 4. Curves of $\delta^{18}O$ and $\delta^{34}S$ mean values in gypsum layers throughout the Wiązownica 1 section

Zmienność wartości średniej $\delta^{18}O$ i $\delta^{34}S$ w warstwach gipsowych w profilu otworu Wiązownica 1

Both sedimentary record and geochemistry evidence that gypsum precipitated directly from evaporating sea-water brines. On the other hand, some lithofacies, as e.g. alabastrine and clastic gypsum, show common recrystallization fabrics. It is suggested that consequent stages of dissolution and re-precipitation resulted in variations of isotopic composition of sulphate, as shown by appropriate samples (nos. 15, 58, 61, and 62 in Figures 2 and 3).

In the vertical section, the isotopic composition is generally characterized by the repeted increasing-decreasing trend of variations of mean δ-values, with a distinct anomaly at the boundary between the lower (autochthonous) and the upper (allochthonous) gypsum members (Fig. 4), which agrees well with results recently obtained by S. Hałas *et al.* (1996). Accordingly, geochemistry supports the earlier sedimentological observations suggesting an essential change of the sedimentary regime during the gypsum deposition (A. Kasprzyk, 1993*b*; T. Peryt, M. Jasionowski, 1994). The thick selenitic complex in the middle section (layers *f–i*), showing distinct depletion in both ^{18}O and ^{34}S relative to the mean δ-values for the section (Fig. 4), seems to represent a generalized brine dilution or, alternatively, to be more affected by fractionation with the isotopically light aqueous sulphate.

For further evidence of the above interpretation, the isotopic data obtained in gypsum samples from Wiązownica 1 section are plotted in Figure 5. The most $\delta^{34}S$ — $\delta^{18}O$ values are clustered around 22 and 12‰, respectively for sulphur and oxygen. However, for some samples (nos. 15, 48', 48", and 6) isotopic enrichments relative to the average δ-values suggest possible effects of partial sulphate reduction or recrystallization (dissolution-precipitation) during deposition and early diagenesis.

Considering the results of the earlier investigations on the isotopic composition of the Badenian gypsum (S. Hałas, L. Mioduchowski, 1978; S. Hałas, 1982; S. Hałas, A. Kurpiewski, 1982; J. Parafiniuk *et al.*, 1994), the new data from Wiązownica 1 borehole give similar $\delta^{34}S$ values, but the $\delta^{18}O$ values are lower by about 1‰, on average. A probable explanation to this local variation in the isotopic composition of the Badenian gypsum is that redox conditions in the sulphate reservoir differed dependent on structural constraints in the basin, salinity gradients and continental water inflow. It seems to reflect a distinct palaeogeographic control on sulphate sedimentation and diagenesis in the peripheral part of the Carpathian Foredeep.

The values obtained undoubtedly confirm the marine origin of the Badenian gypsum in the northern Carpathian Foredeep. All data available evidence primary deposition of gypsum in relatively stable sedimentary conditions, except of an anomalous episode in the middle gypsum section, which may express a distinct evolution of sedimentation, when combined with other geochemical indicators (e.g. A. Kasprzyk, 1993*a*, *c*). Considering the isotope fractionation during the gypsum crystallization, the isotopic composition of aqueous sulphate in the Miocene sea water from which gypsum precipitated would be defined by $\delta^{18}O \approx 8.71$‰ and $\delta^{34}S \approx 20.56$‰. These values are comparable to the isotopic composition of aqueous sulphate of recent sea water (G. E. Claypool *et al.*, 1980).

COMPARISON WITH MESSINIAN GYPSUM

Messinian (Upper Miocene) evaporites of SE Spain formed in intramountainous basins developed from the compressive tectonism in the Betic Cordillera during the Alpine Cycle (J.-M. Rouchy, 1982; C. Montenat *et al.*, 1987).

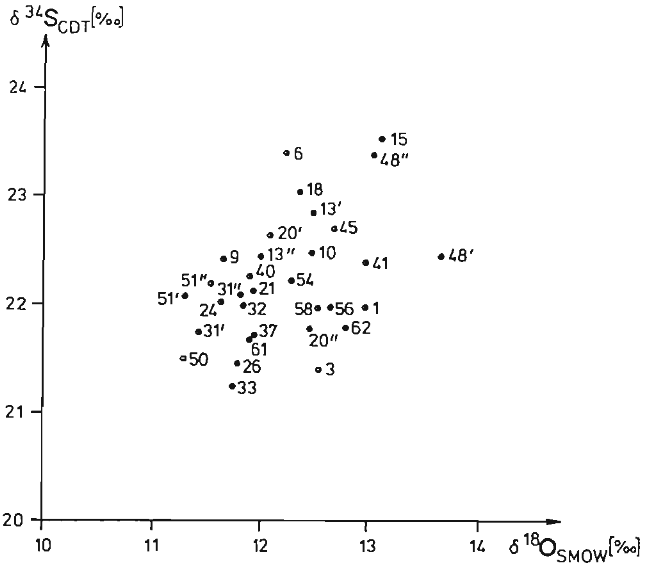

Fig. 5. The $\delta^{18}O$ *vs* $\delta^{34}S$ plot of gypsum from Wiązownica 1 borehole

Zależność między wartościami $\delta^{18}O$ i $\delta^{34}S$ w gipsach z otworu Wiązownica 1

Based on palaeogeographic setting, two primary gypsum facies may be distinguished: (1) selenitic facies displaying cyclicity, which developed in the inner basins: Sorbas, San Miguel de Salinas, Palma de Mallorca, and (2) fine-grained facies (locally with minor intercalations of selenites and halites) transitional to the continental deposits, corresponding to external basins: Abanilla, Lorca, and Fortuna. In the basin of San Miguel de Salinas (Alicante province) several layers of selenitic gypsum showing various fabrics and crystal size, similar to giant gypsum intergrowths from the Badenian of Poland, crop out in the peripheral area (F. Orti, D. J. Shearman, 1977). The main morphological types of selenites are: narrow, vertically elongated, twinned selenites up to several metres high, interpreted to be developed in the inner part of the basin, and wide, assymetrical selenitic intergrowths with twin planes oriented subhorizontally, representative for the more marginal position (L. Rosell *et al.*, in press).

The Table 2 summarizes the earlier oxygen and sulphur isotopic data for the Messinian gypsum. The 17 samples listened represent the primary gypsum lithofacies from Palma de Mallorca, San Miguel de Salinas, Abanilla, Fortuna, Lorca, and Sorbas basins. The δ-values are found to be in a relatively narrow range, from 12.2 to 14.8‰ (mean = 13.7‰) and from 19.4 to 23.8‰ (mean = 21.5‰), respectively for oxygen and sulphur. The appropriate average values in the San Miguel de Salinas section are 14.0‰ (oxygen) and 22.5‰ (sulphur)(*cf.* L. Rosell *et al.*, in press). A slight variation of the isotopic composition, expressed in standard deviation values (σ_{n-1} = 0.2 for oxygen and 0.3 for sulphur), could be related either to processes involving *in situ* dissolution-precipitation or to changing redox potential through sulphate-reducing and sulphur-oxidating bacterial activities. These data are very similar to results obtained in the Badenian gypsum samples, and all are in a good agreement with the sulphur and oxygen age curves for Tertiary (G. E. Claypool *et al.*, 1980).

Table 2

Oxygen and sulphur isotopic composition of primary gypsum from Messinian (Upper Miocene) of SE Spain (according to R. Utrilla, 1989 (1); C. Pierre, 1982 (2); A. Longinelli, 1979 (3))

Location	Sample	$\delta^{18}O_{SMOW}$ [‰]	$\delta^{34}S_{CDT}$ [‰]
Palma de Mallorca (1)	105.9	13.6	21.7
	148	13.0	22.4
	160.2	12.4	22.3
	185	13.0	19.4
San Miguel de Salinas (2)	SM-1	13.5	22.5
	SM	14.5	22.4
	Be-1	13.4	22.0
	Be-1	14,5	23,1
Abanilla (2)	Ab-6	13.7	20.4
	Ab-9	14.2	21.0
Fortuna (1)	MU-6	14.4	23.8
Lorca (2)	Lo-17	13.4	19.8
Sorbas (3)	14	14.8	20.8
	11	14.5	20.3
	9	13.3	20.1
	6	12.2	21.2
	1	14.6	21.9
Mean value		13.7	21.5
Standard deviation		0.2	0.3

CONCLUSIONS

The oxygen and sulphur isotopic composition of the primary gypsum deposits of the two Miocene episodes: Badenian (Middle Miocene) and Messinian (Upper Miocene) fall into narrow range of variability. The average δ-values obtained for representative sections: Wiązownica 1 (S Poland) and San Miguel de Salinas (SE Spain) are respectively: $\delta^{18}O$ = 12.21‰, $\delta^{34}S$ = 22.21‰ for the Badenian gypsum, and $\delta^{18}O$ = 14.0‰, $\delta^{34}S$ = 22.5‰ for the Messinian gypsum. These results correspond very well to data found for the Miocene primary gypsum of the Mediterranean area (e.g. A. Longinelli, 1979), as well as for other Tertiary evaporite formations (G. E. Claypool *et al.*, 1980), and thus provide additional arguments for the marine origin of these evaporites. For the Badenian gypsum, the relative depletion in ^{18}O might reflect a distinct palaeogeographic control on sulphate sedimentation and diagenesis in the northernmost part of Central Paratethys. These results also demonstrate that sedimentary conditions in the peripheral part of the Badenian basin changed drastically at the boundary of autochthonous and allochthonous gypsum members. The minor variations of isotope data are due to dissolution-precipitation and partial bacterial sulphate reduction.

Isotopic composition similar to that of the studied Badenian gypsum are found in sulphate samples from modern marine evaporite environments where variations in $\delta^{18}O$ — $\delta^{34}S$ values relative to those of normal marine gypsum suggest unbalanced sulphur redox reaction between the free solutions and the bottom sediments (*cf.* C. Pierre, 1988; A. Longinelli, 1979).

Similar δ-values of gypsum deposits from both the Badenian of the Carpathian Foredeep and the Messinian of SE Spain might indicate comparable environmental conditions in the peripheral parts of the basins during deposition and diagenesis of these evaporites, which supports the earlier interpretation based on lithofacies and sedimentological studies (*cf.* A. Kasprzyk, 1993*a*, *b*).

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Translated by the Author

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SKŁAD IZOTOPOWY TLENU I SIARKI W GIPSACH BADEŃSKICH POLSKI POŁUDNIOWEJ: BADANIA WSTĘPNE

Streszczenie

Badania składu izotopowego tlenu i siarki w minerałach siarczanowych dostarczają informacji w zakresie warunków fizykochemicznych w środowisku krystalizacji, przeobrażeń diagenetycznych siarczanów i ich udziału w cyklu redukcyjno-utleniającym siarki (np. C. Pierre, 1985, 1988 wraz z literaturą). W celu uzyskania nowych, szczegółowych danych, mających implikacje środowiskowe, autorka wykonała badania izotopowe gipsów badeńskich w reprezentatywnym profilu otworu wiertniczego Wiązownica 1, zlokalizowanym w północnej peryferyjnej części zapadliska przedkarpackiego (fig. 1–2). Badania te przeprowadzono w Laboratoire d'Oceanographie Dynamique et de Climatologie (Universite Pierre et Marie Curie) w Paryżu, przy współpracy i pomocy dr C. Pierre i dr C. Taverner.

W profilu gipsów otworu Wiązownica 1 wyróżniono szereg odmian litologicznych, które tworzą sekwencję kilkunastu warstw litostratygraficznych (litotypów), oznaczonych od *a* do *n* (fig. 2). Na podstawie wykonanych badań izotopowych nie stwierdzono istotnych zmian składu izotopowego tlenu i siarki w gipsach. Wartości $\delta^{18}O$ i $\delta^{34}S$ zawierają się w wąskich przedziałach zmienności, odpowiednio od 11,27 do 13,65‰ oraz od 21,25 do 23,52‰ (wartości średnie wynoszą 12,21 oraz 22,21‰) (fig. 3–4; tab. 1). Są to wartości porównywalne z uzyskanymi przez innych badaczy dla gipsów messyńskich (górny miocen) południowo-wschodniej Hiszpanii (A. Longinelli, 1979; C. Pierre, 1982; R. Utrilla, 1989) (tab. 2) i zawierają się w przedziale zmienności wartości δ dla morskich siarczanów z miocenu innych obszarów (G. E. Claypool i in., 1980). Nie stwierdzono wyraźnego zróżnicowania składu izotopowego w zależności od litologii (tab. 1). Względnie niskie wartości $\delta^{18}O$ i $\delta^{34}S$ wykazują gipsy szkieletowe i szablaste (litotypy *f–i*). W profilu pionowym zaznacza się zmiana składu izotopowego tlenu i siarki na pograniczu gipsów autochtonicznych (litotypy *a–i*) i gipsów allochtonicznych (litotypy *j–n*) (fig. 4). Zmiany te prawdopodobnie rejestrują niestabilne warunki sedymentacji gipsów. Niewielkie zróżnicowanie wartości δ w gipsach wskazuje na wahania potencjału redukcyjno-utleniającego w środowisku sedymentacji, procesy rozpuszczania i rekrystalizacji i/lub dostawę siarczanu izotopowo lżejszego. Podwyższone wartości $\delta^{18}O$ i $\delta^{34}S$ w kilku próbkach (6, 15, 41, 48' i 48"; fig. 5) to efekt frakcjonacji izotopowej w czasie bakteryjnej redukcji siarczanów lub rekrystalizacji, prowadzącej do wzbogacania gipsów w ciężkie izotopy tlenu i siarki (por. A. Longinelli, 1979; C. Pierre, 1982, 1988). Uwzględniając frakcjonację izotopową w czasie krystalizacji gipsu, oszacowano skład izotopowy solanki macierzystej; określają go wartości $\delta^{18}O \approx 8,71$‰ i $\delta^{34}S \approx 20,56$‰, które są porównywalne ze składem izotopowym siarczanu współczesnych wód oceanicznych (G. E. Claypool i in., 1980).

Wyniki wykonanych badań potwierdzają pierwotny charakter gipsów badeńskich południowego obrzeżenia Gór Świętokrzyskich i dowodzą, że zbadane skały tworzyły się w basenie otwartym, przy stałej dostawie wód morskich i względnie stabilnych warunkach sedymentacji. Istotna zmiana środowiskowa pod koniec depozycji gipsów selenitowych, którą rejestrują wyniki nowo wykonanych badań izotopowych, wskazuje prawdopodobnie na początek nowego, większego cyklu sedymentacyjnego, co jest zgodne z wynikami wcześniejszych badań sedymentologicznych i geochemicznych (por. A. Kasprzyk, 1993*b*, *c*; T. Peryt, M. Jasionowski, 1994) oraz uzyskanych ostatnio przez S. Hałasa i in. (1996).