Isotopic composition of the crystallization water of gypsum in the Badenian of the northern Carpathian Foredeep: a case study from the cores Przyborów 1 and Strzegom 143

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The isotopic composition of a crystallization water of gypsum is considered representative of the mother brine. In order to determine its origin for the Badenian primary gypsum in the northern peripheral part of the Carpathian Foredeep, two sections were sampled for the oxygen and hydrogen isotope analyses. The measured δD and $\delta^{18}O$ values for the crystallization water vary from –94.9 to –41.2‰ and from –7.2 to 0.8‰, respectively. Overall, these values are distinctly lower than those expected from isotopic exchange interactions during the gypsum crystallization from the marine brines, which is most likely due to (1) mixing of the original marine (sedimentary) waters with the isotopically light meteoric waters, or (2) isotopic exchange of the crystallization water with secondary solution. There is a clear relationship between the differentiated isotopic composition and variation in lithofacies. Both isotopic components calculated for the mother brine change in parallel fashion and show a decreasing-up trend of changes throughout the section. Most of these values, however, fall above the present-day meteoric water trend line, suggesting either (a) formation of gypsum from connate waters with distinct isotopic signatures, or (b) variation in the isotopic composition of the meteoric waters generated by the general climatic conditions since the late middle Badenian. The difference in the slope of the mother water line for both studied sections may be also explained by differentiated kinetics of the isotopic exchange interactions. Based on the slope of this line and its relationships to the local meteoric water trend line, it may be assumed that the crystallization water in studied gypsum samples has been largely, if not completely, replaced by the meteoric waters or circulating ground waters under relatively cool and humid climatic conditions. Thus, the isotopic signature for gypsum reflects rather very recent history of its diagenesis.

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INTRODUCTION

The stable isotope study of the crystallization water of gypsum is a powerful tool to determine hydrologic systems in which gypsum originated and was changed later during diagenesis (e.g. Z. Sofer, 1978; A. Longinelli, 1979; S. Hałas, H. R. Krouse, 1982; A. H. Bath *et al.*, 1987; M. El Tabakh *et al.*, 1998). In evaporitic environments, gypsum originally forms in isotopic equilibrium with the mother brine. The equilibrium isotopic fractionation is described by the factor:

$$\alpha = \frac{1000 + \delta\ gips}{1000 + \delta\ brine}$$

determined to be 1.004 and 0.980 for oxygen and hydrogen, respectively (R. Gonfiantini, J. C. Fontes, 1963; J. C. Fontes, R. Gonfiantini, 1967; Z. Sofer, 1978). These values are not sensitive to temperature changes during gypsum crystallization or to the salt effect on gypsum saturation (Z. Sofer, J. R. Gat, 1975). Considering the approximate differences on δ-scales during crystallization, the isotopic composition of the crystallization water of gypsum is enriched by 4‰ in oxygen
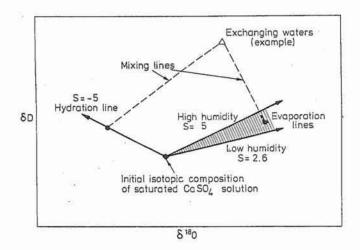
Fig. 1. Predicted isotopic fractionation trends for crystallization water of gypsum during evaporation, hydration and isotopic exchange
A slope of the evaporation line depends mainly on the water salinity and climatic conditions, and it changes (dashed field) from ≈ 5–6 for high atmospheric humidity to 2.5–4 under arid desert conditions (after Z. Sofer, 1978)
Frakcjonacja izotopowa wody krystalizacyjnej gipsów podczas ewaporacji, hydratacji i wymiany izotopowej
Nachylenie linii ewaporacji zależy głównie od zasolenia wód i warunków klimatycznych i zmienia się (obszar zakreślony) od ≈ 5–6 przy dużej wilgotości powietrza do 2,5–4 w suchych warunkach pustynnych (według Z. Sofera, 1978)

and depleted by 20‰ in hydrogen relative to the isotopic ratios of mother solutions (R. Gonfiantini, J. C. Fontes, 1963). Throughout geological time, however, different processes may result in a variation of the original isotopic composition of gypsum due to recrystallization or diffusion of water into an intact crystal during diagenesis (Z. Sofer, 1978). Finally, evolution of an isotopic composition of a crystallization water reflects important geochemical processes in gypsum genesis, including evaporation, hydration and isotopic exchange, all of which are described by appropriate lines in Figure 1.

E v a p o r a t i o n   l i n e s have a positive slope which depends on salinity and, more distinctly, on atmospheric humidity (Z. Sofer, J. R. Gat, 1975). When sulphates are involved in dehydration-hydration processes, equilibrium water composition is enriched in hydrogen and depleted in oxygen. Accordingly, h y d r a t i o n   l i n e s show a characteristic slope for δD vs $\delta^{18}O$ of about –5 (O. Matsubaya, H. Sakai, 1973; Z. Sofer, 1978). In hydrologically open systems, addition of, or exchange with, external circulating waters involve isotopic fractionation ("mixing"), because the crystallization water of gypsum tends to reequilibrate with the surrounding solution along the m i x i n g   l i n e s.

This paper complements earlier scarce isotopic data (S. Hałas, H. R. Krouse, 1982) and provides new results on the hydrogen and oxygen isotope composition of the crystallization water in the Badenian primary gypsum of southern Poland. They offer an opportunity to recognize relationships between the isotopic composition and the lithofacies variation throughout the gypsum section. The main goals of this study are (1) to discuss the origin of the mother waters, and (2) to

deduce the main geochemical processes influencing the gypsum during its deposition and diagenesis. Two cores with primary (sedimentary) gypsum deposits at depth between 113.9 and 288.8 m from the northern peripheral part of the Carpathian Foredeep were chosen and sampled for the isotopic study (Fig. 2).

GEOLOGICAL SETTING

The Carpathian Foredeep of southern Poland (Fig. 2) was a place of a widespread evaporite sedimentation, which resulted from the restriction of the northern part of the Central Paratethys during the Badenian (Middle Miocene), c. 14 Myr BP (N. Oszczypko, 1996). The facies succession and lateral distribution of evaporites express differentiated sedimentary environments including basin margin, shelf and basin centre. In the northern peripheral part of the foredeep, deposition took place in a system of shallow water lagoons (sub-basins) separated by NW–SE-trending elevations or shoals, located on the shelf (S. Kwiatkowski, 1972; A. Kasprzyk, 1991; B. Kubica, 1992). Resulting sulphate deposits are up to 60 m thick and comprise gypsum and anhydrites accompanied by minor siliciclastic and carbonate deposits (A. Kasprzyk, 1993b). Considering the palaeogeographic pattern at the onset of sulphate deposition on the shelf, of the two gypsum sections studied the core Przyborów 1 is located on the NW prolongation of the local shoal ("central elevation" in A. Kasprzyk, 1991), while the core Strzegom 143 represents the lagoonal setting (Fig. 2).

The middle Badenian evaporites are underlain by differentiated siliciclastic and organogenic carbonate deposits with *Lithothamnium* (lower Badenian), and are succeeded by a thick complex of deeper marine clayey-marly sediments of the upper Badenian and Sarmatian.

GYPSUM LITHOFACIES AND SUCCESSION

South of the Holy Cross Mountains (Fig. 2), gypsum deposits form a laterally extensive succession of different lithofacies (from **a** to **n**), which originated in a wide range of depositional settings, from subaqueous (relatively deep water and shallow water) to subaerial (A. Kasprzyk, 1993a; M. Bąbel, 1996). The gypsum lithofacies recognized in both studied sections may be grouped into three main lithological varieties: (1) selenitic gypsum (*szklica*, *sabre-like*, *skeletal*, bedded), (2) massive — fine-grained gypsum (stromatolitic, laminated, alabastrine, nodular), and (3) clastic gypsum (gypsarenites and gypsrudites) (Figs. 3 and 4; Tab. 1). More detailed descriptive data for each of the component lithofacies is presented elsewhere (A. Kasprzyk, 1991, 1993a). It should be noted on the basis of results of the petrographic study, that these lithofacies have not undergone dehydration-hydration diagenesis and are therefore primary in origin.

The measured and calculated (in brackets) values of δD and δ^{18}O for the crystallization water in gypsum
from cores Przyborów 1 and Strzegom 143

Core	Sample no.	Depth [m]	Lithofacies	δD‰		δ^{18}O‰	
	1	262.0	gypsrudite	−85.5	(−66.8)	−6.4	(−10.4)
	2	264.6	gypsrudite	−74.8	(−55.9)	−6.1	(−10.1)
	3	268.5	gypsrudite	−71.5	(−52.6)	−4.2	(−8.2)
Przyborów 1	4	270.6	gypsrudite	−56.0	(−36.7)	−3.8	(−7.8)
	5	274.6	gypsarenite	−59.2	(−40.0)	−3.4	(−7.4)
	6	276.8	gypsarenite	−44.4	(−24.9)	−1.6	(−5.6)
	7	281.5	stromatolitic gypsum-selenite	−41.2	(−21.6)	+0.1	(−3.9)
	1	114.5	stromatolitic gypsum-selenite	−46.5	(−27.0)	+0.8	(−3.2)
	2	115.5	stromatolitic gypsum	−94.9	(−76.4)	−7.1	(−11.1)
	3	122.6	gypsrudite	−87.5	(−68.9)	−6.6	(−10.6)
	4	126.7	laminated gypsum	−85.6	(−66.9)	−4.9	(−8.9)
	5	130.5	laminated gypsum	−91.3	(−72.8)	−6.2	(−10.2)
Strzegom 143	6	134.3	gypsrudite	−92.3	(−73.8)	−6.6	(−10.6)
	7	136.3	bedded selenites	−70.8	(−51.8)	−2.4	(−6.4)
	8	136.8	stromatolitic gypsum	−93.2	(−74.7)	−7.2	(−11.2)
	9	138.2	stromatolitic gypsum	−76.6	(−57.8)	−6.9	(−10.9)
	10	140.2	bedded selenites	−73.0	(−54.0)	−2.8	(−6.8)
	11	143.5	*sabre-like* gypsum	−76.8	(−58.0)	−3.6	(−7.6)

The succession of lithofacies begins with giant crystal intergrowths (*szklica* gypsum) — layer **a** (Fig. 3). Layers **b** to **e** are composed of bedded (grass-like) selenites with intercalations of alabastrine gypsum and cryptomicrobial laminites (stromatolitic gypsum), and locally (Przyborów 1 core) nodular gypsum is present. These layers are overlain by the *skeletal* and *sabre-like* gypsum (layers **f–i**), consisting of elongated selenitic crystals oriented chaotically or uniformly in the uppermost layer **i** (Figs. 3 and 4). Intercalations of laminated gypsum, several centimetres thick, are common within these deposits. They are succeeded by the alternating layers of laminated and/or stromatolitic gypsum with grass-like selenites (layers **j**, **l** and **m**) and of clastic gypsum (layers **k** and **ł**). The overlying deposits up to 26 m thick are mainly gypsarenites and gypsrudites (layer **n**), showing features of redeposition. The clastic gypsum facies are in places intercalated with clays, stromatolitic gypsum and nodular gypsum. Some layers (**f** and **h** to **ł**) in the Przyborów 1 section and the lower sequence (from **a** to **f**) in the Strzegom 143 section are lacking (Figs. 3 and 4) due to synsedimentary exposure of the area or later tectonic movements (A. Kasprzyk, 1991).

ANALYTICAL PROCEDURES

Eighteen gypsum samples, representative of all gypsum lithofacies throughout the sections studied (Figs. 3 and 4), were selected for isotopic analyses of a crystallization water of gypsum. The samples were crushed, put into L-shaped glass tubes and outgassed in a vacuum line at a temperature below 50°C to avoid the escape of a crystallization water. Then, gypsum was dehydrated in a furnace by slow heating to 400°C (R. Gonfiantini, J. C. Fontes, 1963; S. Hałas, H. R. Krouse,

1982); the released water was collected into a tube frozen by liquid nitrogen. The oxygen isotopic composition of water was determined by equilibration of 1 ml of H_2O with 0.2 μmol CO_2 at 25°C (S. Epstein, T. K. Mayeda, 1953). Analyses were made on a *Nier-type* mass spectrometer with some modifications (S. Hałas, 1979; S. Hałas, Z. Skorzyński, 1980). The hydrogen isotopic composition was analysed on hydrogen gas prepared by reduction on zinc shot at 450°C (M. C. Coleman *et al.*, 1982). The δD was measured on cycloidal mass spectrometer (S. Hałas, 1985). This work was performed at the Institute of Physics, Maria Curie-Skłodowska University in Lublin.

RESULTS AND INTERPRETATION

The analytical results for the water of crystallization in gypsum are presented in the δ-notation relative to SMOW (Standard Mean Ocean Water) in Table 1. The δ-values vary within the wide ranges: $-94.9 \leq$ δD‰ ≤ -41.2 and $-7.2 \leq$ δ^{18}O‰ ≤ 0.8, averaging −73.4‰ for hydrogen and −4.4‰ for oxygen. Precision for these values are 2‰ (hydrogen) and 0.2‰ (oxygen). The fractionation factors $\alpha_D = 0.980$ and $\alpha_{18O} = 1.004$ have been used to determine the isotopic composition of water in which gypsum crystallized. The calculated data are plotted on two lithological gypsum profiles (Figs. 3 and 4). Figure 5 shows the relationship between these values in reference to the world meteoric water line (H. Craig, 1961) for both sections studied.

The marine origin of the Badenian gypsum from the northern peripheral part of the Carpathian Foredeep, based on the sulphur and oxygen isotopic data, has been previously stated by many authors (J. Parafiniuk *et al.*, 1994; S. Hałas *et*
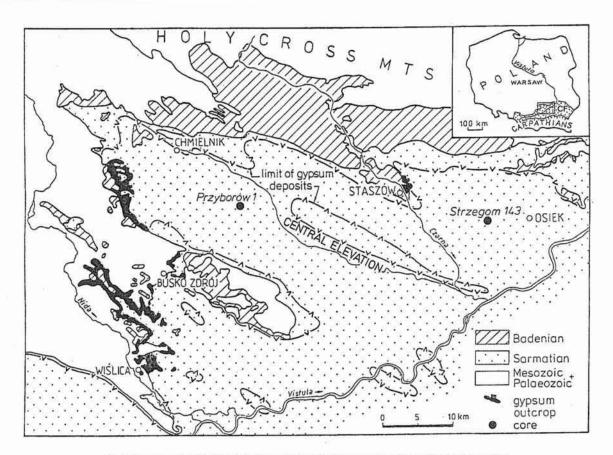
Fig. 2. Location of studied cores in the northern peripheral part of the Carpathian Foredeep (CF)
Lokalizacja zbadanych otworów wiertniczych w północnej peryferyjnej części zapadliska przedkarpackiego (CF)

al., 1996; A. Kasprzyk, 1997, and references therein). The δD values of the crystallization water in all gypsum samples measured for this study are very similar to the previous data reported for the Badenian gypsum (S. Hałas, H. R. Krouse, 1982), whilst the $\delta^{18}O$ values are more differentiated (Tab. 1). These values, however, are distinctly lower than those expected from isotopic exchange interactions during the gypsum crystallization from a marine evaporite water (R. Gonfiantini, J. C. Fontes, 1963). This fact can be explained by: (1) mixing of formation/connate brine with meteoric and freshwater in a depositional environment, resulting generally in isotopic impoverishment of the original brine, and/or (2) isotopic exchange interactions between crystallization water of gypsum and the diagenetic waters.

The hydrogen and oxygen isotopic composition of the crystallization water for various gypsum lithofacies is differentiated (Tab. 1). Selenitic varieties: *sabre-like* gypsum and bedded selenites, including grass-like selenites within the stromatolitic gypsum, show relatively more positive δD and $\delta^{18}O$ values, although they vary in wide ranges: from −76.8 to −41.2‰ and from −3.6 to 0.8‰, respectively. Overall, other gypsum lithofacies (stromatolitic, laminated, gypsarenite, gypsrudite) are isotopically depleted with the δD ranging from −94.9 to −44.4 and the $\delta^{18}O$ from −7.2 to −1.6‰ (Tab. 1). The results obtained for stromatolitic gypsum show a distinct relationship between the measured δ-values for the crystallization water of gypsum and variation in lithology and

chemical composition of these deposits (A. Kasprzyk, 1994). Such relationship may reflect changes in the hydrologic system or kinetics of isotopic exchange interactions, affecting the evaporation and the crystal growth dynamics (C. J. Younge, H. R. Krouse, 1987). On the other hand, however, the average isotope composition of hydrogen and — to a lesser degree — of oxygen for the crystallization water of gypsum is similar to that characteristic of modern shallow ground waters as well as of Tertiary mineralized waters in the northern Carpathian Foredeep, defined by $\delta^{18}O = -10.5‰$ and $\delta D = -73‰$ (K. Osenbrück et al., 1993; J. Szaran et al., 1994, and references therein). These data would suggest isotopic exchange interactions between gypsum and isotopically light diagenetic waters. Main conduits for such ground water input could have been the fracture zones.

Both isotopic components calculated for the mother brine change in a parallel fashion, as shown in Figures 3 and 4. This observation has important implications as to the sedimentary and diagenetic processes involved, which is discussed below. The enrichment in heavy hydrogen associated with the oxygen depletion relative to the local meteoric waters, which is a common isotopic signature of rehydrated secondary gypsum (*cf.* O. Matsubaya, H. Sakai, 1973; Z. Sofer, 1978; A. H. Bath et al., 1987), was recognized for some samples (Fig. 5). However, based on the results of petrographic observations and the sulphur and oxygen isotopic composition, the studied

gypsum deposits are primary and marine in origin and have not been involved in dehydration-hydration diagenesis.

When calculated values for the original brine are compared to the Craig's meteoric water line, three observations are evident (Figs. 3–5): (1) most of the isotopic values fall above the present-day meteoric water trend line, suggesting variable isotopic patterns of connate formation water or meteoric water during late middle Badenian; (2) the different slope of the calculated mother water line is demonstrated for both sections studied, suggesting distinct isotopic signatures of the water, or isotope exchange generated by an interplay of various parameters; and (3) variations in the isotopic values between samples show generally a decreasing-up trend of changes throughout the section.

PRZYBORÓW 1 CORE

In the Przyborów 1 core (Fig. 3), the progressive shift of the δD and $\delta^{18}O$ from relatively high values for the lower samples (nos. 7 and 6) to much lower values in the upper section (samples nos. 1, 2 and 3) suggests that successive isotopic impoverishment of the mother brine took place. This may have resulted from isotopic exchange between either the original evaporite brine and/or the original crystallization water of gypsum and isotopically light meteoric waters. The intensity of isotopic reequilibration is probably expressed as a small step-like variation in δ-values through the profile (Fig. 3). The calculated values for the mother water are located above the present-day meteoric water line (Fig. 5A); the only exception is one sample with the isotopic composition ($\delta D = -21.6\%$; $\delta^{18}O = -3.9\%$) fitting well to this line (sample no. 7 in Tab. 1). The δD vs $\delta^{18}O$ for calculated values plot along a straight line with a steep slope of ≈ 6.7 (Fig. 5A) suggesting mixing of meteoric waters with formation/connate waters (original evaporite brines) of different isotopic compositions under relatively high humidity conditions (Z. Sofer, 1978). The difference between δD values of the mother water and meteoric water lines indicates that solutions to which gypsum reequilibrated during diagenesis must have been largely enriched in heavy hydrogen relative to the local present-day atmospheric precipitation with the mean isotopic composition: $\delta D \approx -70\%$ and and $\delta^{18}O \approx -10\%$ (K. Różański et al., 1993). There is, however, no evidence of dissolution-recrystallization phenomena based on sedimentary structures and microfabrics of gypsum deposits (A. Kasprzyk, 1993a).

STRZEGOM 143 CORE

The δ-values in gypsum samples from the Strzegom 143 core are more variable than those for the Przyborów 1 section discussed above and fall within wide ranges of values ($-94.9 \leq \delta D\% \leq -46.5$ and $-7.2 \leq \delta^{18}O\% \leq 0.8$) (Tab.1). There is a clear relationship between lithology and isotopic data obtained, which has probably palaeoenvironmental implications. In fact, selenitic gypsum samples (nos. 1, 7, 10 and 11) are distinctly isotopically enriched relative to other lithofacies. Thus, the selenitic gypsum seems to preserve more of the original isotopic composition of the crystallization water,
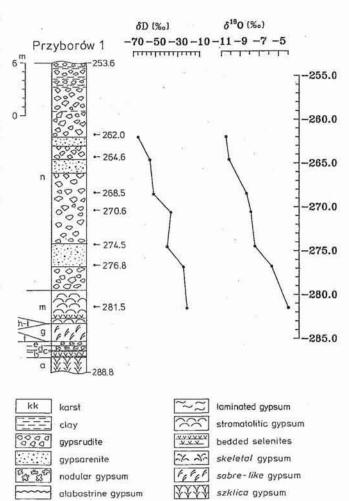

Fig. 3. Isotopic composition of equilibrated crystallization water of gypsum plotted against depth for the Przyborów 1 gypsum section

Zmiany składu izotopowego wody krystalizacyjnej gipsów wraz z głębokością w profilu Przyborów 1 (wartości przeliczone dla solanki macierzystej)

as it has been already suggested by S. Hałas and H. R. Krouse (1982). Most of the fine-grained and clastic gypsum samples show petrographic features, such as granular microfabrics and high porosity, which may have been favourable for the isotopic exchange of an original crystallization water with circulating interstitial waters. Highly negative δ-values of hydrogen and oxygen in some samples (nos. 2, 5, 6 and 8) are thought to be representative of gypsum partly or completely dissolved and reprecipitated, and/or strongly exchanged with D and ^{18}O depleted secondary solutions. Alternatively, but less probably, the δD and $\delta^{18}O$ values calculated for the original brine of different gypsum lithofacies reflect an interplay of various parameters in the sedimentary environment, prior to gypsum crystallization. As such, more positive δ-values for the selenitic gypsum would suggest more concentrated original evaporite brines from which they formed, relative to other gypsum lithofacies (cf. Z. Sofer, 1978; A. Longinelli, 1979; G. N. Dowuona et al., 1992). This interpretation agrees well with the results of previous studies on gypsum lithofacies and Sr geochemistry (A. Kasprzyk, 1991, 1994). In either case, however, the crystallization water of
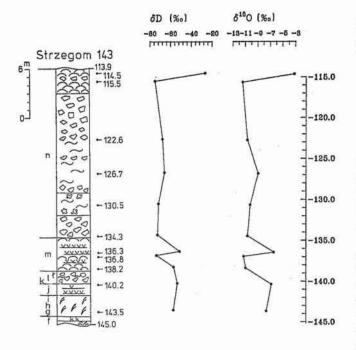
Fig. 4. Isotopic composition of equilibrated crystallization water of gypsum plotted against depth for the Strzegom 143 section
Explanations as in Fig. 3

Zmiany składu izotopowego wody krystalizacyjnej gipsów wraz z głębokością w profilu Strzegom 143 (wartości przeliczone dla solanki macierzystej)
Objaśnienia jak na fig. 3

gypsum for the studied samples depleted in δD and δ^{18}O could continuously reequilibrate with circulating ground waters whenever gypsum came into contact with waters not in isotopic equilibrium with its crystal water.

Distinct changes in lithofacies throughout the section are expressed in a variation of the hydrogen and oxygen isotopic composition between samples, that seems to evolve irregularly but progressively toward the more depleted δ-values (Fig. 4). The anomalously high values at the top of the section may be considered as representative of the original and isotopically enriched mother brine. Thus, the most positive values are related to selenitic crystals preserving most of the original crystallization water unchanged.

When the calculated values of δD and δ^{18}O for the original brine are compared to the present-day meteoric water line, it is evident that selenitic gypsum samples (nos. 1, 7, 10 and 11) are located below the meteoric water line and fall closer to the calculated isotopic composition for the inferred original brines than those representative for other lithofacies (Fig. 5B). The equilibrated δ-values are scattered around a straight line with a slope of ≈ 5 considered as characteristic of humid climatic conditions (Z. Sofer, 1978). The intersection of this line with the meteoric water line would represent the isotopic composition (δD ≈ –60‰; δ^{18}O ≈ –9.2‰), which falls within the range of δ-values for present-day precipitation of relatively cold climate in Central Europe. This could imply that the isotopic exchange of original crystallization water occurred rather recently as a response to climatic cooling, related to Pleistocene glaciation. At that time, exposure and

intensive erosion of Miocene deposits in meteoric regime at the low sea-level stand took place (K. G. Miller et al., 1987; N. Oszczypko, 1996).

DISCUSSION

· The variation in the measured δ-values for the crystallization water in both gypsum sections studied may reflect either (a) formation of gypsum from the connate basin waters with isotopic signatures generated by the general progressive cooling of climate (and indicated by some palaeontological and isotopic records, S. M. Savin et al., 1975; J. Szczechura, 1994), thus favouring gypsum precipitation during late Middle Miocene; (b) changes in the isotopic composition of the input waters into the diagenetic environment with the increasing depth due to mixing of meteoric water and formation/connate water of different isotopic compositions; or (c) variable kinetics of the isotopic exchange. It is quite plausible that an interplay of these different factors took place, prior to the gypsum crystallization or more probably via later isotopic exchange with secondary solutions, resulting in the variation of the isotopic composition between samples. It is clear from the isotopic data, that the original crystallization water of gypsum must have been in isotopic equilibrium with marine water, but it subsequently reequilibrated with meteoric waters toward the more negative δD and δ^{18}O values. There is some evidence, such as the difference in the slope of the calculated mother water line for both studied sections and a hydrogen excess for most studied samples in respect to the local meteoric waters (Fig. 5), suggesting that mixing of the original brine with circulating ground waters of differentiated isotopic compositions took place. In fact, most of the calculated δ-values for the mother brine fall just above the meteoric water line. An alternative possible explanation is to accept that the Badenian meteoric water was enriched in D with respect to the present-day meteoric waters, as shown in Figure 5. As such, this hipothetical line could have climatic implications for the Badenian (Z. Sofer, 1978). It is interesting to note, that this line is also representative of present-day atmospheric precipitation in the Mediterranean climate (Y. Yurtsever, J. R. Gat, 1981), and thus would indicate rather warm and arid climatic conditions during middle Badenian.

On the other hand, however, a progressive depletion in heavy oxygen and hydrogen of the mother brine throughout the gypsum section may express (a) cooling climatic conditions during deposition of gypsum or (b) an isotope exchange trend for the crystallization water of gypsum tending to be in isotopic equilibrium with the input secondary solution. The steep slopes of δD vs δ^{18}O mixing lines (≈ 6.7 and ≈ 5) would suggest crystallization of gypsum under relatively humid climatic conditions. In such environments, mixing of meteoric water with formation/connate water of different isotopic compositions involved isotope exchange interactions between the crystallization water of gypsum and pore solutions. The isotope exchange could take place via two different mechanisms: (1) dissolution and recrystallization, or (2) diffusion of water into the intact crystals, resulting in a new isotopic composition
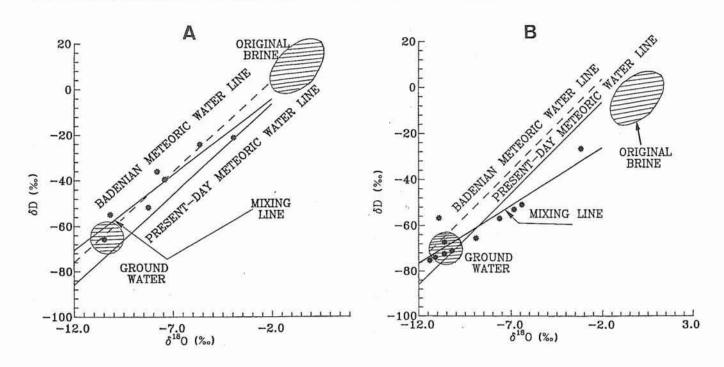
Fig. 5. Crossplot of δD vs δ¹⁸O for the mother brines of gypsum from cores Przyborów 1 (A) and Strzegom 143 (B)

Zależność między wartościami δD i δ¹⁸O solanki macierzystej gipsów w otworach Przyborów 1 (A) i Strzegom 143 (B)

(*cf.* Z. Sofer, 1978; C. Pierre, 1988). Anyway, further investigation is needed for better understanding of this problem.

A large contribution of meteoric water to gypsum beds is thought to be the main trigger force in the water-rock interactions resulting in karst phenomena and mass exchange in the hydrologically open system (*cf.* C. Pierre, 1988; K. Osenbrück *et al.*, 1993). In the structural pattern of the northern Carpathian Feredeep since the late Miocene, gypsum deposits have formed a laterally extensive belt exposed locally to the north and deepening stepwise toward the south (e.g. B. Kubica, 1992; N. Oszczypko, 1996). According to this pattern, the main source areas for the meteoric water supply affecting the gypsum may have been either fracture zones or surficial gypsum exposures owing to local tectonic uplift, erosion and exhumation.

CONCLUSIONS

Hydrogen and oxygen isotope analyses of the crystallization water in Badenian gypsum samples indicate that its original isotopic composition is largely if not completely replaced by the input mixed meteoric/connate waters or the circulating ground waters. The crystallization water of gypsum reequilibrated with isotopically light interstitial solutions

via dissolution and reprecipitation, and mass diffusion. Giant selenitic crystals seem to be less affected by these isotope exchange processes. The δ-values of the original brine, which are located close to the Craig's meteoric water trend line correspond to the equilibrium isotopic compositions of the crystallization water of gypsum with the local ground waters, whilst those values which fall just below this line reflect mixing of the original evaporite brine (sea water) with the input diagenetic water (meteoric water). This is a reason why further isotopic studies aimed to interpret the original (sedimentary) brines of the Badenian gypsum should focus on compact giant crystalline lithofacies unaffected by faulting and/or fracturing (no pathways for circulating ground waters) at relatively large (> 50 m) depths, i.e. below a shallow subsurface karst zone.

Translated by Alicja Kasprzyk

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SKŁAD IZOTOPOWY WODY KRYSTALIZACYJNEJ GIPSÓW W BADENIE W PÓŁNOCNEJ CZĘŚCI ZAPADLISKA PRZEDKARPACKIEGO

Streszczenie

Badania składu izotopowego tlenu i wodoru w wodzie krystalizacyjnej gipsów dostarczają informacji w zakresie pochodzenia i ewolucji roztworów, w których gips krystalizował i podlegał przeobrażeniom w czasie diagenezy (np. Z. Sofer, 1978; A. Longinelli, 1979; S. Hałas, H. R. Krouse, 1982; A. H.

Bath et al., 1987; C. Pierre, 1988; M. El Tabakh et al., 1998) (fig. 1). W tym celu wykonano badania izotopowe badeńskich gipsów pierwotnych pochodzenia morskiego. Do badań wybrano dwa reprezentatywne profile gipsów z północnej peryferyjnej części zapadliska przedkarpackiego, tworzące se-

kwencję różnych litofacji (od **a** do **n**) (fig. 2–4). Zmierzone wartości δD i δ^{18}O zawierają się w szerokim przedziale zmienności: –94,9 ≤ δD‰ ≤ 41,2; –7,2 ≤ δ^{18}O‰ ≤ 0,8 (wartości średnie wynoszą odpowiednio –73,4 i –4,4‰) i wykazują wyraźną zależność od litologii (fig. 3–4; tab. 1). Odmianami najmniej zmienionymi izotopowo są gipsy selenitowe: szablaste i warstwowane, a także kryształy selenitowe w gipsach stromatolitowych. W gipsach tych stwierdzono względnie wysokie wartości δD i δ^{18}O, odpowiednio od –76,8 do –41,2‰ oraz od –3,6 do 0,8‰, najbardziej zbliżone do składu izotopowego solanki macierzystej (fig. 5). Gipsy drobnokrystaliczne i klastyczne wykazują bardziej zróżnicowane i niższe wartości δ: –94,9 ≤ δD‰ ≤ –44,4; –7,2 ≤ δ^{18}O‰ ≤ –2,7. W większości zbadanych próbek zmierzone wartości są wyraźnie niższe od wartości wynikających z frakcjonacji izotopowej w czasie krystalizacji gipsów z wody morskiej (por. R. Gonfiantini, J. C. Fontes, 1963). W obu profilach zaznacza się sukcesywny wzrost wartości δD i δ^{18}O wraz ze wzrastającą głębokością (fig. 3–4), co może być spowodowane: (1) mieszaniem się wód o różnych charakterystykach izotopowych i/lub zmianami klimatycznymi (ochłodzeniem) w czasie depozycji gipsów, lub (2) wtórną wymianą pierwotnej wody krystalizacyjnej z lżejszymi izotopowo wodami podziemnymi lub meteorycznymi w środowisku diagenetycznym. Druga hipoteza, dotycząca wtórnej wymiany, wydaje się bardziej prawdopodobna. Większość wartości δ obliczonych dla roztworu macierzystego leży ponad linią współczesnych wód meteorycznych (fig. 5), co jest prawdopodobnie efektem wzbogacenia izotopowego solanek macierzystych w ciężki wodór, lub odmiennego od współczesnego (wzbogaconego w D) składu izotopowego wód meteorycznych w czasie badenu. Różne współczynniki kierunkowe prostych mieszania (fig. 5) mogą być również związane ze zmiennym tempem wymiany izotopowej między wodą krystalizacyjną a roztworami porowymi (efekt kinetyczny).

Rezultaty wykonanych badań sugerują, że gipsy badeńskie w północnej peryferyjnej części zapadliska przedkarpackiego zawierają wodę krystalizacyjną znacznie, bądź całkowicie wymienioną przez wody meteoryczne późniejszych okresów geologicznych (prawdopodobnie okresu glacjalnego), bądź też cyrkulujące wody podziemne, co jest zgodne z wynikami wcześniejszych badań (S. Hałas, H. R. Krouse, 1982).