Oxygen and sulphur isotopes of gypsum from the Mogilno Salt Dome cap-rock (Central Poland)

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The stable-isotope compositions of oxygen and sulphur from 30 gypsum samples obtained from three drill cores of the Mogilno Salt Dome cap-rock have been analysed; the Mogilno Salt Dome itself is composed of Zechstein evaporites. $\delta^{34}S$ values were measured for SO_4 ions, whereas $\delta^{18}O$ values were measured for SO_4 and H_2O. For the analyses, bulk samples of gypsum ($CaSO_4·2H_2O$) and its dehydrated equivalents ($CaSO_4$) were used. The $\delta^{18}O$ and $\delta^{34}S$ values in SO_4 were analysed using a direct method, but the $\delta^{18}O$ value in H_2O (water of crystallisation) was determined using an indirect method, which influenced the results. The SO_4 appeared to be distinctly enriched in heavy oxygen ($\delta^{18}O = 11.0$–$14.6‰$), which shows that the Zechstein sea was the source of the sulphate; the $\delta^{34}S$ values (10.9–13.6‰) support this conclusion. Variable $\delta^{18}O$ values of the water of crystallisation (–11.3 to 10.7‰) indicate that diagenetic (hydration) processes affected the various samples. Accessory minerals occurring in gypsum probably also influenced the $\delta^{18}O$ values. Five groups of gypsum are distinguished: (1) gypsum in which the $\delta^{18}O$ values of the H_2O are less than –10.2‰ (this gypsum recrystallised in the presence of water enriched in light oxygen isotopes), (2) gypsum in which the $\delta^{18}O$ values of H_2O range between –6.6 and –4.4‰ (interpreted as gypsum in equilibrium with water from the cap-rock), (3) gypsum in which the $\delta^{18}O$ value of the H_2O amounts to 10.7‰ (anhydrite-bearing sandstone near the salt mirror), (4) gypsum in which the $\delta^{18}O$ value of the H_2O ranges between –3.4 and 1.8‰ (samples contaminated by anhydrite; the real $\delta^{18}O$ content is unknown), and (5) gypsum in which the $\delta^{18}O$ value of the H_2O ranges between –8.7 and –6.9‰ (interpreted as gypsum with a mixed isotopic composition due to mixing of water from cap-rock and water enriched in light isotopes of oxygen: recent meteoric water or postglacial water?, or as gypsum formed in a warm interval when the groundwater was somewhat enriched in heavy isotopes of oxygen if compared with the groundwater at present).

INTRODUCTION

Salt diapirs have been the objects of salt mining since the 19th century, but only during the past 30 years they have been investigated and explored in detail as potential hosts for a repository for all kinds of radioactive waste as well as for underground storage of oil and gas by the petroleum industry (Jackson and Seni, 1984; Kreitler *et al*., 1985; Posey and Kyle, 1988; Werner *et al.*, 1988; Bornemann and Bräuer, 1999; Klinge *et al*., 2002; Brewitz and Rothfuchs, 2007).

Cap-rocks cover the tops of salt domes; they are integral parts of the salt bodies, being the products of a sequence of processes near the salt mirror, on top of the salt diapirs. In this salt-dissolution zone, salt rock comes in contact with fresh water or just an NaCl-undersaturated solution, and the rock salt becomes dissolved. Rock salt always contains some impurities:

anhydrite (in particular), and locally carbonates (calcite, dolomite, magnesite), clay minerals and ferrous compounds. All this material, being less soluble, is left on top of the salt body; in the course of time, it becomes compacted and transformed into a rocky cover, the so-called cap-rock. The main diagenetic process is the hydration of anhydrite, transforming it into gypsum, so that a salt body is often covered by a gypsiferous cap-rock.

Some of the cap-rocks have a long-lived diagenetic history, e.g., surface exposure and erosion, fracturing, internal circulation of meteoric water or hydrothermal fluids, metasomatism, and glaciation (Posey and Kyle, 1988; Prikryl *et al*., 1988; Werner *et al*., 1988; Jaworska and Ratajczak, 2008). A key for understanding this history might be a study of the isotopic composition of the sulphates and water of crystallisation that built the gypsum (gypsiferous cap-rock). Isotopic analyses commonly provide information about the conditions and the stages of hydration of the sulphates (Pierre and Fontes, 1978; Hałas

and Krouse, 1982; Kasprzyk and Jasińska, 1998; Peryt *et al*., 2002) and may, in the case of cap-rock, help to reconstruct the processes that have occurred near the salt mirror, particularly the water/sulphates interactions. Examples of such investigations are the studies of the Gyp Hill and Oakwood Domes in Texas (Kreitler and Dutton, 1983) and the Wapno Salt Dome in Poland (Jaworska, 2010).

One of the greatest hazards in mines, including salt mines, are inflows of water; cap-rock, being a cover of the salt body, tends to protect the salt quite well against erosion and groundwater, but not always. Inflow may occur particularly when the cap-rock is partly damaged, by nature or by human activity (see Zuber *et al*., 2000). The results of cap-rock research should be taken into consideration when deciding about the positioning in a salt structure of a salt mine, a repository for radioactive waste or a facility for underground storage of oil or gas.

The purpose of this research was to analyse the $\delta^{18}O$ layout of the crystalisation water of a cap-rock gypsum and assess whether the $\delta^{18}O$ value the same over in the whole cap-rock section or whether it shows different values for different levels. The answer to this question has practical means:

– similar $\delta^{18}O$ values can indicate intense fracturing/karst formation of the cap-rock, subterranean/ground/sub-surface water penetration through it and isotopic exchange between the gypsum crystallisation water and the water from the fractures, resulting in isotopic equilibration;

– variable values of the $\delta^{18}O$ isotope compositions of gypsum crystallisation water may indicate multi-stage

cap-rock genesis. It also allows determination of the type of water with which sulphates forming individual cap-rock parts had contact with.

GEOLOGY

Salt domes belong to the most characteristic structural elements of the Zechstein deposits in the Polish Basin (Fig. 1). The axial zone of the basin has a NW–SE orientation and is called the Mid-Polish Trough (MPT). It is a part of the Southern Permian Basin of Western and Central Europe (Ziegler, 1990; Dadlez *et al*., 2005; Doornenbal and Stevenson, 2010).

The MPT developed along the NW–SE trending Teisseyre-Tornquist Zone during the Permian to Cretaceous (Pożaryski and Brochwicz-Lewiński, 1978; Ziegler, 1990; Dadlez, 1997; Guterch and Grad, 2006); it became filled with a succession of siliciclastic deposoits, carbonates and evaporites (in the Zechstein) several kilometres thick. The Zechstein deposits were buried by Triassic, Jurassic, Cretaceous and Cenozoic strata, while a complex system of more than 90 salt structures evolved simultaneously in the Polish Basin (Dadlez *et al.*, 1998; Krzywiec, 2006). They are of various size and occur in various levels of Mesozoic rocks in which the salt had intruded (Fig. 1). Ten of the salt diapirs cut the upper denudation or structural surface of the Mesozoic, and intrude into the Cenozoic cover.

The Mogilno Salt Dome (MSD) is the only one that reaches the present-day surface. The development of this structure oc-
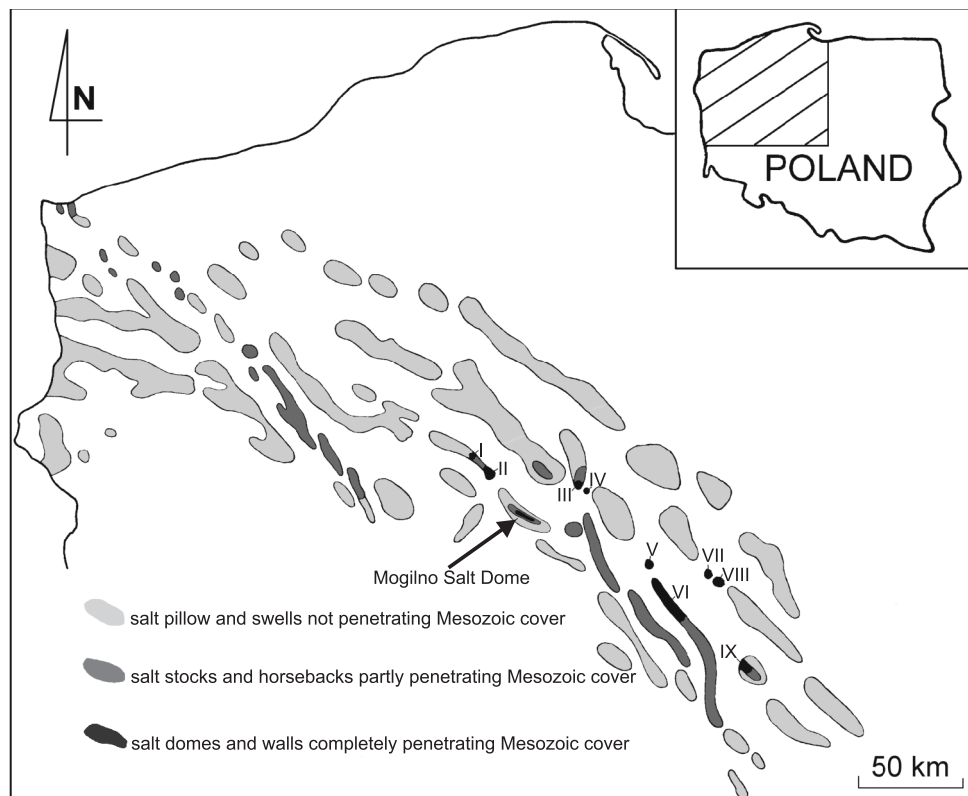
Fig. 1. Location map of the Mogilno Salt Dome and other salt structures in Poland (based on Dadlez, 1997)

I – Wapno Salt Dome, II – Damasławek Salt Dome, III – Inowrocław Salt Dome, IV – Góra Salt Dome,
V – Izbica Kujawska Salt Dome, VI – Kłodawa Salt Dome, VII – Lubień Salt Dome,
VIII – Łanięta Salt Dome, IX – Rogoźno Salt Dome
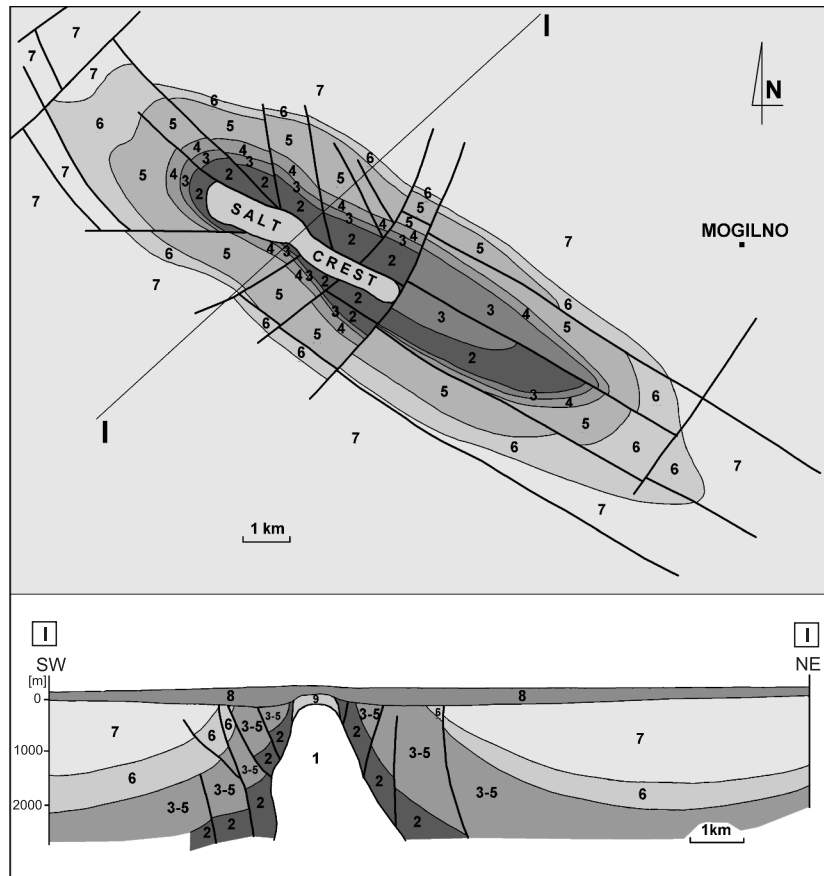
Fig. 2. Geological sketch-map of the Mogilno Salt Dome structure without Cenozoic deposits, with geological cross-section (Wilkosz, 2005, modified after Sokołowski, 1966)

1 – Zechstein rock salt, 2 – Upper Triassic, 3 – Lower Jurassic, 4 – Middle Jurassic, 5 – Upper Jurassic, 6 – Lower Cretaceous, 8 – Cenozoic, 9 – cap-rock

curred in three main phases (Wilkosz, 2005), forming a pillow, a diapir and a post-diapir structure, respectively. Halokinesis started during Mid to Late Triassic times. A thick salt pillow was formed during the Late Triassic to Early Cretaceous. The diapir stage was reached in the Early Cretaceous and diapirism continued during the Paleocene and late Eocene. The post-diapir stage began in the late Eocene to early Oligocene and has continued to the present.

The MSD is located in Central Poland (Fig. 1). It is about 30 km long, up to 7 km wide, and up to 6 km high (Fig. 2); it stretches in a NW–SE direction. At present, this dome is used for gas storage and salt mining (Czapowski and Bukowski, 2010). It is a typical diapir with a central zone where a small salt crest rises up. This asymmetric form is about 5 km long, and up to 1 km wide; it intrudes the Cenozoic cover. The salt crest consists of a sequence of PZ2 (Stassfurt) and, on the flanks, PZ3 (Leine) and PZ4 (Aller) deposits. Characteristic of this structure is the vertical arrangement of strata of the three Zechstein salt cycles. The internal structure of the salt body is complex, including folds with vertical, steeply inclined and overturned axes.

The salt crest is surrounded by Triassic, Jurassic and Cretaceous deposits. The Mesozoic deposits in the area of the MSD show a distinct increase in thickness from the centre of the dome to its periphery. Numerous hiatuses occur in the elevated parts of the structure.

The salt crest has a mantle of cap-rock resting on the top of the salt core (Wilkosz, 2005; Wilkosz *et al.*, 2006). This cap-rock varies in thickness, lithology and morphology of the top surface. The irregular topography of the top results in a number of outcrops of the salt crest. The cap-rock immediately under the Cenozoic cover is about 5 km long and varies in width from 250 to 750 m. Its thickness ranges from 77 to 190 m, most frequently from 130 to 170 m. The upper surface of the cap-rock is undulose, with height differences exceeding 100 m, from 30.4 m beneath sea level (b.s.l) to 78 m above sea level (a.s.l.). Two areas, situated in the NW and SE parts of the dome, contain cap-rock above 70 m a.s.l.; these areas are separated by an area where the central part of the cap has a maximal height of 30.4 m b.s.l.

The lithology and internal structure are interpreted mainly on the basis of cores from boreholes M III, M IX and M XIII (Fig. 3A, B). On this basis, the following five rock types and deposits building the so-called "gypsiferous cap" covering the salt crest of the MSD have been distinguished.
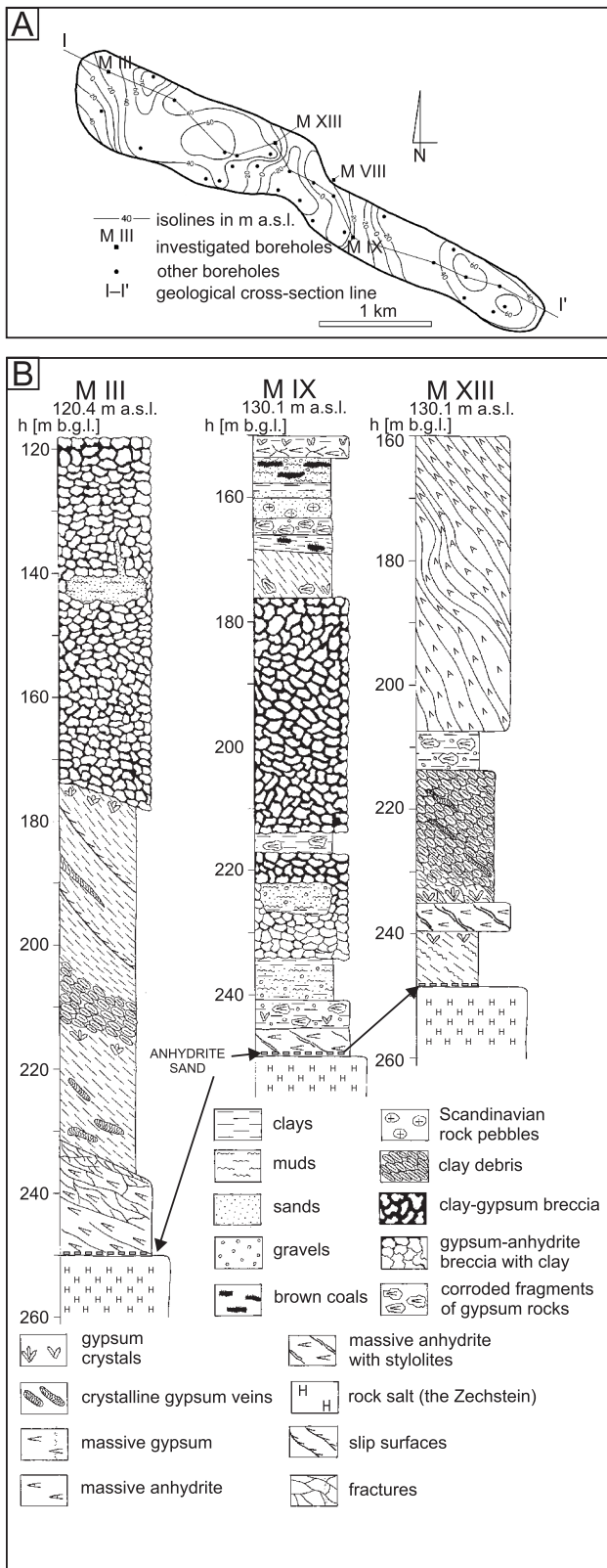
Fig. 3A – topographic surface of the Mogilno Salt Dome cap-rock, with location of the geological cross-section I–I' (Wilkosz, 2001); B – geological profiles of the drill cores from the boreholes M III, M IX and M XIII (Wilkosz, 2005)

1. The main (almost exclusive) component of the cap-rock is gypsum, which occurs in variable shape and size. It forms auto-, hypidio- and xenomorphic crystals, and shows fine-, medium and coarse-crystalline textures. Two specific forms of gypsum are present; lenticular crystals (Fig. 4) and selenite (Fig. 5). Auto- and hypidio-, coarse- to medium-crystalline gypsum dominates near the bottom of the cap-rock, which gradually becomes finer and more xenomorphic upwards.

2. Anhydrite is the main component at the bottom of the cap-rock: it constitutes a layer of anhydrite-bearing sandstone about 20–40 cm thick (Figs. 3B and 4) in boreholes M III, M IX and M XIII, at a depth of 245–250 m below ground level (b.g.l.), just above the salt mirror.

3. Sulphate rocks (Zechstein anhydrites – Fig. 6 – chemically transformed into gypsum in the outer parts of the blocks) are locally intensively corroded and fractured (fractures are frequently healed with gypsum and carbonates). This facies shows a wide array of textures, ranging from cloudy amaeboid-xenotopic with anhydrite relics to idiotopic without anhydrite relics.

4. Sulphate-terrigenous rocks in the form of a breccia of gypsiferous clay (Fig. 7) were formed by complete chemical transformation of anhydrites into gypsum, their secondary dissolution, fracturing and gravitational and tectonic redeposition.

5. Allochthonous fillings of karst caverns, tectonic slits and collapse forms comprising Oligocene sands and muds, Miocene and Oligocene sands and brown coal and Quaternary sands with gravel and small boulders of crystalline rocks.

MATERIAL

Thirty representative calcium-sulphate core samples (29 gypsum and 1 anhydrite) were analysed for their $\delta^{18}O$ and $\delta^{34}S$ values. They are from three boreholes (Mogilno III, Mogilno IX, Mogilno XIII); 9 samples from Mogilno III, 14 from Mogilno IX and 7 from Mogilno XIII. The samples represent all types of gypsum and derive from depths of the cap-rock from 150.4 m to 249.5 m b.g.l. Some samples included carbonate (calcite or magnesite, Fig. 8) and inclusions of anhydrite in the gypsum crystals.

METHODS

The gypsum samples were analysed for their $\delta^{18}O$ and $\delta^{34}S$ values by Dr. S. Poulson, at the University of Nevada (Department of Geological Science, Reno). The values were measured using an *Eurovector model 3000* (elemental analyser to a Micromass IsoPrime stable-isotope ratio mass spectrometer) in a continuous flow mode.

Two methods were applied. The first was used to determine the $\delta^{34}S$ value (*cf.* Giesemann *et al.*, 1994); V_2O_5 was added to the sulphate samples as a combustion aid. The values found are expressed in per mil, relative to the Vienna-Canyon Diablo Troilite standard (V-CDT); the analytical precision is ±0.2‰. The second method (*cf.* Kornexl *et al.*, 1999) was used for the $\delta^{18}O$ analysis; nickelised graphite was added to each sample to promote CO formation. These values are also expressed in per
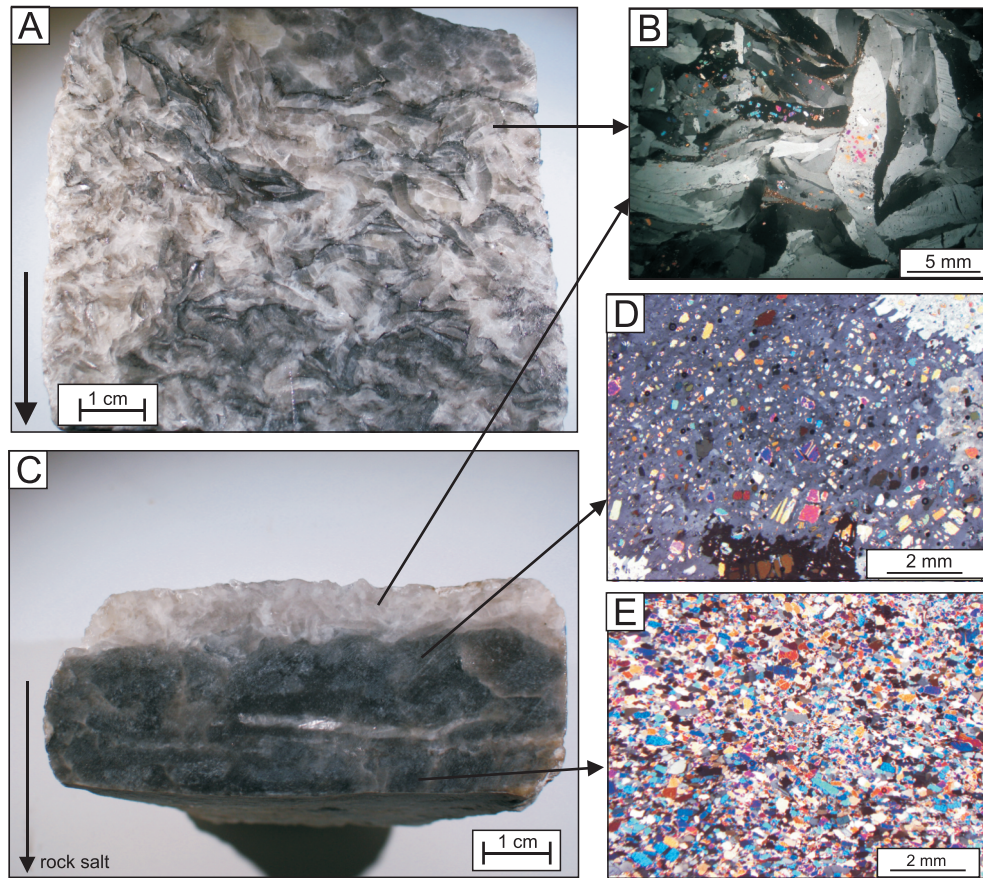
Fig. 4. Micro- and macrophotos of rocks from the contact zone between the salt mirror and the cap-rock

A – lenticular crystals of gypsum (borehole M III, 249.3 m b.g.l.); **B** and **D** – gypsum with anhydrite sand relics (borehole M III, 249.2–249.5 m b.g.l.); **C** – anhydrite sand from the bottom of the cap-rock directly on the salt mirror (borehole M III, 249.5 m b.g.l.); **E** – anhydrite sands level; crossed polars

Fig. 5. Selenite gypsum generally occurs in tectonic slits and karstic caves; single crystals have lengths to 10 cm (M XIII, 237.6 m b.g.l.)

mil, relative to the Vienna-Standard Mean Ocean Water (V-SMOW); the analytical precision is ±0.4‰.

The $\delta^{18}O$ values were measured twice for both the bulk sample ($CaSO_4\cdot2H_2O$) and for its dehydrated form ($CaSO_4$ residue after dehydration). The isotopic composition of the oxygen in the bulk sample ($CaSO_4\cdot2H_2O$) is a mixture of $\delta^{18}O$ from the SO_4 and from the H_2O (crystallisation water). In order to investigate the differences of the $\delta^{18}O$ content in both components, the gypsum powder was therefore slowly heated (to eliminate water) under vacuum to 450°C for 30 minutes (see: Dowuona *et al.*, 1992). The $\delta^{18}O$ values in the dehydrated form in SO_4 were measured directly by mass spectrometry, whereas the isotopic composition of the water of crystallisation was determined indirectly, by calculating the mean $\delta^{18}O$ value of the bulk gypsum sample ($CaSO_4\cdot2H_2O$) and its SO_4 component (from the residue after dehydration). The results obtained using the indirect method have not been verified by a direct method.

RESULTS

SULPHUR

The $\delta^{34}S$ values in the gypsum cap-rock samples investigated show a range from 10.9 to 13.6 ±0.2‰ and thus indicate
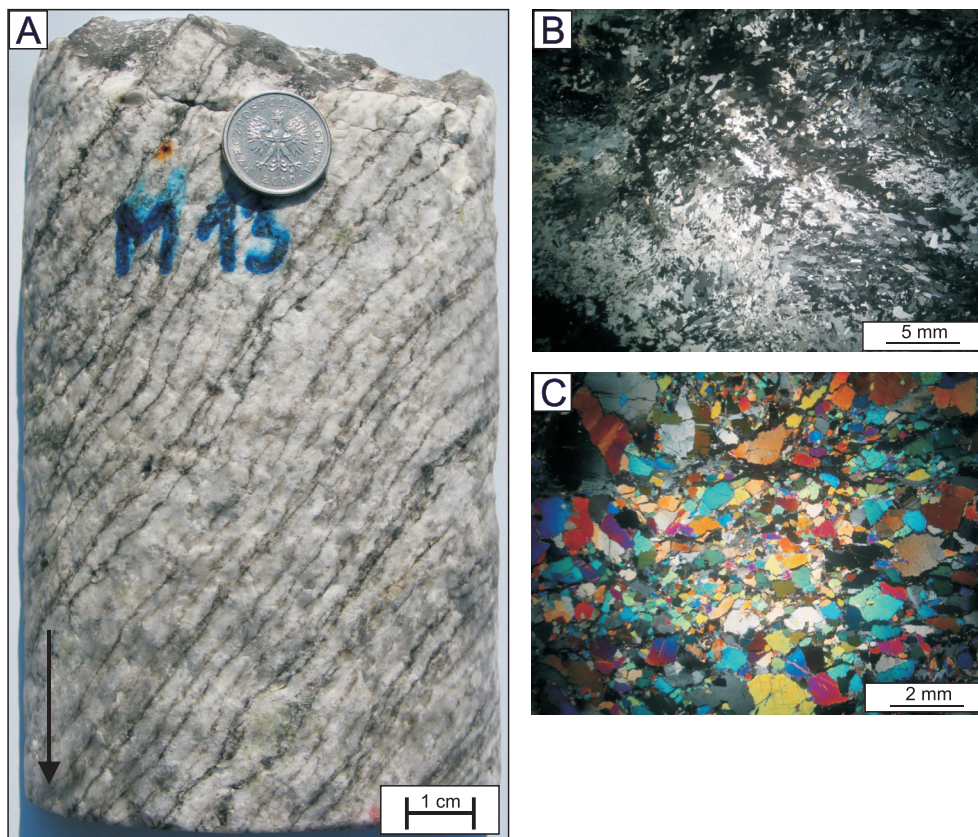
Fig. 6. Zechstein anhydrite (M XIII, 192 m b.g.l.)

A – detached block of Main Anhydrite incorporated in the cap-rock; **B** – the outer parts of the block are completely transformed into gypsum, **C** – in the central parts of the block anhydrites relics are preserved; crossed polars
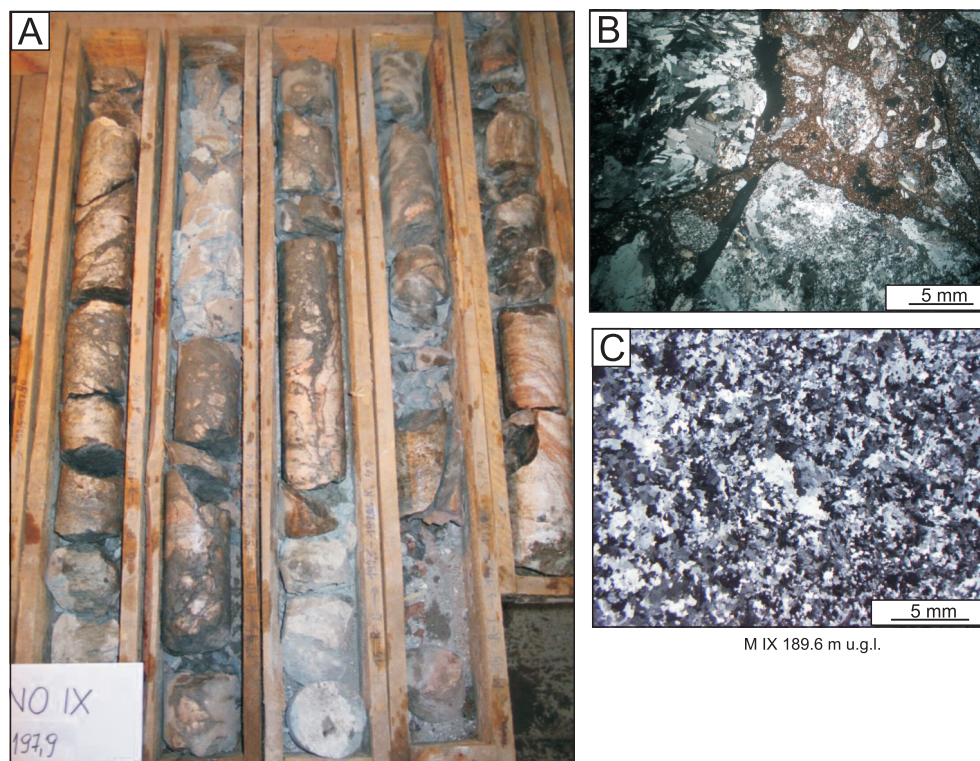
Fig. 7. Breccia of sulphate rocks (A) – M IX, 192.6–197.9 m b.g.l.;
B, C – blocks of gypsum rock, clay and mud material; crossed polars
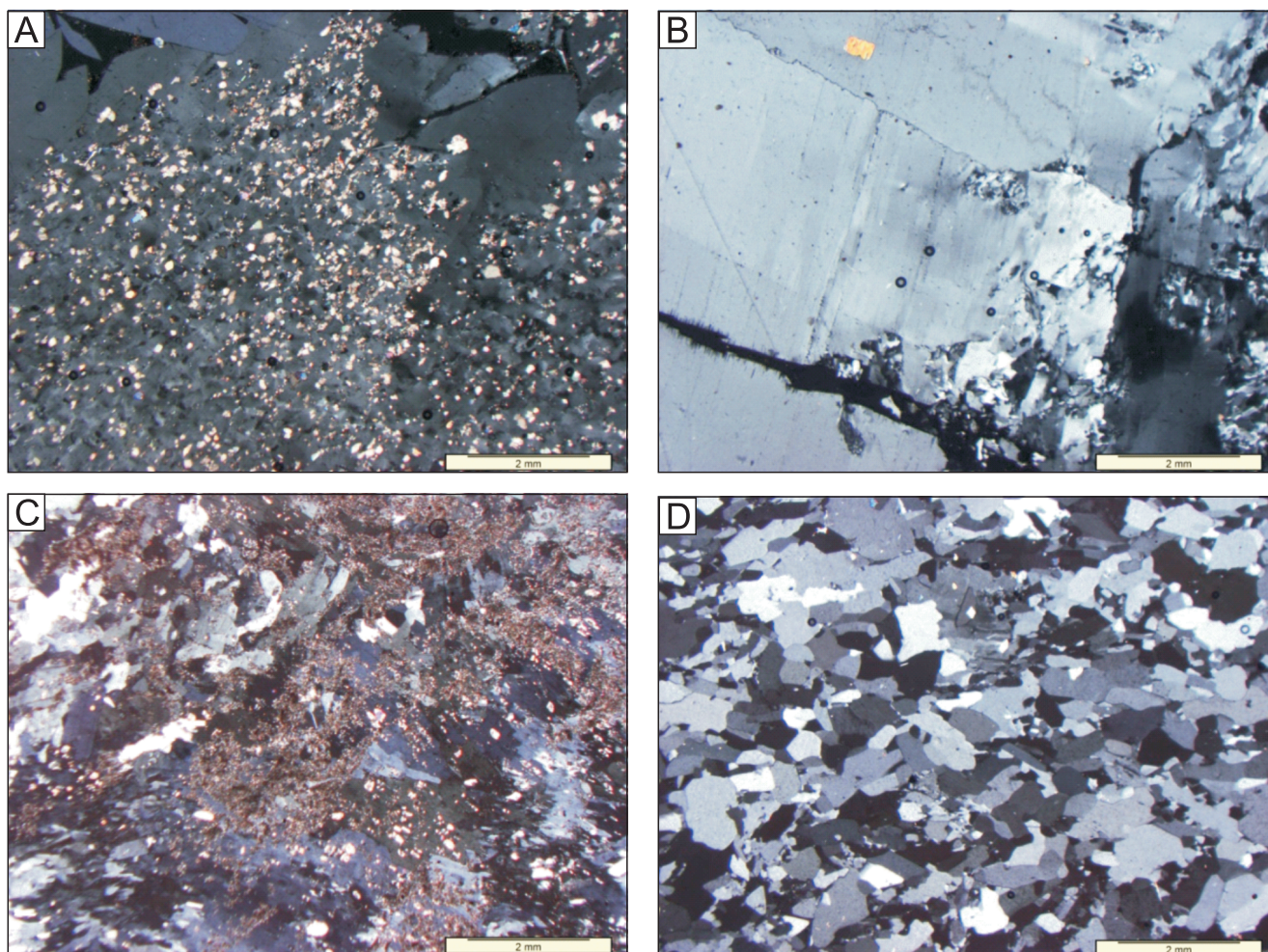
Fig. 8. Microphotos from thin sections of gypsum samples

A – lenticular gypsum with calcium (3–5%), M IX, 153 m b.g.l.; **B** – lenticular gypsum without calcium, M IX, 153.5 m b.g.l.; **C** – fine-crystalline gypsum with magnesite (10%), M XIII, 174.1 m b.g.l.; **D** – fine-crystalline gypsum with magnesite (1%), M XIII, 198.1 m b.g.l.; crossed polars

that these sulphates are distinctly enriched – with respect to V-CDT – in the heavy isotope; the mean $\delta^{34}S$ value is 11.9‰ for the core samples from Mogilno III, 11.8‰ for the core samples from Mogilno IX and 11.6‰ for the core samples from Mogilno XIII (all ±0.2‰; Table 1).

OXYGEN

The $\delta^{18}O$ values for the SO_4 from the gypsum samples range from 11.0 to 14.6‰; the mean $\delta^{18}O$ value is 13.5‰ for the core samples from Mogilno III, 13.0‰ for the core samples from Mogilno IX and 13.1‰ for the core samples from Mogilno XIII.

The $\delta^{18}O$ values for the water of crystallisation from the gypsum samples are highly variable and range from –11.3 to 10.7‰; their mean $\delta^{18}O$ value is –4.9‰ (–5.7‰ if the two gypsum samples enriched in anhydrite are excluded) for the core samples from Mogilno III, –4.8‰ (–6.0‰ if the sample of anhydrite sandstone is excluded) for the core samples from Mogilno IX and –8.3‰ for the core samples from Mogilno XIII (Table 1).

DISCUSSION

SULPHUR

Sulphur isotopes are useful indicators of the origin of sulphates because they preserve their primary isotopic composition very well. Diagenesis (hydration/dehydration), reduction and weathering do not lead to considerable fractionation of the sulphur isotopes; these factors can jointly make a difference only of about –1.3‰, which can commonly be neglected (Holser *et al.*, 1989; Worden *et al.*, 1997; Hoefs, 2004).

The $^{34}S/^{32}S$ ratio of present-day sulphates (marine evaporites) in oceanic water is fairly constant (+20 ±0.5‰ with respect to V-CDT; Pierre, 1988). The fractionation distinguishing dissolved calcium sulphates in oceanic water from gypsum or anhydrite is negligible (Thode and Monster, 1965; Raab and Spiro, 1991), so that recently deposited sulphates in marine evaporite basins have the same $\delta^{34}S$ value as the sea water (Claypool *et al.*, 1980). The $\delta^{34}S$ values for calcium sulphates in the geological past have changed, but the general trends (S-isotope age curve), including minor oscillations (Nielsen,

Results of isotope analysis with comments

Sample	Depth [m b.g.l.]	Comment	Gypsum–$\delta^{18}O$ V-SMOW [‰]	CaSO$_4$–$\delta^{18}O$ V-SMOW [‰]	H$_2$O–$\delta^{18}O$ [‰]	$\delta^{34}S$ V-CDT [‰]	Major, minor, trace components:calcite (C), magnesite (M), anhydrite (A)	H$_2$O–$\delta^{18}O$ comment
M IX	150.4		8.4	13.6	−2	12.4	no data	
	152.25		6.8	13.3	−6.2	11.7	no data	
	153		8,1	13.8	−3.3	12.2	C − 5%	overstated value
	153.5		7.3	13.3	−4.7	12.3	C <1%	actual value
	175.5		7.1	13.6	−5.9	12.1	C, A<1%	actual value
	180.7		7.3	13.8	−5.7	13.6	no data	
	183.1		7,1	14.6	−7.9	11.6	no data	
	189.6		5.9	12	−6.3	11.3	–	actual value
	191.1		7.7	14	−4.9	11.4	C, M − 10–15%, A − 3%	problematic
	213.2		5.8	12.2	−7	11.5	A, C −1%	actual value
	229.9		6.1	12.6	−6.9	11.5	C <1%	actual value
	249.3		5.5	12.6	−8.7	11.3	A − 15%	overstated value
	249.35		4.5	11	−8.5	11	A − 15%	overstated value
	249.5		11.7	12.2	10.7	10.9	anhydrite-bearing sandstone	
Average M IX			7.1	13	−4.8	11.8		
M III	239.3		6.5	12.7	−5.9	11.5	–	actual value
	240.7		6.3	13.3	−7.7	11.6	–	actual value
	244	lenticular	7.9	14.6	−5.5	12.4	–	actual value
	244	massive	7	13.4	−5.8	11.9	A − 1%	actual value
	244.3		7.2	13.4	−5.2	11.9	–	actual value
	244.9		7.6	13.1	−3.4	11.9	C − 5%	overstated value
	244.9		6.9	13.4	−6.1	11.8	A − 30%	overstated value
	249.5	lenticular	7.8	14.6	−5.8	12.3	A − 10–15%	overstated value
	249.5	massive	9.3	13.1	1.7	11.6	A − 50%	high overstated value
Average M III			7.4	13.5	−4.9	11.9		
M XIII	174.1		5.1	13.3	−11.3	11.7	M − 10%	probably no influence
	175.35		4.8	12.6	−10.8	11.5	M − 10%	probably no influence
	186.2		5.8	12.9	−8.4	11.7	M − 10%	probably no influence
	198		6.1	13.5	−8.7	11.6	C − 1%	actual value
	242.7		6.2	12.6	−6.6	11.3	A − 1%	actual value
	242.7	vein	6.9	13.6	−6.5	11.5	A − 1%	actual value
	244.8		6.7	13.1	−6.1	11.6	–	actual value
Average M XIII			5.9	13.1	−8.3	11.6		

A – anhydrite, C – calcite, M – magnesite

1989), are well-known (see Claypool *et al*., 1980; Holser *et al*., 1989; Strauss, 1999, 2004).

Zechstein evaporites are characterized by minimum $\delta^{34}S$ values for the Phanerozoic (close to 10–12‰; see Garcia-Veigas *et al.*, 2011). The values found for the gypsum samples from investigated the Mogilno samples (10.9–13.6‰) are characteristic of late Permian sulphates; the isotopic composition of the sulphur in these samples (1.65‰) reflects, taking into consideration the fractionation factor (Thode and Monster, 1965; Pierre, 1988), the isotopic composition of Zechstein brines. This result is consistent with the sulphur-isotope data for Zechstein evaporites from Northern Germany (9.7–12.6‰: Kampschulte *et al.*, 1998), northeastern Poland (polyhalite)

(10.0–12.1‰; Peryt *et al.*, 2005), southwestern Poland (9.4–13.3‰; Vovnyuk and Czapowski, 2007) and West Poland (9.6–12.6‰ in anhydrite; Peryt *et al.*, 2010).

OXYGEN

In comparison to the sulphur analysis, the oxygen-isotope composition of gypsum is complex, because it consists of two "kinds" of oxygen: from SO$_4$ (sulphate ion) and H$_2$O (water of crystallisation). Both calcium sulphates and their crystallisation water are commonly formed in isotopic equilibrium with the mother brine (Sofer, 1978), but this may change during

diagenesis. The rate of isotope exchange between a sulphate (SO_4) and surrounding water is extremely low (Lloyd, 1968; Holt and Kumar, 1991), so that the isotopic composition in sulphate ions is quite stable; it barely changes and remains in equilibrium with the mother brine of the directly precipitated calcium sulphate.

It is different for the water of hydration. Gypsum easily loses its original water of crystallisation during contact with sea water or groundwater. Recrystallisation, dehydration and hydration (sometimes repeated) affect the primary isotopic composition of the gypsum crystallisation water due to diffusion of water of whatever origin (meteoric, open-marine, interstitial brine or a mixture of these) into the crystal. Changes in the $\delta^{18}O$ value of the water of crystallisation of calcium sulphates may thus originate from the absorption of "new" water.

Modern ocean water contains sulphates of which the $\delta^{18}O$ values amount to 9.5 ±0.5‰ with respect to V-SMOW (Longinelli and Craig, 1967). During recrystallisation of oceanic sulphates, the $\delta^{18}O$ value rises by 3.5–3.6‰ (the fractionation factor; Lloyd, 1968; Pierre, 1988) with respect to the mother water; the gypsum water of hydration is then enriched by about 4.0‰ (Gonfiantini and Fontens, 1963). This implies that the $\delta^{18}O$ value of evaporites that precipitated from sea water should be 13.0 ±0.5‰ (13.5 ±0.5‰ in the crystallisation water of gypsum).

The $\delta^{18}O$ value of marine sulphates in the geological past has been more stable than that of sulphur. The $^{18}O/^{16}O$ ratio in evaporites has changed slightly over geological time and the general trend is known. The resultant O-isotope age curve can be used to determine the time of evaporite precipitation, and Zechstein evaporites show, like the $\delta^{34}S$ values, a minimum $\delta^{18}O$ value for the Phanerozoic, close to 10‰ (see Claypool *et al.*, 1980). This is consistent with the oxygen-isotope data for Zechstein evaporites from northeastern Poland (polyhalite) (10.0–13.5‰; Peryt *et al.*, 2005), southwestern Poland (9.4–10.4‰; Vovnyuk and Czapowski, 2007) and West Poland (9.4–15.5‰ in anhydrite; Peryt *et al.*, 2010).

The data shown in Table 1 indicate that the oxygen-isotope composition of sulphate ions (SO_4) and water of crystallisation (H_2O) of gypsum are very different. The $\delta^{18}O$ value in SO_4 from the Mogilno gypsum samples ranges from 11.0 to 14.6‰ (Fig. 9). The measured ratio corresponds to the value known for precipitated calcium sulphates in the isolated evaporite basin of the Zechstein sea and demonstrates the marine origin of this salt.

The $\delta^{18}O$ values in the water of crystallisation from the Mogilno gypsum samples range from –11.3 to +1.7‰ (mostly between –8 and –5‰). This gypsum is secondary: it does not consist of primary calcium sulphates that precipitated from solution but rather of hydrated anhydrites; consequently, their water of crystallisation is not in isotopic equilibrium with the mother brine. The variable $\delta^{18}O$ values of the H_2O indicate that the calcium sulphates have been in contact with non-marine (meteoric and/or ground) water that was enriched in light isotopes during the various stages of diagenesis that formed the cap-rock.

The Mogilno cap-rock formed from the Cretaceous on, when the salt intruded the Mesozoic overburden, reaching the zone of percolating groundwater. The salt then started to go into solution, and the residue (anhydrite sand) started to trans-
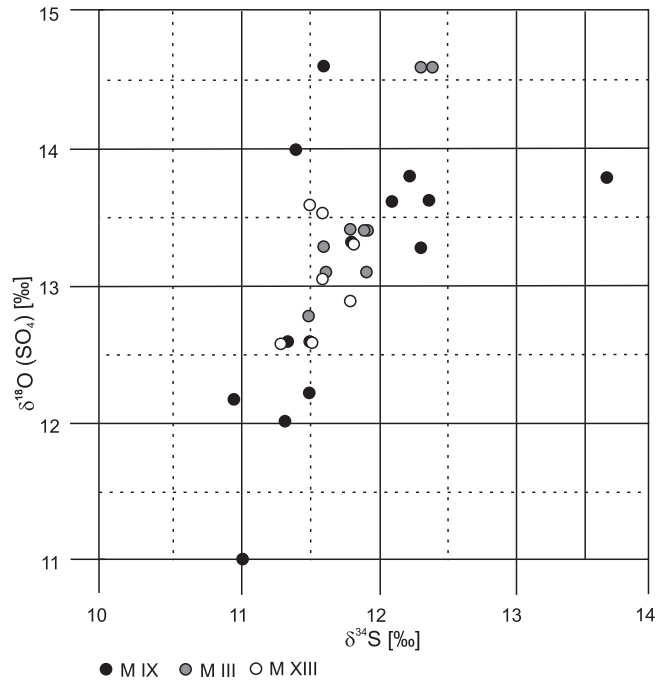

Fig. 9. Values of $\delta^{34}S$ *vs.* $\delta^{18}O$ of residual sulphate depth – 191.1 (m b.g.l.)

form into gypsum. The formation of the incipient cap-rock continued and karst processes affected the material during that time-span; this enabled "new" water, from the surface or the surrounding diapir, to penetrate the cap-rock and the gypsum underwent recrystallisation; the water of hydration then reached a new equilibrium. An assumption has been made that in the case of the gypsum samples, the crystallisation water $\delta^{18}O$ values correspond to the meteoric water $\delta^{18}O$ values; the sulphates underwent hydration under the influence of meteoric water, and therefore the crystallisation water of gypsum is in isotope equilibrium with the meteoric water.

Analyses of the crystallisation water of the gypsum from the Mogilno cap-rock give results that are comparable to those of the analyses of water of crystallisation from the cap-rock of the Gorleben Salt Dome (Herbert *et al.*, 1990), where the $\delta^{18}O$ values in the H_2O of the gypsum samples range from –12.4 to –5.2‰, and of the Wapno Salt Dome (Jaworska, 2010), where the $\delta^{18}O$ values in the H_2O of the gypsum samples range from –13.1 to –5.6‰.

In the Polish Lowland area, the mean isotopic composition of oxygen in modern meteoric water and in recent infiltration water ranges, as a rule, from –10.2 to –9.2‰ (d'Obryn *et al.*, 1997; Duliński *et al.*, 1997). During ancient times of low temperatures such as the Pleistocene, as well as immediately after cold intervals, the groundwater (derived from melt water) was enriched in the light oxygen isotope, so that its $\delta^{18}O$ values were more negative than those of the water from warm and hot times such as the Paleogene and Neogene, when the groundwater became enriched in the heavy oxygen isotope (Duliński *et al.*, 1997). The stable-isotope composition of water collected from the Mogilno boreholes shows a significantly larger enrichment in the heavy oxygen isotope than is to be expected for infiltration water in this part of Poland (Górski and Rasała,

2008). The δ^{18}O values of water from the Kg-1 and Kp-2 bore-holes were (in 2005) –4.3 and –6.6‰ with respect to V-SMOW, accordingly.

The δ^{18}O analyses (using the indirect method) of water of crystallisation in the Mogilno gypsum samples suggest the fol-lowing five groups of calcium sulphates (Fig. 10):

1. Two samples in which the δ^{18}O values of the H_2O are less than –10.2‰; this gypsum was recrystallised in the presence of water enriched, in comparison to recent meteoric water, in the light isotopes of oxygen. This implies that these gypsum sam-ples (i.e., this part of the cap-rock) came in contact with water supplied during cooler time-spans such as, possibly, the Pleis-tocene. The δ^{18}O values of this crystallisation water probably reflect the $^{18}O/^{16}O$ ratio of postglacial meltwater;

2. A group of 15 samples in which the δ^{18}O values of H_2O range between –6.6 and –4.4‰; this gypsum was recrystallised in the presence of water from the cap-rock and has reached isotopic equilibrium with this water;

3. One single analysis of the δ^{18}O value of the H_2O amounts to +10.7‰; this value was not found for a true gypsum sample but for a sample of gypsum from the anhydrite sandstone that occurs near the salt mirror; this value therefore does not reflect the real oxygen-isotope ratio of hydration water, but rather the slightly modified/lower isotope ratio from the sul-phate ion;

4. A group of 4 samples in which the δ^{18}O values of the H_2O range between –3.4 and 1.7‰; these samples represent gyp-sum with anhydrite, so that the values found do not reflect the real isotope ratio of the hydration water. The δ^{18}O values indicate rather a mixture the oxygen-isotope ratio in sul-phate ions and the oxygen-isotope ratio in the water of crystallisation of gypsum; in short, the real δ^{18}O content is unknown;

5. A group of 8 samples in which the δ^{18}O values of the H_2O range between –8.7 and –6.9‰; these samples are interpreted as either gypsum with an isotopic composition that represents a mixture of water from the cap-rock and water enriched in light isotopes of oxygen (for example recent meteoric water or postglacial water) or gypsum which was formed in a warmer climate than the present one, when the groundwater was slightly enriched in the heavy isotopes of oxygen.

Comparing the data of the cap-rock gypsum isotope compo-sition of the Mogilno Salt Dome with analogous data from the Wapno Salt Dome cap-rock (Jaworska, 2010), it seems that:

– in the gypsum of both cap-rocks the δ^{18}O values indicate the involvement of water: (a) mixed, (b) enriched with light oxygen isotope – indicating the presence of water from colder periods;

– nearly half of the gypsum from the Mogilno cap-rock contains crystallisation water which represents the δ^{18}O values corresponding to water inside the cap-rock (from –6.6 to –4.3‰), while there is practically no gypsum with δ^{18}O corresponding to the present water (class of –10.2 to –9.2‰); only two samples got close to this value, reaching –8.7‰, while four of eight samples from Wapno contained crystallisation water with δ^{18}O values corresponding to the present water; additionally, regarding the samples from Mogilno, the high percent-
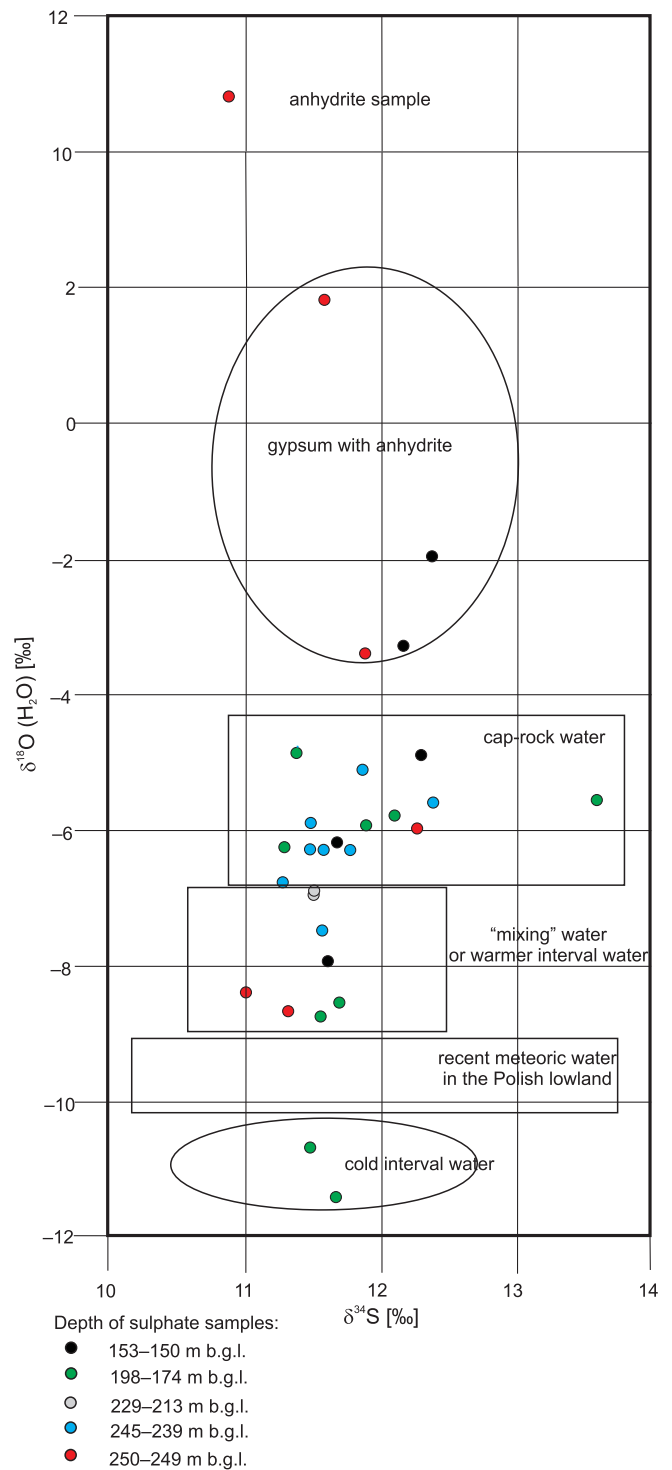

Fig. 10. Values of δ^{34}S vs. δ^{18}O of water of crystallisation

age of gypsum shows the δ^{18}O value slightly enriched in the heavy oxygen isotope (between –8.7 and –6.8‰);

– gypsum material in samples from Wapno were lacking impurities such as carbonates, so all analyses corre-sponded to the actual state; in Mogilno, part of the sam-ples contained carbonate impurities, (calcite) or anhydrite, which falsified the proper results.

SUMMARY

The gypsum from the cap-rock of the Mogilno Salt Dome is not a primary precipitate from solution but hydrated anhydrite. The oxygen- and sulphur-isotope compositions in the sulphate ion of the gypsum clearly show that sea water/brine is the source of these calcium sulphates. The $\delta^{18}O$ and $\delta^{34}S$ values measured in the SO_4 point to the Zechstein evaporite basin as the primary source of these sulphates.

The primary isotopic composition of the SO_4 was preserved despite repeated recrystallisation (hydration and dehydration) phases. The isotopic composition of the crystallisation water of this gypsum is a useful diagnostic tool to unravel the diagenetic history of this mineral. Two gypsum samples indicate probably Pleistocene or post-Pleistocene diagenetic processes, because the water of hydration is in equilibrium with water enriched in the light oxygen isotope (–11.3 and –10.8‰), probably postglacial water. These two gypsum samples come from borehole M XIII, situated near the centre of the cap-rock, at a depth of 174–175 m b.g.l. (near the surface of the cap-rock) where the gypsum cover is probably cut by fissures that form pathways for circulating water. The cap-rock is in this place quite easily penetrated by water; it is probably "the weakest" point of this cap-rock.

A majority of the gypsum samples crystallised in the presence of water enriched in the heavy oxygen isotope. The $\delta^{18}O$ values of the crystallisation water can be grouped into two main categories: (1) a group where the values are slightly enriched in the heavy isotopes of oxygen ("mixing" water or water from a warmer interval of time) and (2) a group with water from the cap-rock.

The results of some samples are problematic because these samples show values that are mixtures of real $\delta^{18}O$ values of crystallisation water and $\delta^{18}O$ values of impurities in the gypsum samples such as anhydrite and carbonate minerals (see Table 1). The actual isotopic composition of the crystallisation water of these calcium sulphates remains unknown.

The presence of a small percentage of anhydrite impurities in the gypsum samples also suggests that the meteoric water which influenced the sulphates underwent hydration, could not have had free access to the cap-rock, and in reality, the crystallisation water of gypsum had not obtained an equilibrium state with the meteoric water (Bath et al., 1987). Difficult access of the meteoric water to the cap-rock can indicate that the cap-rock in this area has remained an impenetrable body (without larger fractures and joints) – without water circulation and migration routes; and has functioned properly as effective protection for the upper parts of the salt deposit.

One of the main objectives of the study was to test whether the oxygen-isotope ratio of gypsum samples from cap-rock can be measured reliably with the indirect method. It was found that the analysis of pure gypsum samples gives reliable values but that the analytical results of other gypsum samples (gypsum with anhydrite and gypsum with calcite) yield problematic values, which needs to be taken into account when analysing such gypsum samples.

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