An oxygen and sulfur isotopic study of gypsum
from the Wapno Salt Dome cap-rock (Poland)

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The stable isotope compositions of oxygen and sulfur from gypsum samples derived from borehole cores of the Wapno Salt Dome cap-rock have been determined. The $\delta^{18}O$ values were measured (for both the SO_4 and the H_2O) in bulk samples of gypsum ($CaSO_4 \cdot 2H_2O$) and in its dehydrated equivalents ($CaSO_4$). The SO_4 is enriched in the heavy oxygen isotope, which unequivocally indicates the Zechstein sea as the place of origin of the sulfate. The variable $\delta^{18}O$ values of the H_2O (water of crystallization) indicate different conditions (and stages) of diagenetic processes of these samples, primarily recrystallization (hydration) episodes. Two groups of gypsum were distinguished: (1) a group in which the $\delta^{18}O$ values of H_2O range between –9.0 and –10.2‰ (interpreted as gypsum in equilibrium with recent or subrecent meteoric water), (2) a group in which the $\delta^{18}O$ values of the H_2O were less than –10.2‰ (this gypsum has recrystallized in the presence of water enriched in the light isotopes of oxygen). In addition, in one single analysis the $\delta^{18}O$ value of the H_2O amounts to –5.6‰ (gypsum with mixed isotopic composition).

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INTRODUCTION

Cap-rocks are integral and important parts of salt bodies. They overlie salt domes, result from multiple processes and have a long diagenetic history (e.g., Posey and Kyle, 1988; Prikryl *et al*., 1988; Werner *et al*., 1988; Jaworska and Ratajczak, 2008). On top of the salt diapirs (salt mirror area), salt rock comes into contact with water that is fresh or NaCl⁻-undersaturated, and the rock salt is dissolved; this is the salt dissolution zone. Rock salt is commonly impure, containing anhydrite in particular, but also clay minerals and carbonates. On top of salt domes therefore anhydrite (in the form of anhydrite sand, later anhydrite sandstone) is left with the rest of the less soluble minerals. Diagenetic processes transform the anhydrites by hydration into gypsum, and compaction results thus in a rocky cover, the so-called cap-rock. The youngest levels of the cap-rock are always at its base, and the oldest ones are found at its top, in an inverted stratigraphy.

Since the end of the 1970s, salt domes have been thoroughly investigated and explored as potential repository sites for radioactive waste and 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; Warren, 2006). Cap-rocks are natural covers and usually protect salt bodies quite well against erosion (groundwater dissolution) although not always (Zuber *et al*., 2000).

The isotopic composition of the sulfates and water of crystallization that build gypsum may provide information about the conditions and stages of hydration of the sulfates, and help understand the processes that occur near the salt mirror, particularly the water/sulfates interactions that are responsible for the creation and evolution of the cap-rock. Results of cap-rock research may therefore help to decide whether a specific cap-rock is stable and dry enough to act as a "protector" of the salt body beneath. A good example of such an investigation is Kreitler and Dutton's (1983) study of the Gyp Hill and Oakwood Domes in Texas.

GEOLOGICAL SETTING

The Wapno Salt Dome is one of the smallest diapirs in the Polish Lowland; it is located about 70 km to the north-east of Pozna , between the Pomeranian Swell (which forms part of the
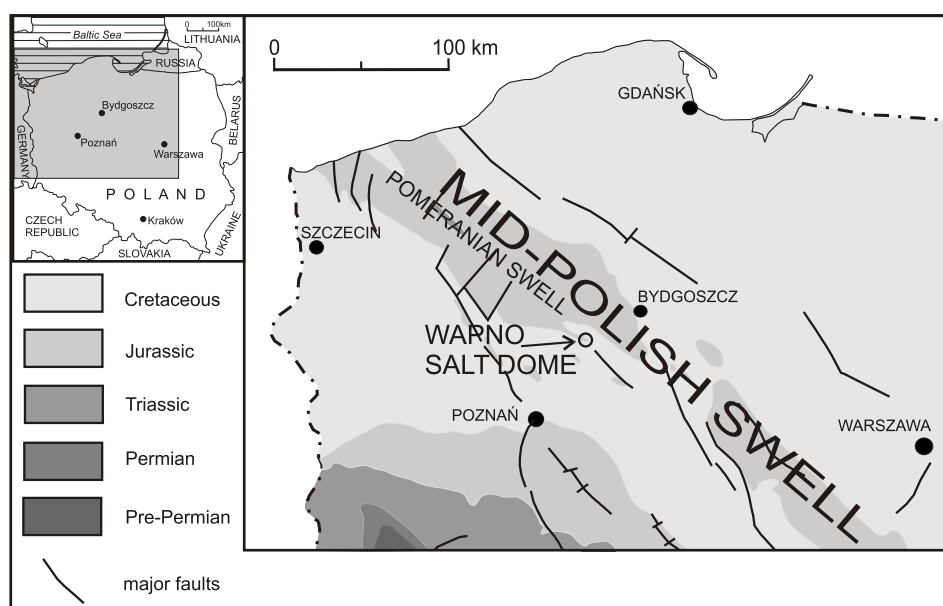
Fig. 1. Simplified geological map of NW and central part of Poland without Cenozoic and location of Wapno Salt Dome (after Marek and Leszczyński in Narkiewicz, 1997)

Mid-Polish Swell; Fig. 1) and the Mogilno Trough. It consists of two elements: a salt stock and a gypsum cap-rock. The salt dome is 1000 m long and approx. 600 m wide and its surface area is 0.5 km^2; the salt mirror is located at a depth of 160–180 m below the surface (Jaworska and Ratajczak, 2008). The salt forming the Wapno Salt Dome comes from a depth of approx. 6000 m (Marek and Raczyńska, 1974) and pierces through the entire Mesozoic and almost all the Cenozoic. The central part of the diapir is built by Zechstein (late Permian) evaporites: the older salt rocks, belonging to PZ2, represent 90% of all salt rock in the diapir (Jaworska and Ratajczak, 2008).

The origin and development of the Wapno Salt Dome is related to the subsidence and inversion of the Mid-Polish Trough (Dadlez *et al.*, 2005; Guterch and Grad, 2006; Krzywiec *et al.*, 2006). The trough was inverted during the Late Cretaceous and Paleocene. This regional antiform structure, referred to as the Mid-Polish Swell, is outlined by the Cenozoic subcrop of Cretaceous and older rocks (Dadlez *et al.*, 2005; Guterch and Grad, 2006; Krzywiec, 2006).

The Wapno Salt Dome is covered by a cap-rock; the thickness of the cap-rock ranges from 20 to 160 m (Jaworska and Ratajczak, 2008). The cap-rock, which crops out at two places, is cut by a deep trough/furrow (the C1 borehole area; Figs. 2 and 3) reaching a depth of approx. 130 m (Jaworska and Ratajczak, 2008).

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 has fine-, medium and coarse-crystalline textures (Fig. 4A and B). Two specific forms of gypsum, i.e. lenticular and selenite gypsum (Fig. 4C and D), were also observed. Auto- and hypidio-, coarse- to medium-crystalline gypsum dominates near the bottom of the cap-rock. The cap-rock changes upwards gradually to become fine and xenomorphic. The Wapno cap-rock still contains some small amounts of anhydrite. These are com-

monly remnants of larger anhydrite crystals, now forming inclusions within large gypsum grains. In one case, however, anhydrite is the main component of the cap-rock: it constitutes a 20-cm thick layer of anhydrite sandstone at the bottom of borehole C1, at a depth of 157.5 m below the surface, just above the salt mirror. Carbonates, automorphic quartz crystals and iron sulfides occur also in small amounts (Jaworska and Ratajczak, 2008).
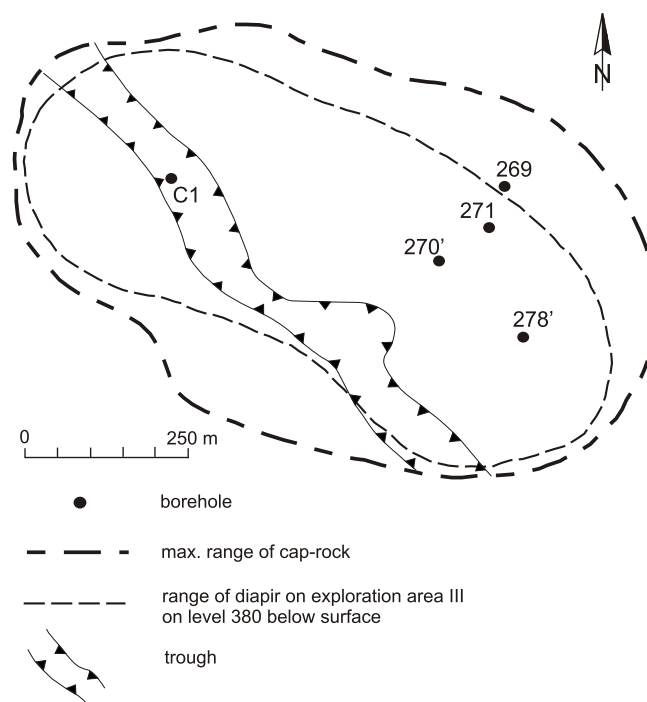

Fig. 2. Subsurface range of the Wapno Salt Dome (after Jaworska and Ratajczak, 2008; changed by author) showing the location of boreholes and trough
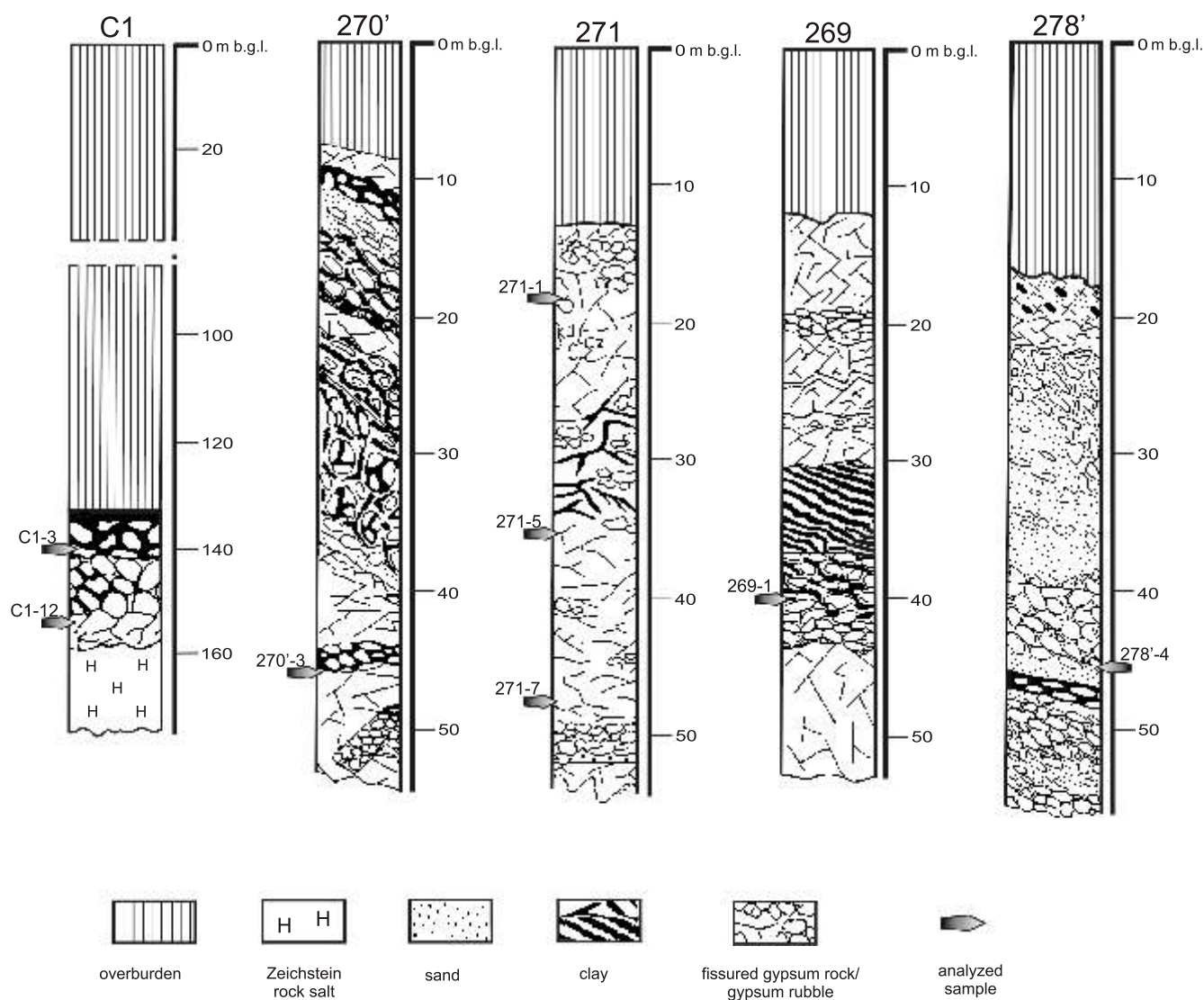
Fig. 3. Analysed core-profiles (after Jaworska and Ratajczak, 2008; changed by author)

MATERIAL

Eight representative gypsum samples (chosen from the 46-sample collection) from 5 borehole cores: C1, 270', 271, 269, 278' (Figs. 2 and 3) were analyzed for their $\delta^{18}O$ and $\delta^{34}S$ values. The samples reflect the full variety of gypsum textures (hetero-, fine-, medium-, coarse-crystalline, lenticular and selenite gypsum; Fig. 4) and come from different depths of the cap-rock – from 18.5 to 154–157 m.

METHODS

The gypsum samples were analyzed by Dr. S. Poulson at the University of Nevada (Department of Geological Sciences) for their $\delta^{18}O$ and $\delta^{34}S$ values. The isotope analyses were performed in a continuous flow mode, using an *Eurovector* model 3000 elemental analyzer to a *Micromass IsoPrime* stable-isotope ratio mass spectrometer, following two methods. The first was used to determine the $\delta^{34}S$ value (*cf.* Giesemann *et al*., 1994); V_2O_5 was added to the sulfate samples as a combustion aid; the analyses are reported as per mil relative to the Vienna-Canyon Diablo Troilite standard (V-CDT) and have uncertainties of $\pm0.2‰$. The second method (*cf.* Kornexl *et al.,* 1999) was used for the $\delta^{18}O$ analysis; nickelized graphite was added to each sample to promote CO formation; the analyses are reported as per mil relative to the Vienna-Standard Mean Ocean Water (V-SMOW) and have uncertainties of $\pm0.4‰$.

The $\delta^{18}O$ values were measured for both the bulk sample ($CaSO_4 2 \cdot H_2O$) and for its dehydrated form ($CaSO_4$ residue after dehydration); the gypsum powder was slowly heated under vacuum to 450°C for 30 minutes (see Dowuona *et al*., 1992). The isotopic composition of the oxygen in the gypsum is a mixture of $\delta^{18}O$ coming from SO_4 and H_2O (water of crystallization). The sulfates studied (gypsum samples) were therefore also analyzed twice, in order to investigate the differences of the $\delta^{18}O$ content in both components. The $\delta^{18}O$ values in the SO_4 were detected directly by mass spectrometry, whereas the isotopic composition was determined indirectly in the case of
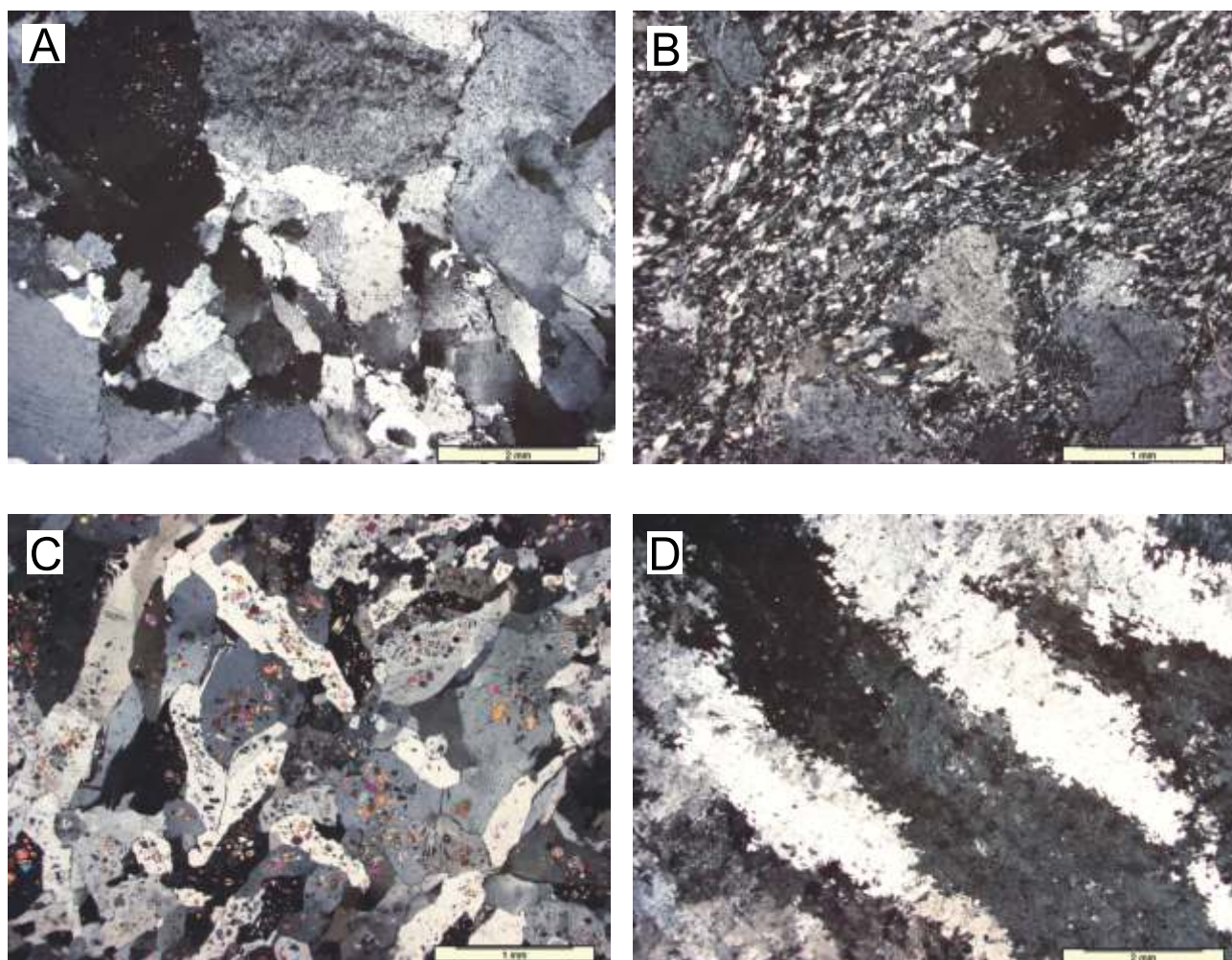
Fig. 4. Photos from thin sections of gypsum samples

A – coarse-crystalline gypsum (271-5); **B** – fine- to midium-crystalline gypsum (278'-4);
C – lenticular gypsum (C1-12); **D** – selenite gypsum (270'-3); sected nicols

the water of crystallization), by calculating the mean $\delta^{18}O$ value of the bulk gypsum sample ($CaSO_4 \cdot 2H_2O$) and of its SO_4 component (from the residue after dehydration).

RESULTS
OF THE ISOTOPE ANALYSES

Sulfur. The isotopic analyses of the sulfur in the gypsum samples investigated show a range from 11.2 to 12.5‰ and thus they indicate that these sulfates are distinctly enriched – with respect to V-CDT – in the heavy isotope (mean $\delta^{34}S$ value is 11.7‰; see Table 1, Figs. 5 and 6).

Oxygen. The $\delta^{18}O$ value in SO_4 from the Wapno gypsum samples ranges between 11.7 and 14.0‰ (mean 12.8‰; see Table 1, Fig. 5). The $\delta^{18}O$ values in the water of crystallization from the Wapno gypsum samples are completely different and range between –5.6 to –13.1‰ (Fig. 6).
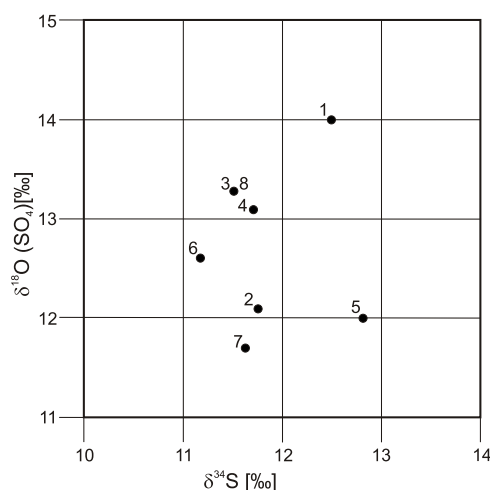

Fig. 5. Values of $\delta^{34}S$ *vs*. $\delta^{18}O$ of residual sulfate

For sample description and location see Table 1

Results of isotope analysis

	Sample number and depth	Type of gypsum rock	$\delta^{18}O$ (‰, V-SMOW) in $CaSO_4 \cdot 2H_2O$	$\delta^{18}O$ (‰, V-SMOW) in $CaSO_4$	$\delta^{18}O$ (‰, V-SMOW) in H_2O	$\delta^{34}S$ (‰, V-CDT)
1	C1-3 140 m	hetero-crystalline	6.0	14.0	–10.0	12.5
2	C1-12 154–157 m	lenticular (hypautomorphic)	6.2	12.1	–5.6	11.8
3	269-1 40 m	coarse-crystalline	4.5	13.3	–13.1	11.5
4	270'-3 45.5 m	selenite	4.8	13.1	–11.8	11.7
5	271-1 18.5 m	medium-crystalline	4.3	12.0	–11.1	11.8
6	271-5 34.5 m	coarse-crystalline	5.4	12.6	–9.0	11.2
7	271-7 47.5 m	coarse-crystalline	4.7	11.7	–9.3	11.6
8	278'-4 46.5 m	fine-crystalline and medium-crystalline	5.5	13.3	–10.1	11.5

DISCUSSION

SULFUR

Sulfur in sulfates very well preserves its primary isotopic composition, including during diagenesis as the chemical evolution of sulfates (hydration/dehydration) does not involve significant isotopic fractionation; nor does chemical sulfate reduction (Worden *et al.*, 1997). Weathering does not lead to consid-
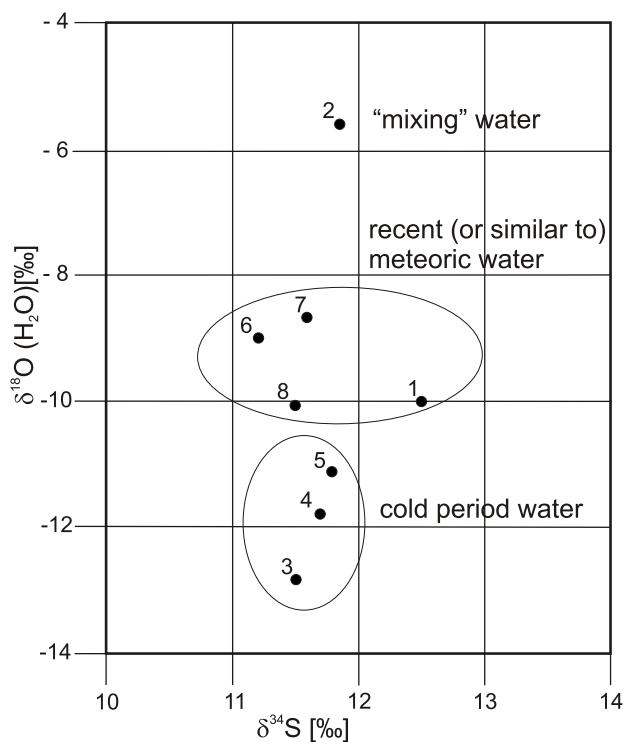

Fig. 6. Values of $\delta^{34}S$ *vs.* $\delta^{18}O$ of water of crystallization

For sample description and location see Table 1

erable fractionation of sulfur isotopes either (Hoefs, 2004). Present-day sulfates in oceanic water are characterized by a fairly constant $^{34}S/^{32}S$ ratio, with values that reach +20 ±0.5‰ with respect to V-CDT (Pierre, 1988); the fractionation between dissolved sulfates in oceanic water and gypsum or anhydrite is negligible (Thode and Monster, 1965; Raab and Spiro, 1991). In the past, this relationship changed continuously, but the general trends of the $\delta^{34}S$ value in the geological past (S-isotope age curve) is known, so that it is possible approximately to define the time of evaporite crystallization (e.g., gypsum; see Claypool *et al.*, 1980; Strauss, 1999).

The value $\delta^{34}S$ (11.7‰) in the gypsum samples investigated from Wapno is characteristic of Permian evaporites; for instance, the sulfur isotope data for Zechstein evaporites from N Germany range from 9.8 to 12.0‰ (Kampschulte *et al.*, 1998) and those for Zechstein evaporites from SW Poland range from 9.4 to 13.3‰ (Vovnyuk and Czapowski, 2007). This implies that the isotopic composition of the sulfur in these samples, taking into consideration the fractionation factor, amounting to 1.65‰ (Thode and Monster, 1965; Pierre, 1988), reflects the isotopic composition of the Zechstein brines.

OXYGEN

Analysis of the oxygen-isotope composition of gypsum is more complicated, because oxygen is present in the form of SO_4 and of water of crystallization. Initially, the gypsum and its water of crystallization were formed in isotopic equilibrium with the mother brine (Sofer, 1978), but the gypsum later easily loses its original water of crystallization (primary composition of H_2O) during contact with sea or groundwater. Changes in the $\delta^{18}O$ of water of crystallization may thus arise from repeated phases of dehydration and hydration (sometimes many times), by absorption of "fresh" water.

Present-day oceanic water contains sulfates of which the $\delta^{18}O$ values amount to 9.5 ±0.5‰ with respect to V-SMOW (Longinelli and Craig, 1967). During recrystallization of the oceanic sulfates, the $\delta^{18}O$ is raised by 3.5‰ (the factor of frac-

tionation; Lloyd, 1968; Pierre, 1988). It indicates that the $\delta^{18}O$ value of evaporites crystallizing from seawater should be 13.0 ±0.5‰.

The data shown in Table 1 indicate that the oxygen-isotope composition of the two gypsum components (SO_4 and H_2O) differs significantly. The $\delta^{18}O$ value in SO_4 from the Wapno gypsum samples (distinctly enriched in the heavy isotope of oxygen, mean $\delta^{18}O$ value is 12.8‰) indicates the Zechstein evaporite basin as the environment of the sulfate crystallization and is consistent with the "marine" origin of these sulfates.

On the other hand, the $\delta^{18}O$ values in the water of crystallization from the Wapno gypsum samples (ranges between –5.6 to –13.1‰) means that the water of crystallization is not in isotopic equilibrium with the mother brine. The variable $\delta^{18}O$ values of the H_2O indicate that the sulfates have had contact with meteoric and/or groundwater (enriched in light isotopes) and indicate different stages of diagenetic processes, primarily recrystallization (hydration) of the sulfate. These analyses are comparable to the analyses of water of crystallization from the cap-rock of the Gorleben Salt Dome (Herbert *et al.*, 1990), where the $\delta^{18}O$ value in the H_2O of the gypsum samples ranges between –5.2 and –12.4‰.

In the Polish Lowland area, the mean isotope composition of oxygen in meteoric water and in recent infiltration water ranges between –9.2 and –10.2‰ (D'Obryn *et al.*, 1997; Duli ski *et al.*, 1997). The water supplied during cold periods (such as Pleistocene meltwater) is enriched in the light isotope of oxygen and its $\delta^{18}O$ values are more negative than in the water from warm periods such as the Paleogene and Neogene, which is enriched in the heavy isotope of oxygen (Duli ski *et al.*, 1997). The stable-isotope composition of water collected from the boreholes in the Wapno area is slightly richer in the heavy isotope of oxygen than expected for infiltration water in this part of Poland (Górski and Rasała, 2008). The $\delta^{18}O$ values of water from the C1 borehole range between –8.5 and –8.7‰ with respect to V-SMOW. This discrepancy is probably caused by a small admixture of water coming from the inclusions of dissolved rock-salts or alternatively results from the presence of crystallization water released from dissolved evaporite minerals (Duli ski *et al.*, 2001).

The analyses of the $\delta^{18}O$ of water of crystallization of the Wapno gypsum samples suggest the presence of two groups (Fig. 6): (1) a group in which the $\delta^{18}O$ values of the H_2O lie between –9.0 and –10.2 ‰ (this is the gypsum which came into contact with recent meteoric water or with water that was supplied during the geological past when conditions were similar to the present-day ones, and that achieved an isotopic equilibrium with that water), and (2) a group with $\delta^{18}O$ values of the H_2O below –10.2‰, thus enriched in the light isotopes of oxygen (this comes from gypsum that recrystallized in the presence of water supplied during cooler time spans such as – possibly – the Pleistocene). In addition, one analysis shows a $\delta^{18}O$ value of H_2O of –5.6‰ which is probably the effect of partial mixing of isotopic "materials", possibly of Zechstein age with more recent ones. The high content of heavy oxygen isotopes suggests the beginning of the recrystallization processes.

CONCLUSIONS

Summing up the results, the following conclusions can be drawn.

1. The oxygen-isotope composition (in both sulfate and water of crystallization) of the gypsum is a highly useful diagnostic tool for identification of the source of the sulfate and of its diagenetic history.

2. The $\delta^{18}O$ and $\delta^{34}S$ measured in the SO_4 preserved its primary Zechstein isotope composition despite diagenesis.

3. The isotope composition of the crystallization water indicates a probably Pleistocene character of the diagenetic processes.

4. Meteoric (probably recent/postglacial) water from near the surface and outside the cap-rock quite easily penetrates the cap-rock, which does not form a tight, hermetic cover, but is cut by fissures. Consequently, the cap-rock of the Wapno Salt Dome does not fulfill the requirements for a seal which protects the rock salt and salt mirror against inflows of freshwater. This finding may have consequences for salt structures which are prepared for underground disposal of radioactive waste or for the storage of hydrocarbons.

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