

## ORIGIN OF THE BADENIAN SALTS FROM EAST SLOVAKIAN BASIN INDICATED BY THE ANALYSIS OF FLUID INCLUSIONS

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**Abstract:** Chemical composition of the brines of primary fluid inclusions in sedimentary halite (from the boreholes: P-2, P-3, P-6, P-7 and P-8) of the Badenian evaporite of the Zbudza Fm. from East Slovakian basin indicates that the basinal brines belong to the Na-K-Mg-Cl-SO<sub>4</sub> type. The ratios of K<sup>+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> ions are practically the same as they were in the Badenian seawater.

Taking into account the information on the chemical evolution of seawater in the Phanerozoic (Kovalevich *et al.*, 1998) and the calculations of this evolution for the Cenozoic (Zimmermann, 2000) it is suggested that the Badenian seawater was characterized by the reduced contents of Mg (by approximately 20%) and SO<sub>4</sub><sup>2-</sup> (by approximately 40%) in comparison with the recent seawater.

The postsedimentary recrystallization of salts occurred under the effect of buried brines, which inherited their composition from the primary basinal brines. The intensive recrystallization of salts occurred during the tectonic movements.

**Key words:** Miocene, evaporites, halite, fluid inclusions, Carpathian region.

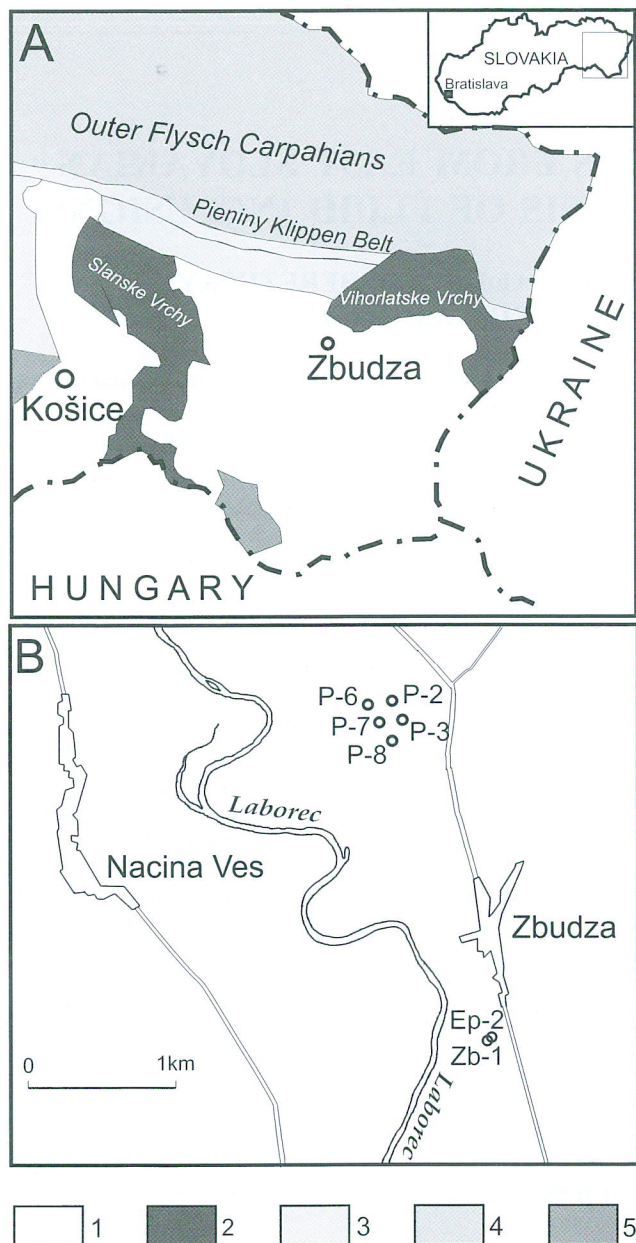
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### INTRODUCTION

Many geochemical studies of the Badenian salts of the Carpathian region were done so far, including study of fluid inclusions, Br content in halite, and isotopic composition of sulfate sulfur (e.g. Khrushchov & Petrichenko, 1979; Garlicki & Wiewiórka, 1981; Kovalevich, 1994, 1997; Bukowski, 1997; Bukowski & Szaran, 1997; Galamay, 1997; Galamay *et al.*, 1997; Galamay & Karoli, 1997; Kovalevich & Petrichenko, 1997; Shaidetska, 1997; Poberezhskyy & Kovalevych, 2001). These data indicate that the geochemical conditions for the formation of salts in all Badenian evaporite basins of the Carpathian region (Carpathian Fore-deep, Transcarpathian, East Slovakian and Transylvanian basins) were in many respects similar, in spite of essential differences in their paleogeography and volume of the accumulated salts in each of them. However, a question about the basic source of salts of the region is a subject to controversies (see for example: Garlicki, 1979; Liszkowski, 1989; Kovalevich & Petrichenko, 1997; Garcia-Viegas *et al.*, 1997; Eastoe & Peryt, 1999; Poberezhskyy & Kovalevych,

2001; Cendón *et al.*, 2004). The reasons for the existing differences were partially caused by differences in the a priori ideas about the chemical composition of ancient seawater (Valiashko, 1962; Holland, 1972, 1984; Kovalevich, 1990; Hardie, 1996; Kovalevich *et al.*, 1998; Zimmermann, 2000; Holland *et al.*, 1996; Ayora *et al.*, 2001; Lowenstein *et al.*, 2001; Horita *et al.*, 2002). Those ideas depend on the selection of a standard (contemporary or Badenian seawater) for the comparison with the chemical composition of brines in primary fluid inclusions hosted in halite of the Badenian evaporites.

Geochemical features of fluid inclusions in halite from the East Slovakian Basin were earlier studied on scarce samples (Panov *et al.*, 1989; Kovalevich & Petrichenko, 1997) and a complete section cut by one borehole (Ep-2; Galamay & Karoli, 1997). In this work we present new results obtained from five new boreholes (P-2, P-3, P-6, P-7, P-8, Fig. 1; see: Bukowski *et al.*, 2003).



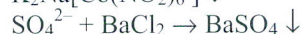
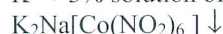
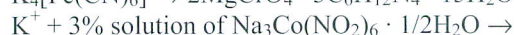
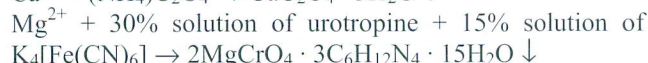
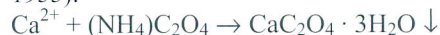
**Fig. 1.** Location of boreholes in the East Slovakian Basin (A) and in vicinity of Zbudza (B). 1 – East Slovakian Basin; 2 – Neogene volcanics; 3 – Mesozoic and Palaeogene of the Inner Carpathians; 4 – Outer Flysch Carpathians; 5 – pre-Mesozoic units of the Inner Carpathians

During the determination of the role of sea and other sources in the formation of salts we proceeded from the ideas that Badenian seawater differed from the contemporary one in terms of a slightly reduced Mg and a substantially reduced  $\text{SO}_4^{2-}$  contents. In this work a significant attention is given to the study of sedimentary structures in halite in connection with the numerous traces of tectonic deformations. Such deformations substantially effect determination of the genetic type of inclusions (primary or secondary) and respectively they can lead to the erroneous conclusions about the genesis of these salts.

## METHODS

Polished plates (1 to 5 mm thick) cut parallel to cleavage were made for study fluid inclusions, analysis of the chemical composition of brines of individual inclusions, and determination of their homogenization temperature.

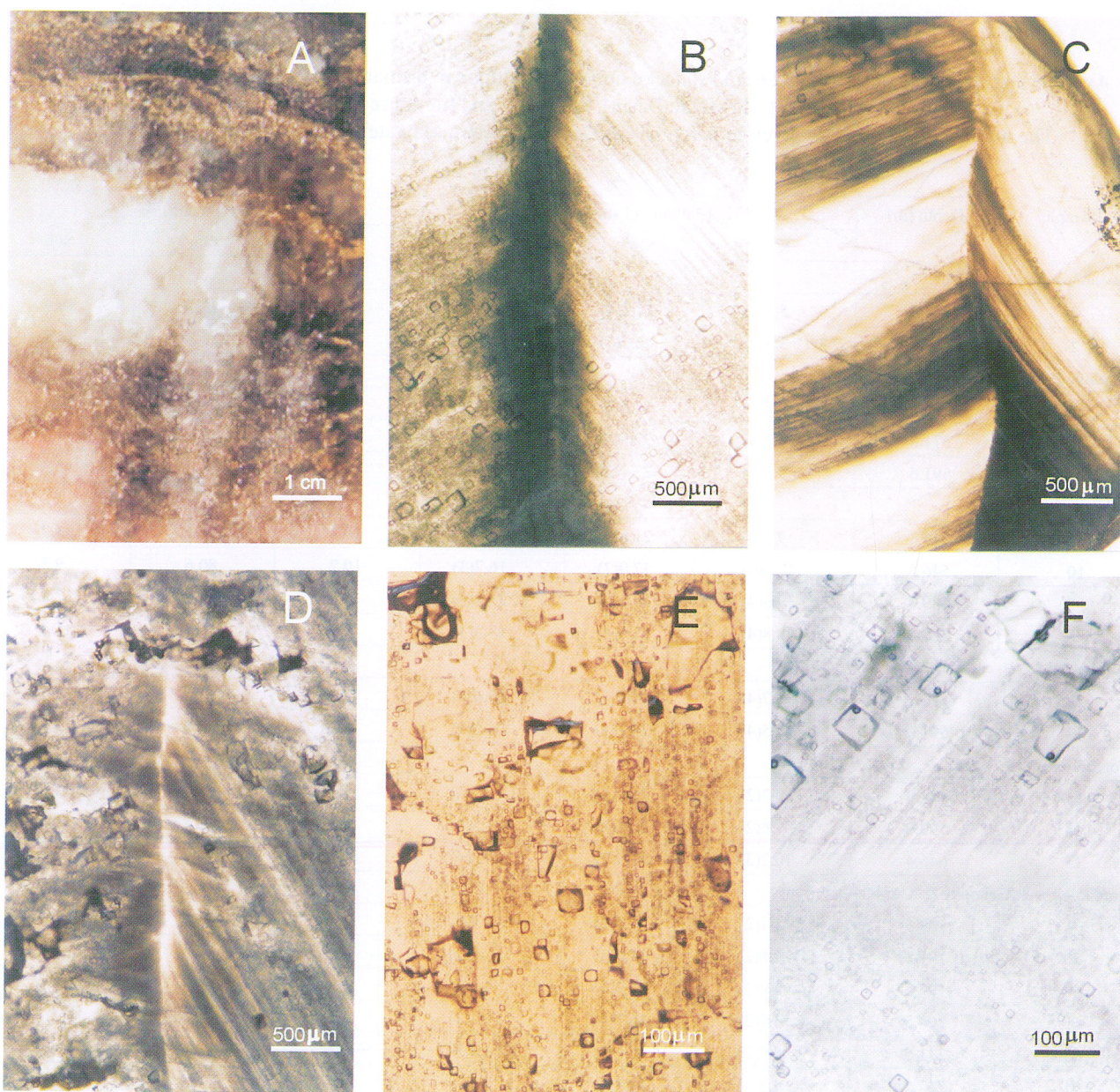
Chemical composition of the inclusion brines was determined with the aid of the method developed by Petrichenko (1973). The essence of this method (see also Lazar & Holland, 1988) is the application of a traditional chemical analysis to very small samples. The selected plate of halite was dissolved by thin water jet before reaching the wall thickness of several ten micrometers above the inclusion. The plate was then dried and the inclusion opened by a needle. Brine from the inclusion was extracted with a glass capillary, and a reagent is then added to determine the solutes in the inclusion fluid, following the recommendations by Korenman (1955): 30% solution of  $\text{BaCl}_2$  for determination of the  $\text{SO}_4^{2-}$  ion, 3% solution of  $\text{Na}_3\text{Co}(\text{NO}_2)_6 \cdot (1/2)\text{H}_2\text{O}$  for the  $\text{K}^+$  ion, 5% solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  for the  $\text{Ca}^{2+}$  ion, and one part of a 30% solution of urotropine and one part of a 15% solution of  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  for the  $\text{Mg}^{2+}$  ion (assuming that its content is  $<6$  g/l) or 15% solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . When the Ca value is  $>6$  g/l, Ca begins to precipitate; in the remnant solution the Mg value is determined in the reactive (i.e. one part of a 30% solution of urotropine and one-part of a 15% solution of  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ). The reagent is added until the process of precipitation is completed according to the reactions (Korenman, 1955):



The capillary was sealed and centrifuged. Volume of the sediment, formed as a result of reaction of the brine with the reagent was compared (under microscope) with the same volume of standard brine.

With the aid of this method the contents of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions can be determined. However, method does not make it possible to determine the  $\text{Na}^+$  and  $\text{Cl}^-$  contents because the error of analysis is large. The analytical error of the applied method is 15–23% (for  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) and 37–43% (for  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ ) when a single measurement is done. To decrease the error of determination, a number of analyses of each component in inclusion brines of each sample were carried out; two to three parallel analyses decrease the error to 16–17% (see Petrichenko, 1973: Table 4). The minimum concentrations of the studied ions needed for such an error are (in g/l): 0.8 for  $\text{K}^+$ , 1.0 for  $\text{Mg}^{2+}$ , 0.9 for  $\text{Ca}^{2+}$ , and 0.5 for  $\text{SO}_4^{2-}$  ion, and the lower values are semi-quantitative. The minimal size of inclusions which are suitable for such analysis is 40  $\mu\text{m}$ , although the larger inclusions ( $>100$   $\mu\text{m}$ ) are preferred since it is possible to run two or three parallel analyses.

Temperature of homogenization of two-phase (gas-liquid) inclusions was determined in the microscope heating stage constructed by Kaluzhny (1982). The heating rate was



**Fig. 2.** Photographs of characteristic chevron structures and fluid inclusions in halite. **A.** Primary chevron halite ("milky") overlain by halite arenites. Borehole P-8, depth 561.6–561.8 m. **B.** Chevron halite crystal of rhythmic zonation with size of inclusion increasing from axis toward the peripheries of the chevron structure. Borehole P-6, depth 559.4 m. **C.** Chevron structure of halite with the traces of tectonic deformations. Borehole P-6, depth 543.3 m. **D.** Fragment of chevron structure with systems of cracks which are connected large secondary fluid inclusions of irregular shape. Borehole P-8, depth 636.3 m. **E.** Fragment of chevron structure with irregular fluid inclusions. Borehole P-6, depth 480.7 m. **F.** Fragment of chevron structure in halite. Inclusions are liquid with gas bubbles. Borehole P-7, depth 599.7 m

0.2–0.5°C/min and the accuracy of measurement is about 1°C. To establish the temperature of salt crystallization based on one-phase, liquid inclusions (at room temperature) the cryometric method, proposed by Roberts & Spencer (1995) was applied with the modification of the process of obtaining the gas phase in inclusions and the method of their homogenization (Galamay, 2003). Samples of halite (with one-phase liquid inclusions) were cooled at a temperature from 0 to –7°C during 3–5 days (before the appearance of gas phase in the inclusions). Then the halite samples were immersed in the transparent cuvette filled glycerine with cooled to +10°C. Homogenization of inclusions was con-

ducted under the microscope by heating the glycerine by illuminating quartz lamp, and the heating temperature was fixed with mercury thermometer with the accuracy of  $\pm 0.5^\circ\text{C}/\text{min}$ .

#### PETROLOGY OF SAMPLES AND THE CHARACTERISTICS OF THE INCLUSIONS IN HALITE

Small (up to 200 g) samples of coarse-grained salts with chevron crystals of halite were selected for inclusion inves-

Table 1

Average contents of major ion species and Jänecke units for solutions in primary fluid inclusions in Badenian halite (East Slovakian Basin), this study and literature data.

The number of analyses is given in parentheses. Data on modern seawater after McCaffrey *et al.* (1987)

Sample	Depth (m)	Content, g/l solution			Jänecke unit, %		
		K <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	2K	Mg	SO <sub>4</sub>
Borehole P-2							
3	513.8	5.3(2)	21.2(4)	11.0 (3)	6.4	82.7	10.9
1	540.3	3.5(2)	16.2(3)	11.9(1)	5.4	79.8	14.8
Borehole P-3							
6	550.0	8.5(2)	24.5(2)	13.3(2)	8.7	80.3	11.0
5	571.3	9.8(4)	29.9(2)	14.2(3)	8.3	81.8	9.8
4	591.6	9.2(3)	27.1(3)	13.6(2)	8.6	81.1	10.3
Borehole P-6							
12	543.3	9.6(4)	21.8(3)	18.3(4)	10.1	74.1	15.7
10	546.5	15.1(5)	37.0(2)	16.7(3)	10.2	80.6	9.2
9	549.8	19.9(4)	37.1(1)	25.1(4)	12.5	74.7	12.8
8	559.4	8.8(4)	22.0(5)	18.3(3)	9.3	74.9	15.8
Borehole P-7							
28	539.7	16.7(4)	40.9(3)	26.4(4)	9.8	77.5	12.7
14	591.0	12.5(4)	24.9(4)	21.2(3)	11.4	72.9	15.7
Borehole P-8							
18	544.9	9.7(2)	28.0(2)	16.7(3)	8.5	79.5	12.0
15	590.0	7.6(2)	28.4(2)	13.3(3)	6.9	83.2	9.9
13	646.4	10.2(3)	29.4(2)	12.3(4)	8.9	82.4	8.7
Borehole Ep-2 (Galamay & Karoli, 1997)							
71	189.5	5.1(2)	13.9(3)	8.7(3)	9.0	78.6	12.4
70	191.8	4.8(2)	13.4(3)	8.8(2)	8.7	78.3	13.0
68	195.5	3.9(2)	13.0(3)	8.5(3)	7.4	79.4	13.1
65	204.5	5.5(2)	16.7(3)	9.1(3)	8.3	80.6	11.1
63	211.5	5.2(2)	12.9(3)	9.4(3)	9.6	76.4	14.1
61	217.5	4.5(3)	11.4(2)	8.3(2)	9.4	76.5	14.1
59	225.8	4.4(3)	13.5(3)	8.6(2)	7.9	79.4	12.8
57	232.0	4.8(2)	12.8(2)	9.0(3)	9.0	77.3	13.7
56	236.4	5.1(2)	12.4(2)	8.8(3)	9.8	76.5	13.7
55	238.4	5.2(2)	13.0(2)	9.8(2)	9.5	76.0	14.5
54	239.2	4.7(2)	12.1(3)	8.6(3)	9.3	76.9	13.8
53	241.0	4.5(2)	13.3(2)	9.7(3)	8.2	77.5	14.3
52	243.5	4.5(3)	12.6(2)	9.6(3)	8.5	76.7	14.8
50	246.0	3.3(2)	11.0(2)	8.2(2)	7.3	78.0	14.7
Borehole Ep-2 (Kovalevich & Petrichenko, 1997)							
56	236.4	4.4(3)	17.6(2)	11.7(3)	6.2	80.3	13.5
55	238.4	5.4(3)	17.7(3)	14.0(3)	7.3	77.2	15.5
54	239.2	5.2(4)	17.3(3)	13.7	7.2	77.3	15.5
Borehole Zb-1 (Kovalevich & Petrichenko, 1997)							
	132.0	6.2(3)	22.8(2)	10.3(4)	7.1	83.4	9.5
Modern seawater saturated NaCl		3.9	12.6	17.6			
Modern seawater saturated MgSO <sub>4</sub>		21.6	85.9	115.0			

tigation. Chevron structure is well visible macroscopically as the white spots (Fig. 2A). Nodules of white anhydrite (up to 1.5 cm in diameter) are common at the boundaries of separate halite grains.

Up to 3 cm long chevron structures formed by one-phase liquid inclusions of cubic form were found in halite from the borehole Ep-2 (Galamay & Karoli, 1997, see figs 4–6). Among these structures occur such having symmetrical and asymmetrical structure and a clear rhythmic zonation. The size of the inclusions in these chevrons is from a fraction of micrometer to 300  $\mu\text{m}$  (rarely up to 450  $\mu\text{m}$ ). But considerably more frequent in the large crystals of halite are very small inclusions (to several micrometers in the diameter), which occur near the axis, and with the distance from the axis their size gradually increases (up to several tens of micrometers, Fig. 2B).

Traces of tectonic deformations are common in chevrons, especially in the crystals of halite from P-6 and P-7 boreholes. These deformations were recorded through the bent lines of zonality (Fig. 2C), the systems of cracks which intersect the entire chevron structure (Fig. 2D). Large inclusions of irregular shape (as on Fig. 2E) or network of small inclusions are developed along such cracks.

Some chevron structures are modified by secondary processes to such an extent that it is difficult to find the zoned parts with the preserved primary appearance (Fig. 2E). In such chevrons large secondary inclusions of irregular shape, arranged without the visible regularity, seem to be superimposed on the primary zoned structure formed by small cubic inclusions. This intensive post-sedimentary transformation of chevron crystals was the reason that in some samples from the boreholes P-6 and P-7 we could not find unquestionable primary inclusions suitable for studies.

In some cases zones or sections of the intensive transformation of chevron crystals become well visible under the microscope (in the crossed polars) due to the presence of the numerous anisotropic crystals (gypsum, anhydrite) arranged along the cracks or inside large secondary inclusions. The same large secondary inclusions of irregular shape, frequently with the anisotropic small crystals of gypsum or anhydrite, are encountered in the periphery of chevron crystals or in the transparent halite. They are also placed without a visible regularity, and they are sometimes connected with the healed cracks.

In one sample of halite (P-7/13) the inclusions in chevron crystals were two-phase (gas-liquid; Fig. 2F). The volume of gas phase with respect to the volume of inclusion was approximately 1%.

## RESULTS OF ANALYSES

### COMPOSITION OF THE INCLUSION BRINES

The chemical composition of the brines from primary inclusions in chevron halite is given in Table 1. Besides the data obtained during this study, we report also on the previously published data from the boreholes Zb-1 and Ep-2. At

**Table 2**

Content of major ion species in solutions of secondary fluid inclusion in Badenian halite, East Slovakian Basin.  
Boreholes: P-6, P-7 (Zbudza).  
The number of analyses is given in parentheses

Sample	Depth (m)	Content, g/l		
		K <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
Borehole P-6				
29	459.1	5.8 - 18.2 (4)	13.3	11.6
25	473.5	5.0 - 15.0 (6)	37.8	13.6
24	480.7	5.8 - 13.7 (5)	40.8	14.2
20	505.3	9.7 - 11.4 (3)	12.9 - 17.9 (3)	12.8
12	534.3	5.4 - 6.1 (2)	18.0	4.1 - 10.2 (3)
10	546.5	4.8 - 8.9 (2)	24.3	7.0 - 8.6 (3)
9	549.8	3.9 - 9.4 (11)	12.7 - 25.1 (5)	11.3 - 15.5 (5)
8	559.4	4.7 - 19.2 (3)	17.0	9.7
Borehole P-7				
34	502.2	10.5 - 18.8 (5)	10.9 - 33.7 (5)	3.2 - 26.0 (4)
32	526.9	6.1 - 10.7 (3)	30.4	12.4 - 15.3 (2)
31	533.5	9.6 - 12.6 (3)	26.0	6.1
29	536.2	3.6	18.9	8.7
28	539.75	5.4 - 10.9 (9)	19.4 - 21.5 (3)	7.8 - 14.5 (4)
14	591.0	6.7	33.1	13.2
13	599.7	3.8 - 5.5 (3)	22.5	12.4

the end of table 1 the contents of ions in the recent seawater, concentrated to the stage of the precipitation of halite and magnesium sulfates are shown for comparison. Taking into account relatively small dimensions of the primary inclusions in the investigated crystals, the content of each ion was determined in separate inclusions. All investigated inclusions were located in one or several adjacent zones of the same chevron crystal. For the majority of samples 3–4 parallel analyses were done for each ion, i.e. we investigated 3–4 various inclusions. Table 1 gives only average contents, since all obtained values were found within the limits of analytical errors.

Table 2 gives all analyses of the ion contents in the brines of secondary inclusions in the halite samples from boreholes P-6 and P-7. The average contents of ions K<sup>+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> were not calculated, since the obtained values are characterized by wide fluctuations.

The investigated secondary inclusions were located, as a rule, in the same chevron structures, but they differed from primary inclusions in terms of irregular shape, large dimensions and common visible connection with the healed cracks. For a number of samples only one measurement of the K<sup>+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> content was done due to a relatively small number of secondary inclusions.

Table 3

Temperatures of homogenization of the inclusions in primary halite, borehole of Ep-2 Zbudza

Sample	Depth (m)	Temperature, °C									
		19.0	19.5	19.5	20.0	21.5	21.5	22.0	23.0	23.0	23.5
		24.0	24.5	24.5	25.5	25.5	26.0	26.0			
70	191.8	16.0	17.5	17.5	18.5	19.0	19.0	19.5			
68	195.5	20.5	21.0	21.0	21.0	21.0	22.0	22.0	22.0	23.0	23.0
65	204.5	18.0	19.0	19.0	19.5	19.5	19.5	20.0	20.0	20.0	20.5
63	211.5	17.0	17.0	18.0	18.0	19.5	20.0	20.0	20.5		
61	217.5	19.5	20.2	20.0	21.5	21.5	22.0	22.5	22.5	23.0	23.0
		23.0	23.0	23.5	23.5	24.0	25.0	25.0	25.0	25.0	25.0
59	225.8	18.5	21.0	22.5	22.5	23.0	23.0	23.0			
56	236.4	17.5	18.0	18.0	18.0	18.0	19.0	19.0			
54	239.2	15.0	15.5	15.5	15.5	16.0	16.0	17.5	17.5	17.5	18.0
		18.0	18.5	18.5	19.0	19.0					
53	241.0	19.0	19.5	19.5	20.0	20.5	21.0	21.0	21.0	21.5	21.5
		22.5	23.0	23.0	23.0	23.5	23.5				
52	243.5	19.5	21.5	22.0	22.0	23.5	23.5	23.5	23.5	23.5	24.0
		24.0	24.0	24.0							
50	246.0	17.5	18.5	18.5	18.5	20.5	20.5	21.5	21.5	21.5	21.5
		21.5	22.0	22.5	22.5	22.5	22.5	23.5	24.0		

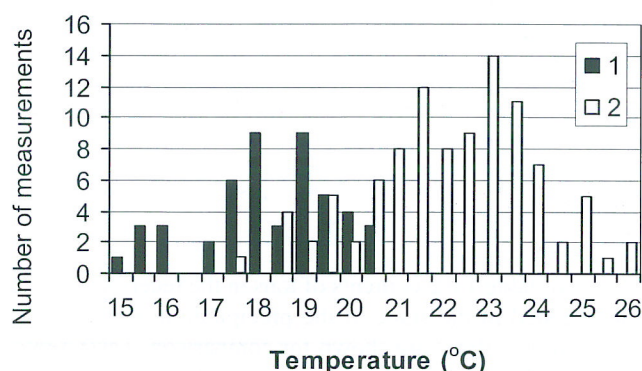


Fig. 3. Distribution of temperatures of homogenization of the inclusions in sedimentary halite from borehole Ep-2 Zbudza. 1 – relatively low values (48 measurements on 5 samples); 2 – relatively high values (99 measurements on 7 samples)

#### HOMOGENIZATION TEMPERATURE OF INCLUSIONS

The determination of the temperature of homogenization of inclusions, in which the appearance of gas phase was artificially caused by cooling the halite samples, was done earlier on one sample (Galamay, 2003). We studied 12 halite samples from borehole Ep-2 and the homogenization temperatures of 147 inclusions were determined (Table 3). It was found that in each sample, the inclusions homogenized in a narrow temperature interval. Within the entire interval of values, two groups of data were distinguished, with low and high values (Fig. 3). Two-phase (gas-liquid at room

temperature) inclusions in the sample P-7/13 (depth 597.0), homogenized between 70 and 77°C.

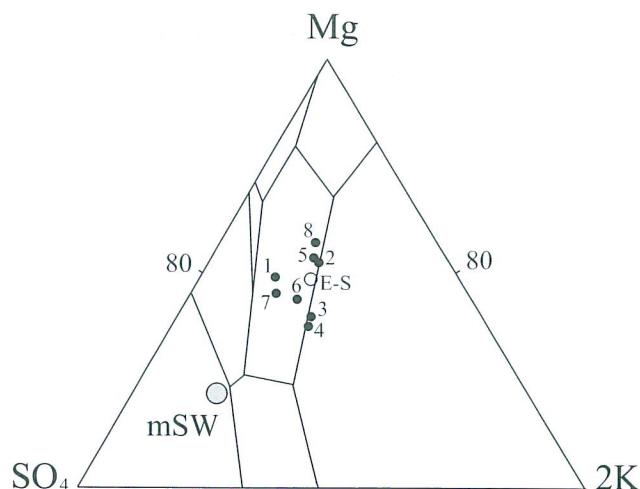
## INTERPRETATION AND DISCUSSION

### THE CHEMICAL COMPOSITION OF BRINES

The results of all analyses of primary fluid inclusions in chevron crystals of halite (given in Table 1) indicate that the brines of the basin were of the Na-K-Mg-Cl-SO<sub>4</sub> (SO<sub>4</sub>-rich) type. The contents of K<sup>+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions were close to the recent seawater, concentrated to beginning of halite precipitation (see Table 1). However, the ratios of these ions differ compared to those in the recent seawater. The basic difference is the substantial decrease of relative content of SO<sub>4</sub><sup>2-</sup> what is indicated by the location of the point of the average brine composition (for each borehole and the entire basin) on the Jänecke (1923) diagram (Fig. 4). The scatter of points on the diagram around the average value for the basin is relatively small and it is partially caused by the analytical error (about 20%).

### SOURCE OF SALTS

In order to estimate the effect of non-marine sources of salts on the composition of brines in the East Slovakian basin, it is necessary to reconstruct composition of Badenian seawater, considering the results of investigation of primary inclusions in halite and the general chemical evolution of seawater in the Phanerozoic (Kovalevich, 1990; Hardie, 1996; Kovalevich *et al.*, 1998; Zimmermann, 2000; Lowen-

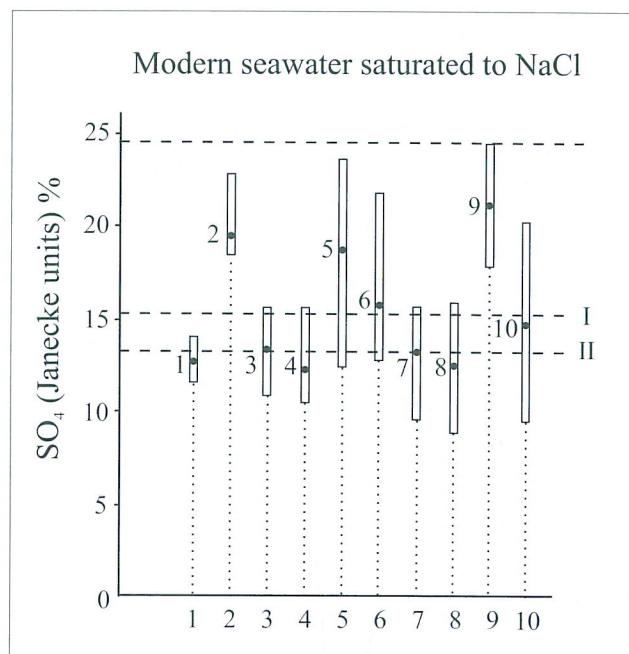


**Fig. 4.** Average ion contents of the inclusion brines (as shown in Table 1) in primary inclusions of sedimentary halite from different boreholes of the Badenian East-Slovakian Basin plotted on the Jänecke projection of the quinary system Na-K-Mg-SO<sub>4</sub>-Cl-H<sub>2</sub>O at 25°C. mSW – modern seawater saturated with respect to halite. E-S – average for the East Slovakian basin as a whole. Dots: 1 – borehole P-2; 2 – borehole P-3; 3 – borehole P-6; 4 – borehole P-7; 5 – borehole P-8; 6 – borehole Ed-2 (Galamay & Karoli, 1997); 7 – borehole Ed-2 (Kovalevich & Petrichenko, 1997); 8 – borehole Zb-1 (Kovalevich & Petrichenko, 1997)

stein *et al.*, 2001; Poberezhskyy & Kovalevych, 2001; Horita *et al.*, 2002). The best substantiated calculations of the composition of Badenian seawater are given by Zimmermann (2000) who showed that the Badenian seawater differed from the recent seawater by the reduced content of Mg<sup>2+</sup> (by approximately 20%) and SO<sub>4</sub><sup>2-</sup> (by approximately 38%). On the Jänecke diagram the point of the composition of such water corresponds quite precisely to the composition of the brines of the East Slovakian basin. However, it should be noted that Zimmermann (2000) conducted her calculations on the basis of only two basins: East Slovakian (boreholes Ep-2 and Zb-1) and Carpathian Foredeep (Wieliczka, Poland).

All data on the content of SO<sub>4</sub><sup>2-</sup> in the brines of the Badenian evaporite formations of the Carpathian region are summarized in figure 5, except for one section in the Transcarpathian Basin (Chop - Mukachevo depression, borehole 6-T; see Shaidetska, 1997), where all fluid inclusions in the halite contained gas phase. These data shows that the average content of the SO<sub>4</sub><sup>2-</sup> ions in the studied sections is within the interval ranging from 12.2 to 21.2 Jänecke units and thus all values are smaller than those characteristic for recent seawater (24.4).

The average SO<sub>4</sub><sup>2-</sup> values (in Jänecke units) given by Zimmermann (2000) and by us for the Badenian salts of the Carpathian region are 13.2 and 15.2, respectively, and the difference between them is relatively small. Nevertheless, some sections, included by us, significantly differ considering the range of fluctuation and the average values of the SO<sub>4</sub><sup>2-</sup> contents from the average for the Carpathian region. The reason for such deviations can be partly caused by systematic errors. In these cases content of SO<sub>4</sub><sup>2-</sup> ions were studied, by different methods. Sections of the boreholes



**Fig. 5.** Content of SO<sub>4</sub> ion (in the Jänecke units) in primary fluid inclusions of sedimentary halite from different boreholes, mines and localities on the territory of the Badenian evaporate in the Carpathian region. I – Badenian seawater (this study); II – Badenian seawater (Zimmermann, 2000). Dots: 1 – Bochnia mine, Carpathian Foredeep, Poland (Kovalevich, 1997; n = 2 samples); 2 – Lezkowice Z-1 and Woszczyce IG-1 boreholes, Carpathian Foredeep, Poland (Garcia-Veigas *et al.*, 1997; n = 6 samples); 3 – Wieliczka mine, Carpathian Foredeep, Poland (Kovalevich & Petrichenko, 1997; n = 5 samples); 4 – Wieliczka mine, Carpathian Foredeep, Poland (Galamay *et al.*, 1997; n = 20 samples); 5 – Selets-Stupnitsy and Zabolotiv localities, Carpathian Foredeep, Ukraine (Kovalevich & Petrichenko, 1997; n = 20 samples); 6 – Slanic-Prahova mine, Carpathian Foredeep, Romania (Kovalevich & Petrichenko, 1997; n = 5 samples); 7 – Ep-2 and Zb-1 boreholes, East-Slovakian basin (Kovalevich & Petrichenko, 1997; n = 4 samples); 8 – all data, East-Slovakian basin (n = 32 samples); 9 – Solotvyn mine, Transcarpathian Trough (Kityk *et al.*, 1983; n = 7); 10 – Transylvanian Basin, Romania (Kovalevich & Petrichenko, 1977; n = 4 samples)

Łęzkowice Z-1 and Woszczyce IG-1 (Polish part of Carpathian Foredeep) was studied by Garcia-Veigas *et al.*, (1997) by the aid of the Cryo-SEM-EDS method, sections in the Ukrainian Carpathian Foredeep (Selets-Stupnitsa and Zabolotiv) and the Transcarpathian region were studied by Kovalevich & Petrichenko (1997) and Kityk *et al.*, (1983), respectively, with the aid of the method introduced by Petrichenko (1973).

We think that of the decisive importance are not analytical errors, but instead the errors in determination of the genetic type of fluid inclusions (the secondary inclusions) which occur inside the chevron structures of halite. However, it is not possible to exclude that the described deviations caused, to a considerable extent, by the influence of some local factors on the brine composition in these regions or sub-basins, for example, by the inflow of continental waters or terrigenous material. In any case, on the basis of available data we consider that the composition of seawater in the Badenian time was characterized by the reduced con-

tent of  $\text{SO}_4^{2-}$  ion (within the range of 13.2 to 15.2 in Jänecke units), i.e., by approximately 40% less than in the contemporaneous seawater. Taking into account the calculations done by Zimmermann (2000), we assume the equivalent (in moles) deficit of  $\text{Mg}^{2+}$  in the Badenian seawater, although with respect to its content in the recent seawater this deficit did not exceed 20%. Thus, on the basis of study of primary fluid inclusions in the Badenian salts of the Carpathian region we conclude that the salt composition of the brines of the East Slovakian evaporite basin was formed in the major part from the Badenian seawater, which differed from contemporaneous seawater in terms of the reduced contents of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions.

The oxygen and sulphur isotope compositions in anhydrite from the salts of the East Slovakian basin show a wide scatter of a values from 11.16‰ to 13.15‰ SMOW for oxygen and from 18.28‰ to 24.45‰ CDT for sulphur (Galamay 1997). Average values  $12.34 \pm 0.47\%$  and  $22.22 \pm 0.87\%$  respectively correspond to typical Miocene evaporites of marine origin (Claypool *et al.*, 1980).

The isotopic data reported from Badenian evaporite formations of the Carpathian region, including marginal gypsum-anhydrite series (Claypool *et al.*, 1980; Halas *et al.*, 1996; Bukowski & Szaran, 1997; Galamay 1997; Kasprzyk, 1997; Parafiniuk & Halas, 1997; Peryt *et al.*, 1998; Peryt *et al.*, 2002; Cendón *et al.*, 2004), are plotted against normal values for Miocene marine sulfates; however, a significant part of them shows a somewhat heavier isotopic composition of sulfur and oxygen. On this basis some authors assume the significant role of the redeposition of evaporites during their sedimentation (Peryt *et al.*, 1998; Cendón *et al.*, 1999; Cendón *et al.*, 2004) and the significant inflow of continental waters into the basin. Such a possibility is supported by the reduced contents of bromine in halite (Bukowski *et al.*, 2003) and the presence of sedimentary salt breccias in some sections of the Badenian evaporites of the region (e.g., Ślaczka & Kolasa, 1997).

### COMPOSITION OF POSTSEDIMENTARY BRINES

Postsedimentary brines are those formed from primary basinal brines buried together with the sediments and modified during water-rock interactions. Thus, they originated in the subsurface conditions due to a partial recrystallization of salts. In halite crystals, they were preserved in form of secondary fluid inclusions (see Table 2; Fig. 2D, E). In the studied salts their composition is very close to the composition of brines in the primary inclusions and thus one can conclude that the postsedimentary brines to a considerable extent inherited the composition of the basinal brines. However, in a number of samples very wide fluctuations of the contents of the  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions were recorded in the inclusions within the same crystal. Such a modification of brines in the subsurface is a typical phenomenon. For example brines of the  $\text{SO}_4$ -rich and Ca-rich types were found in the secondary inclusions in the Triassic salts of Switzerland whereas the brines of the primary inclusions were exclusively  $\text{SO}_4$ -rich. (Kovalevych & Hauber, 2000). Therefore, during a study of fluid inclusions in halite the correct identification of their genetic type is very important.

### TEMPERATURE CONDITIONS OF SALT CRYSTALLIZATION

Two groups of halite crystals have been distinguished according to homogenization temperature of fluid inclusions (see Table 3):

- 1 – with the relatively low temperature (15.0–20.5°C),
- 2 – with the relatively high temperature (17.5–26.0°C).

Experimental studies (Acros & Ayora, 1997) showed that the homogenization of the inclusions in the halite grown from low-temperature (30.0–40.0°C) solutions occurs both above and below the actual temperature crystallization. The distribution of values on the histogram (Acros & Ayora, 1997) shows that a number of decreased values is bigger and directly after its last maximum is the actual temperature of the mineral crystallization. This and the dispersion of temperatures of the homogenization of inclusions (Fig. 3) lead to the conclusion that the temperature on the bottom of salt basin during the crystallization of halite varied from 19.5°C (with respect to measurements on the first group of crystals) to 23.5°C (with respect to measurements on the second group of crystals). Strakhov (1962, p. 229) noted that a fast growth of crystals on the bottom of modern salt lakes with the formation of numerous liquid inclusions is in the evening and night time more concentrated and cooled surface brines. Therefore, this suggests that in the arid and warm semiarid climate (Stoica & Gherasie, 1981) the temperature of surface brines was slightly higher.

The results of the homogenization of two-phase inclusions with high homogenization temperatures (70–77°C) are difficult to interpret because such inclusions are revealed in only one sample. Similar two-phase inclusions were observed also in halite from other saliferous formations (Shaidetska, 1997; Kovalevych *et al.*, 2000), but there they originated due to the overheating of the entire saliferous series. In our case it is difficult to assume that the studied salt series was thoroughly heated only in the interval of one sample. Most likely, this sample was overheated because of the influence of some special technical conditions of boring in this interval. The possibility of the artificial conversion of the one-phase inclusions in two-phase ones through the warming up of the sample of halite was proven by Petrichenko (1973). The subsequent homogenization of such inclusions shows the actual temperature of the warming up of the samples.

### CONCLUSIONS

New and previously published data on the chemical composition of the brines in primary inclusions in the chevron crystals of the halite from the Zbudza Fm. indicate that the brines of this basin were of the Na-K-Mg- $\text{SO}_4$  type. The ratio of the  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions were almost the same to the ratios in the Badenian seawater, which differed from the recent seawater in terms of the reduced content of  $\text{Mg}^{2+}$  ions (by approximately 20%) and  $\text{SO}_4^{2-}$  ions (by approximately 40%) (Kovalevich *et al.*, 1998; Zimmermann, 2000; Poberezhskyy & Kovalevych, 2001).



Postsedimentary transformations of salts occurred due to the buried brines, which inherited their composition from the primary brines of the basin. Their partial modification is evidenced by a relatively wide fluctuation of  $K^+$ ,  $Mg^{2+}$  and  $SO_4^{2-}$  ions in the brines of the secondary inclusions even within the one sample. The wide distribution of the deformed chevron structures and the connection of secondary inclusions indicates that the most intensive postsedimentary transformations of salts of Zbudza Fm. occurred in the stage of the salt tectonics.

The homogenization temperatures of fluid inclusions show that during the separate stages of the accumulation of salts the temperature of the bottom brines of the basin was from 19.5 to 23.5°C, what as a whole will support the idea of semiarid climate at that time in the region.

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### Streszczenie

#### POCHODZENIE BADEŃSKICH SOLI BASENU WSCHODNIOŚLÓWACKIEGO NA PODSTAWIE ANALIZY CIEKŁYCH INKLUZJI

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W pracy przedstawiono rezultaty badań kilkudziesięciu próbek soli z 5 nowych otworów (P-2, P-3, P-6, P-7, P-8, Fig. 1) oraz porównano je z wcześniej publikowanymi danymi. Skład chemiczny solanek pochodzących z inkluzji był określany za pomocą metody rozwiniętej przez Petrichenko (1973). Metoda ta opiera się na zastosowaniu tradycyjnej chemicznej analizy do mikroobjętości substancji (solanka z inkluzji pobierana jest szklaną kapiłarą). Za pomocą tej metody może być określana zawartość jonów  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  i  $\text{SO}_4^{2-}$ .

Badania składu chemicznego ciekłych inkluzji pochodzących z halitu o strukturze szewronowej (Fig. 2) wskazują, że solanki w basenie wschodniosłowackim były typu Na-K-Mg-Cl-SO<sub>4</sub>. Charakteryzowały się one zredukowaną zawartością  $\text{Mg}^{2+}$  (o ok. 20%) oraz  $\text{SO}_4^{2-}$  (o ok. 40%) w stosunku do współczesnej wody morskiej.

Na podstawie oznaczeń temperatury homogenizacji ochłodzonych inkluzji jednofazowych - fazowych (w temperaturze pokojowej) występujących w strukturach szewronowych, można wyróżnić dwie grupy kryształów halitu: z relatywnie niską temperaturą (15–20.5°C) oraz relatywnie wysoką temperaturą (17–26°C) homogenizacji (Fig. 3). Przedstawione wyniki składu chemicznego inkluzji wskazują na morskie pochodzenie soli w basenie wschodniosłowackim (Fig. 4, 5)