

SLOVAK GEOLOGICAL MAGAZINE

VOLUME 3 NO 3

ISSN 1335-96X

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Geological Survey of Slovak Republic, Bratislava
Dionýz Štúr Publishers

3/97

SLOVAK GEOLOGICAL MAGAZINE

Periodical of Geological Survey of Slovak Republic is a quarterly presenting the results of investigation and researches in a wide range of topics:

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Address of the publishers: Geological Survey of Slovak Republic, Mlynská dolina 1, 817 04 Bratislava, Slovakia

Printed at: IBI-print Bratislava

Annual subscription
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3902001018558

SLOVAK GEOLOGICAL MAGAZINE

VOLUME 3 NO 3

ISSN 1335-96X

Evaporite Formations of the Carpathians Mts.

Part II.



Geological Survey of Slovak Republic, Bratislava
Dionýz Štúr Publishers

3/97

Chemical composition of brines in Miocene evaporite basins of the Carpathian region

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Abstract. The chemical composition of brines in primary inclusions of primary halite from Miocene evaporite formations in the Carpathian region including the Carpathian Foredeep, East Slovakian, Transcarpathian, and Transylvanian basins, have been studied in order to determine the similarities and differences in composition of basin brines. The chemical compositions of fluid inclusions indicate that brines from all basins studied belong to the Na-K-Mg-Cl-SO₄ type and the proportion of the ions was close to modern seawater saturated with NaCl. The slightly decreased content of SO₄ is found in all basins, that is probably caused by the inflow of continental water. An especially low content of SO₄ was typical for evaporite formations in the smallest, East Slovakian basin. The geochemical data on Miocene evaporites of the Carpathian region confirm the idea that seawater was the main source of the salts and had the composition close to modern seawater.

Key words: Miocene, evaporite, salt, halite, fluid inclusions, Carpathian region.

Introduction

The question of genesis of Miocene evaporites in the Carpathian region is still under discussion because of peculiarities of evaporite sequences in that region. Salt-bearing sequences in the Carpathian Foredeep are characterized by a high content of terrigenous material and by the presence of potassium-magnesium sulfate salts, and the East Slovakian basin differs by its small area. Most evaporite sequences have a very complicated tectonic structure and a wide distribution of breccia. In the Transcarpathian and Transylvanian basins, salt diapirs are developed. Data on the chemical compositions of brines in inclusions in sedimentary halite are very important sources of information for revealing evaporite genesis. They permit the reconstruction of the composition of brines in ancient basins, and thus provide information about the source of salts. The results of analyses of fluid inclusions in halite from Miocene evaporites are especially important, because the chemical composition of seawater (as a standard for correlation) at that time is known; it could not differ significantly from modern seawater taking into account the age of these evaporites (*cf.* Holland, 1978).

Up to now, the fluid inclusions in sedimentary halite from several evaporite sections from the Ukrainian Fore-

carpathian and Transcarpathian regions have been studied in detail (Kovalevich, 1978, 1994; Khrushchov & Petrichenko, 1980; Kityk *et al.*, 1983; Petrichenko, 1988). From the Badenian evaporites of East Slovakia and Transylvania, only a few samples have been investigated (Petrichenko, 1988). In this paper, new geochemical data for these four basins are presented, and the existing information on brine composition in basins and genesis of evaporites in this region are summarized.

For three reasons, we present data on the composition of brine inclusions in halite that has precipitated at relatively early stages of brine saturation: (1) The potash salts were formed only in evaporite sequences of the Forecarpathian basin, and they have been studied in detail (Kovalevich, 1978, 1994; Peryt & Kovalevich, 1997). (2) For reconstruction of seawater composition, in our opinion, it is necessary to use samples from the lowest parts of halite sequences that were formed from brines of relatively low concentration, because further evaporation leads to significant changes in ion ratios up to the complete loss of sulfate ion. Specifically, such a picture of brines evolution has been established for the Permian basin of the Uralian Foredeep (Kovalevich & Petrichenko, 1994). (3) The halite sequences with a relatively low concentration of brine inclusions have been found in all evaporite formations of the region.

Geological setting

The Miocene evaporite basins in the Carpathian region are in Slovakia, Poland, Ukraine and Romania in foremountain and intermountain depressions (Fig. 1; Sonnenfeld, 1974). The ages of evaporite sequences range from 14 to 22 Ma, although the stratigraphic position of some of them is doubtful.

Forecarpathian basin. Evaporite deposits of the Carpathian Foredeep belong to a thick Miocene molasse unit. Questions about the number of evaporite formations in the molasse section, their thicknesses, stratigraphy and tectonics are still being discussed.

According to recent views (Dzhinoridze *et al.*, 1980; Korin, 1992, 1994), there are only two evaporite formations in the Carpathian Foredeep: Vorotyshcha and Tyras of Eggenburgian and Badenian age, respectively. The deposits of both series occur as narrow bands along the entire foredeep. The real thickness of each series is 100-130 m. Salt-bearing parts of these sections are composed of salt breccias, rock salt and lenticular beds of potassium-magnesium salts of chloride-sulfate type in the middle parts of the series. Gypsum-anhydrite rocks are widely developed only in the upper (Tyras) formation, and in the marginal part of the basin they make up the entire formation. Salt deposits of both sequences are

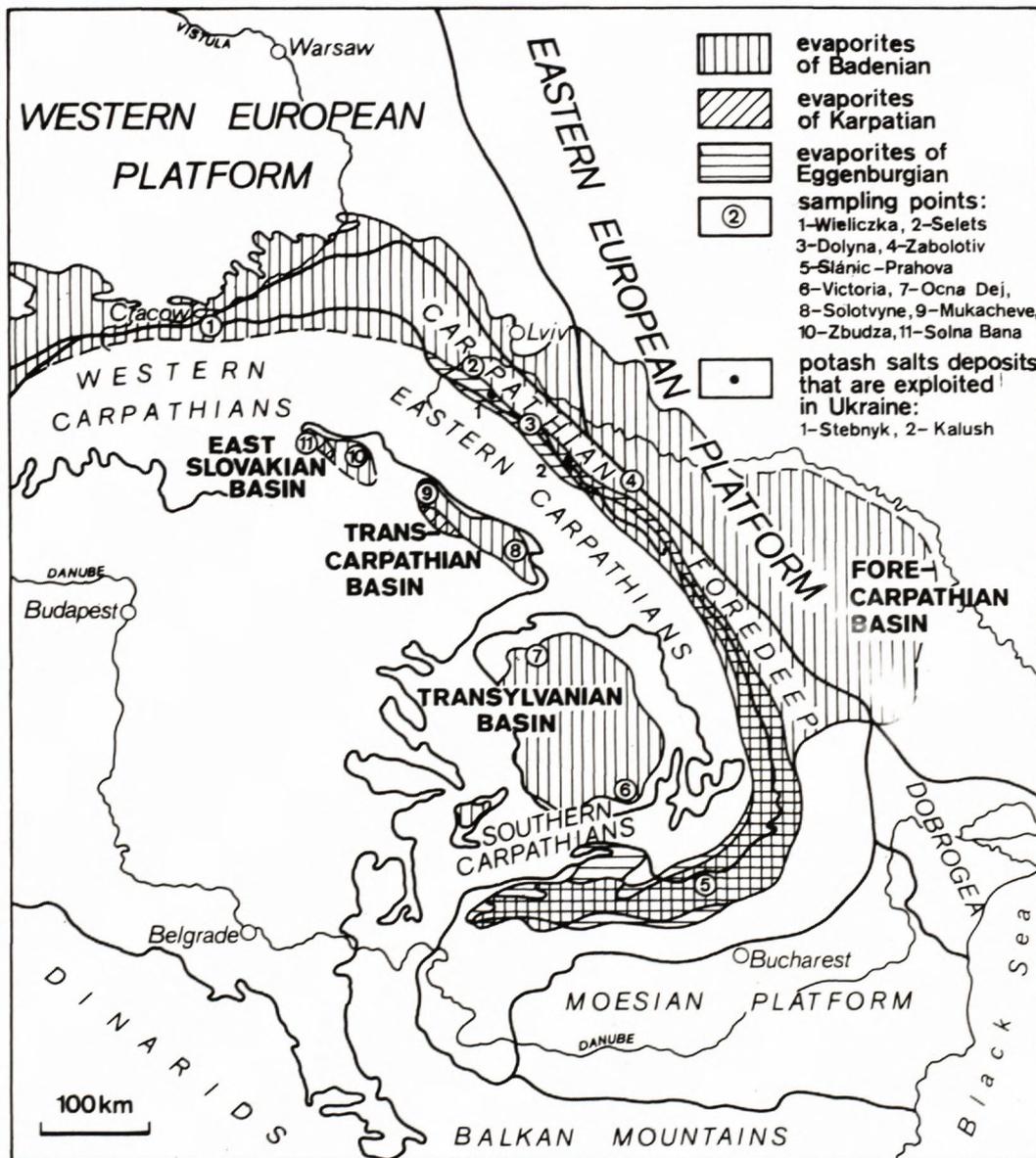


Fig. 1. Occurrence of Miocene evaporites in the Carpathian region (after Garlicki, 1979; Popescu *et al.*, 1973; Stoica & Gherasie, 1981; Panow & Plotnikow, 1996).

pressed into narrow, often recumbent, folds and are offset by reverse faults. Such a complicated folded-thrust construction caused the salt-bearing deposits to be 1000 and more meters thick in parts of the Carpathian Foredeep.

Kainite and langbeinite as well as less frequent sylvite, kieserite and polyhalite are the most common minerals in the potassium-magnesium salt deposits. Within the Carpathian Foredeep more than 10 deposits of potash salts are known and two of them are exploited - Stebnyk and Kalush (Fig. 1).

In the Eggenburgian evaporite formation, the primary sedimentary forms of halite (chevron and hopper crystals) are rare, and in the Badenian evaporites they are widespread. The largest chevron crystals are observed in the Wieliczka rock salt deposit in Poland (15 cm in length). From data on inclusions in halite from the Eggenburgian formation, in this paper we use only those that have been obtained from the lowest parts of underlying rock salt (Ukraine, three boreholes near Dolyna, see Table 1). Several sections without potash salts from the Badenian formation of the Carpathian Foredeep have been studied, particularly in the Wieliczka (Poland), Slanic-Prahova (Romania) and in Selets and Zabolotiv (Ukraine) regions.

Intracarpathian depressions. The smallest is the East Slovakian basin. Two salt formations have been cut by boreholes in the Miocene in this basin (Karoli, 1994). The lower, Solna Bania Formation, is Karpatian age and 300 m thick. It contains a lot of terrigenous material, and its upper part is composed of breccia. In borehole 131 we have studied the sedimentary relics in halite, but the relatively large fluid inclusions suitable for analysis have been found only in one sample. The upper, Zbudza Formation (see Fig. 1), is Badenian age and about 200 m thick. The most typical section of the formation includes the rock salt sequence within clayey deposits. In studied sections of rock salt from boreholes Zb-1 and Ep-2, we have found many large chevron crystals of halite.

The Transcarpathian basin is a medium size basin. Rock salts occurring there have a thickness of about 500-600 m (Korenevsky *et al.*, 1977) and belong to the Badenian Tereblin Formation. The older (Karpatian) evaporites (Fig. 1) in that basin consist of sulfates only (Kityk *et al.*, 1983). Two depressions - Solotvyne and Mukacheve - are distinguished within the Transcarpathian basin. In the most complete sections, the Tereblin Formation is subdivided into three horizons: the lower and upper are salt-bearing, and the middle is terrigenous (Kityk *et al.*, 1983). The rock salt deposits have a low content of terrigenous material and are characterized by well-preserved bedding in rocks with chevron relics in halite. Due to tectonic movements, the disharmonic folding has been formed. It is better expressed in the Solotvyne Depression,

where the large diapiric structures, that partly or completely cut the capping rocks, are present. One such diapiric structure is the Solotvyne rock salt deposit. The rock salt we sampled for investigation comes from the upper horizon. The section of salts from the Mukacheve Depression has been studied in borehole 6-T near Mukacheve.

The Transylvanian basin is the largest one among the Intracarpathian depressions. The salt-bearing sequence of this basin is similar to those described from the Solotvyne Depression and is also to Badenian. Korenevsky *et al.* (1977) have distinguished three tectonic zones within the Transylvanian Depression: a monoclinical zone (in margins of depression); a zone of salt massifs and diapirs (closer to the centre) and dome-like folds (in the centre). Most of the salt massifs, as a matter of fact, are deposits of relatively clean rock salt. The visible thickness of salt in some massifs is more than 2000 m. In studied samples from the "Victoria" and "Ocna Dej" rock salt deposits, numerous relics of chevron halite have been recorded.

Primary fluid inclusions in primary halite

The specimens were sampled only from bedded rock salt. The thickness of individual layers in sampled sections ranged from several to a few tens of cm. The sizes of halite grains (or crystals) also vary, from 1 mm to 15 cm. We sampled the most coarse-grained varieties of the salt with macroscopic chevron structures except the Eggenburgian Vorotyshcha Formation in the Carpathian Foredeep where we sampled the relatively fine-grained rock salt (with grain sizes less than 8 mm across). By size and structure, the sedimentary forms of halite in studied evaporites show a considerable variability. Structures, with or without rhythmic zonation and sometimes both occurring within the same sample, differ by inclusion sizes and their amount per volume unit of the crystal (Fig. 2-5). In many cases, the processes of recrystallization have led to sedimentary forms preserved only as rare relics. The largest chevron structures were preserved in the Badenian formations of all basins. Inclusions in sedimentary structures are usually one-phase fluid, have a cubic, or close to cubic, shape and are oriented along the growth zones of crystals. The size of inclusions ranges from a fraction of μm to 200-300 μm , but rarely reaches 1 mm. It is important to emphasize that we have found a lot of fluid inclusions with sizes above 100 μm in halite and these are suitable for chemical analyses.

Fluid inclusions in chevron and hopper crystals are the microdrops of brines trapped during the growth of these crystals. Such a concept is shared by most investigators that have studied the process of crystallization of halite sedimentary forms (Valiashko, 1951, 1962; Dellwig, 1955; Raup, 1970; Roedder, 1984). We think that

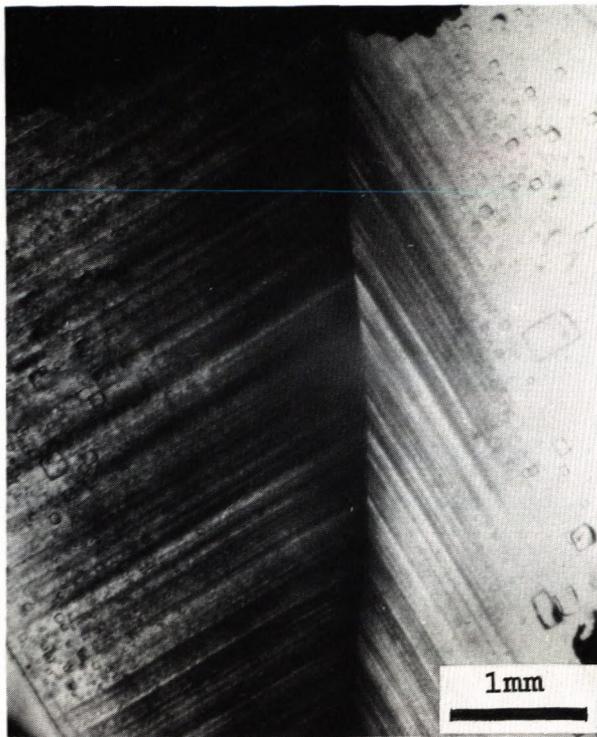


Fig. 2. Chevron structure in halite with asymmetric construction and very thin zonation and minute fluid inclusions. East Slovakia, Badenian, borehole Zb-1, depth 132 m.

this conclusion has been especially substantiated during last years, after obtaining the data about alteration of composition and concentration of inclusion brines in

sections coming from many evaporite formations throughout the world (Petrichenko, 1988; Kovalevich, 1990).

In chevron halite from the Mukacheve Depression (borehole 6-T), two-phase gas-fluid inclusions are present (see Fig. 5). The gas phase does not exceed 1% of inclusion volume. It should be emphasized here that a gas phase is present in all inclusions (not depending on their sizes) and the homogenization temperature is similar within every sample from the same depth. We suppose that the gas bubbles result from partial splitting of inclusions due to a high geothermal gradient in the region, and these inclusions are also of use for reconstruction of the chemical composition of brines in basins, considering the small volume of possible loss of brine from inclusions.

The results of chemical analyses of inclusion brines and interpretation

The analysis of inclusion brines was done using the Petrichenko (1973) method of glass capillaries. The contents of K, Mg, SO_4 were determined. The analytical error of the applied method is *ca.* 20% when one measurement is done so, to decrease the error of determination, a few analyses for each compound in inclusion brines in each sample have been carried out. The inclusions over 100 μm across were used for analyses, although the method permits the analysis also of smaller inclusions (about 40 μm). The results are presented in Table 1.

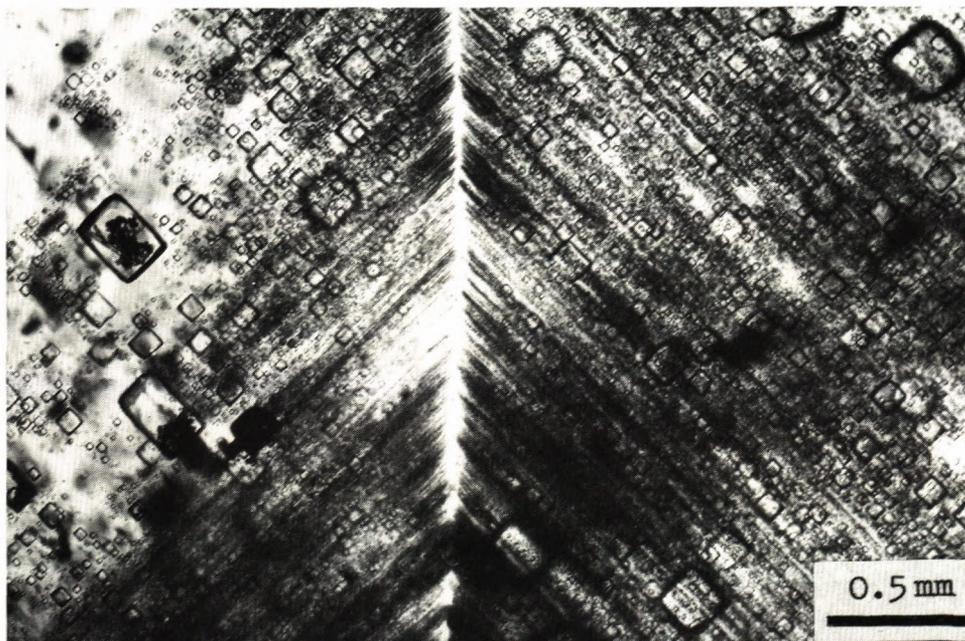


Fig. 3. Fragment of chevron structure in halite with symmetric construction and relatively large fluid inclusions. Carpathian Foredeep, Wieliczka deposit, Badenian.



Fig. 4. Fragment of chevron structure in halite in part with rhythmic zonation. Inclusions are liquid with gas bubbles. Transcarpathians. Mukacheve depression, borehole 6-T, depth 1074 m.



Fig. 5. The detail of chevron structure in halite shown in Fig. 4. The gas phase in inclusions is distinctly seen.

Because of the numerous data, only the average values for separate samples or groups of samples are shown. The grouping of results is applied only when the distinct stratigraphic location of samples in sections is unknown and when the obtained data are similar by total concentration of brines as well as by ratio of ion content. Specifically, the average data are presented for groups of samples from salt diapirs Solotvyne and Slanic-Prahova

and for boreholes cutting the Vorotyshcha and Tyras deposits in the Ukrainian part of Carpathian Foredeep.

Considering the data in Table 1, the average contents of ions in brine inclusions in halite from all studied formations (Table 2) have been calculated. We consider these results to correspond to the composition of brines in evaporite basins during crystallization of halite from sampled sections. The data indicate that the brines of all

Table 1. The chemical composition of brine inclusions in primary halite of Miocene evaporite formations of the Carpathian region (g/l of solution)

Location, depth; number of samples	K	Mg	SO ₄
FORECARPATHIAN BASIN, VOROTYSHCHA FORMATION, EGGENBURGIAN (UKRAINE, near DOLYNA)			
Borehole Dolyna-9MD, 73-152 m; 5	2.6 (14)*	23.4 (13)	17.0 (16)
Borehole Strutyn-819, 487-518 m; 2	2.3 (5)	28.2 (6)	32.3 (6)
Borehole Jasenovets-17, 319 m; 1	2.0 (4)	26.4 (5)	27.5 (5)
EAST-SLOVAKIAN BASIN, SOLNA BANIA FORMATION, KARPATIAN			
The rock salt deposit Solevar, borehole 131, 374.6 m; 1	0.5 (3)	12.0 (3)	7.2 (3)
FORECARPATHIAN BASIN, WIELICZKA FORMATION, BADENIAN (POLAND)			
The rock salt deposit Wieliczka, 5 samples:			
green salt in breccia	5.1 (3)	18.0 (3)	11.8 (3)
spiza salt	5.5 (3)	20.2 (3)	16.0 (2)
spiza salt	9.7 (2)	26.3 (3)	16.8 (2)
shaft salt	8.0 (5)	20.8 (2)	11.3 (4)
green salt	9.3 (3)	19.3 (3)	17.5 (2)
FORECARPATHIAN BASIN, TYRAS FORMATION, BADENIAN (UKRAINE)			
Borehole Selets-Stupnitsy-348, 117.5-176.0 m; 6	10.6 (25)	22.7 (15)	29.8 (15)
Borehole Selets-Stupnitsy-671, 272-506 m; 13	10.6 (45)	30.9 (19)	24.5 (19)
Borehole Zabolotiv-3847, 660 m; 1**	14.5 (8)	25.8 (8)	31.0 (8)
FORECARPATHIAN BASIN, BADENIAN (ROMANIA)			
The rock salt deposit Slanic-Prahova; 5	6.1 (16)	19.8 (15)	16.1 (12)
EAST SLOVAKIAN BASIN, ZBUDZA FORMATION, BADENIAN			
Borehole Zb-1, 132 m; 1	6.2 (3)	22.8 (2)	10.3 (4)
Borehole Ep-2; 3 :			
depth 236.4 m	4.4 (3)	17.6 (2)	11.7 (3)
depth 238.4 m	5.4 (3)	17.7 (3)	14.0 (3)
depth 239.2 m	5.2 (4)	17.3 (3)	13.7 (3)
TRANSCARPATHIAN BASIN, TEREBLIN FORMATION, BADENIAN (UKRAINE)			
The rock salt deposit Sotolyne; 7	15.5 (40)	28.5 (35)	36.5 (35)
Mukacheve depression, borehole 6-T, 1047.0-1318.0 m; 17***	9.5 (34)	18.0 (34)	20.0 (34)
TRANSYLVANIAN BASIN, BADENIAN (ROMANIA)			
Mine "Victoria", sample P-4	9.0 (4)	20.4 (5)	17.3 (3)
Mine "Victoria", sample P-11	9.3 (5)	14.2 (3)	7.0 (3)
Mine "Victoria", sample P-12	9.8 (2)	24.8 (4)	29.5 (1)
Mine "Ocna Dej", sample P-50	6.8 (2)	13.6 (1)	8.2 (2)

* In brackets - number of analyses; ** After Poberevsky (1991); *** After Shaidetska (1997)

basins of the region belonged to the Na-K-Mg-Cl-SO₄ type during the formation of all Miocene evaporite formations, i.e. the same chemical type as modern seawater. The correlation with data on modern seawater evaporation (see Table 2) shows that we have established the brine composition at the initial stages of halite precipitation.

The peculiarities of ion ratios in brines of each basin result when the data are put in the diagram of the seawater system (Fig. 6). All points of composition are located slightly up from the point of modern seawater composition and are scattered in relation to the average value for

Miocene basins in the region. The location of points and their scattering show the impact of local paleogeographic conditions on the brine composition in each basin. The most significant alterations took place during the deposition of both formations in the smallest, East Slovakian basin. The essence of these alterations was the decrease of SO₄-ion content (in comparison to modern saturated seawater), which was, probably, caused by sulfate reduction, inflow of surface or underground water and run-off of terrigenous material to the basins. Despite the decreased content of SO₄-ion, seawater was the main source

Table 2. The average composition of brines in Miocene basins of the Carpathian region

Basin, the age of evaporites	Content, g/l		
	K	Mg	SO ₄
Forecarpathian, Eggenburgian	2.3	26.0	25.0
Forecarpathian, Badenian	8.5	22.4	19.7
East Slovakian, Karpatian	0.5	12.0	7.2
East Slovakian, Badenian	5.3	18.8	12.4
Transcarpathian, Badenian	12.5	23.2	28.2
Transylvanian, Badenian	8.2	18.2	15.5
The average value	6.2	20.1	18.0
The average value (leveled by Mg content in modern seawater saturated to NaCl)	4.8	15.5	13.9
Modern seawater (saturated with NaCl)	3.3	15.5	21.0

* Calculated from Valiashko (1962).

Table 3. The average composition of brines in Miocene evaporite basins, leveled by magnesium content in modern seawater saturated to the beginning stage of halite precipitation.

	Content, g/l		
	K	Mg	SO ₄
Miocene basins	4.8	15.5	13.9
Modern seawater saturated with NaCl	3.3	15.5	21.0

of salts in Miocene basins of the region, and its composition was similar to the modern one. This is also proved by previous investigations of the mineralogy, petrography and geochemistry of salts (Korobtsova, 1955; Khodkova, 1971; Valiashko, 1962), and especially of bromine and some other trace elements (Bilonizhka, 1972, 1975; Garlicki & Wiewiórka, 1981; Kovalevich, 1978, 1994; Malikova, 1967; Slivko & Petrichenko, 1967), as well as isotopic composition of sulfate sulfur (Claypool *et al.*, 1980; Kovalevich & Vityk, 1995).

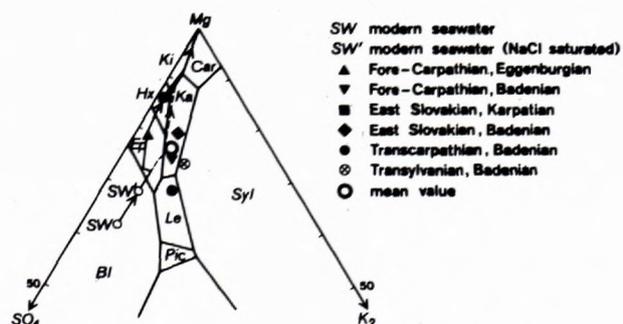


Fig. 6. Analyses of inclusion brines from chevron halite of Miocene evaporites (Carpathian region) plotted on a Jänecke projection of the quinary system Na-K-Mg-SO₄-Cl-H₂O saturated with respect to halite at 25°C (Eugster *et al.*, 1980). The stability fields of Bl, bloedite; Car, carnallite; Ep, epsomite; Hx, hexahydrate; Ka, kainite; Ki, kieserite; Le, leonite; Pic, picromerite; Syl, sylvite, are indicated.

The location of points in the diagram makes it possible to predict the probable composition of potash salts in new, not yet studied sections of evaporite formations in the region. In case when the brines has reached the higher stage of saturation, the salts may be of complex chloride-sulfate composition, like those found in the Carpathian Foredeep.

We made an attempt to reconstruct the composition of Miocene seawater. For this purpose we calculated the average composition of brines in studied basins, leveled by Mg content with modern seawater, and saturated to the corresponding stage (Table 3). As shown in the table, the brines from Miocene basins differed by the slightly decreased content of SO₄-ion and increased content of K-ion. The Miocene seawater could not significantly differ from modern one, as the residence time of many compounds in seawater was close to or greater than this time (Holland, 1978). Accordingly, the results of analyses of inclusions in primary halite permit reconstruction of the composition of ancient seawater, but with taking into account some alteration of brines within the basin. The most reliable information may be obtained during the study of relatively large basins. In our case they are the Forecarpathian and Transylvanian basins with compositions of brines very close to the composition of modern seawater saturated with NaCl.

Conclusions

The chemical composition of brines in chevron and hopper crystals of halite from bedded rock salt of Miocene evaporite formations in Poland, Slovakia, Ukraine and Romania has been studied. Such basins are located in intermountain and foremountain depressions of the Carpathians: Carpathian Foredeep (Eggenburgian and Badenian), East Slovakian (Karpatian and Badenian), Transcarpathian Foredeep (Badenian) and Transylvanian depression (Badenian).

Results of analyses indicate that the brines of all studied evaporite basins during salt deposition belonged to Na-K-Mg-Cl-SO₄ type. These brines differed from modern seawater saturated to a corresponding stage by slightly decreased content of SO₄. Small differences have been also established in the composition of brines in each basin, that can be explained by peculiarities in local paleogeographic conditions during salt accumulation. Specifically the lowest content of SO₄-ion was characteristic for the smallest, East Slovakian basin. Nevertheless, the results of the analyses permit us to suppose that the seawater with composition close to the modern one was the main source of salts in the Miocene basins.

Acknowledgments

We acknowledge grant No. UCM000 from the International Science Foundation and thank "Derzhkomgeologii" of Ukraine for support. We also thank T.M.Peryt, K.Bukowski, J.Przybyto, S.Karoli and S.Redan for their help in sampling the Miocene salt deposits in Poland, Slovakia and Romania. Bromine content in halite was determined by V.Kryzhevich (Chemical Laboratory, Institute of Geology and Geochemistry of Combustible Minerals, Lviv). Drawings were done by T. Dobroszycka.

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Petrology and geochemistry (fluid inclusions) of Miocene halite rock salts (Badenian, Poland)

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Abstract. Within Badenian evaporites of southern Poland, three sections have been selected for petrological and geochemical study. Rock salt samples from the vicinity of Wieliczka and Upper Silesia were studied in thin sections under microscope and examined by XRD analysis. A number of selected samples were tested by fluid inclusions microanalysis using the Cryo-SEM-EDS methodology. As a result of this study, the mineralogical components and characteristic textures of the rock salt have been established. Fine to coarse crystalline halite is the main constituent of the rock salt. Relics of large hopper crystals are abundant in two of the studied sections. Anhydrite and gypsum are the occurring sulphate minerals, the latter being derived mainly from partial anhydrite hydration. Polyhalite is absent or very scarce. The chemical composition of primary fluid inclusions is in accordance with a marine origin of the deposit. The homogeneity of the fluid inclusion composition in the analyzed samples suggests that the mother brines reached a steady state during the halite deposition. To reach this steady state, Na and Cl lost by halite precipitation had to be added by inflow waters enriched in both elements so that a recycling mechanism was needed. With the available data it is not possible to determine the source (marine, continental or mixed waters) of the inflow implicated in the recycling mechanism.

Key words: Badenian salts, evaporite petrology, halite, fluid inclusions composition, Poland.

Introduction

Halite is the most frequent mineral precipitated during the evaporation of marine, continental, mixed, or hydrothermal waters. However, the solute composition of these saline brines undergoes important variations that are not recorded in the mineral precipitation. The direct analysis of the electrolyte composition of primary fluid inclusions in the halite crystals of ancient evaporite formations is the best method to identify the evaporation stage attained by the original brines.

The aim of the present paper is to characterize the chemical composition and origin of the mother brines of the Badenian halite rock salts of Poland by means of the analysis of fluid inclusions in primary halite crystals. Prior to fluid inclusion study, the mineralogical composition and textures of the halite salt rocks were established in order to recognize the sedimentary and diagenetic features of the deposit.

Geological setting

The Badenian Stage (M₄, Middle Miocene) of the Carpathian Foredeep in Poland has been subdivided into a

number of lithostratigraphic units. The oldest unit is known as the Skawina Beds (Fm) and consists of marly mudstones, siltstones, and shales. These sediments are up to 500 m thick in Upper Silesia and from 600 to 800 m thick in the area east of Kraków, Poland (Fig. 1).

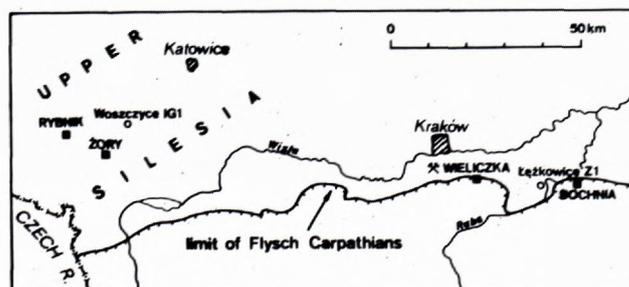


Figure 1 Location of profiles in Upper Silesia and in vicinity of Wieliczka salt deposit.

The Wieliczka Beds (Fm) overlie the Skawina Beds and are composed predominantly of evaporites (Garlicki, 1994a). In the southern part of the Badenian basin (Upper Silesia and the area east of Kraków) the Wieliczka Beds consist of rock salt and anhydrite. The normal thickness of

these sediments does not exceed 100 m. The Chodenice Beds overlie the Wieliczka Beds and were deposited during the final stage of an evaporite basin, in an euxinic environment. These sediments are therefore dark, thinly laminated, and contain a considerable amount of chlorides, sulphates, and carbonates.

Within the Badenian evaporites of southern Poland, several salt sections in the area of Upper Silesia and vicinity of Wieliczka have been recognized and correlated (Garlicki, 1971, 1974, 1993). Besides the Wieliczka salt deposit, among these sections, Woszczyce IG-1 and Łęzkowice Z-1 have given recently new materials for core examination and sampling (Fig. 1). However, the rock salt beds at the Wieliczka salt deposit are of utmost significance (Garlicki & Wiewiórka, 1983).

Sedimentary cyclothems and marker beds distinguished in the bedded part of the Wieliczka salt mine made it possible to carry out a lithostratigraphic correlation in a regional scale (Garlicki, 1979, 1994b). It has been stated that salts of cyclothem I were deposited only in the area between Bochnia and Tarnów. In cycle II, the sedimentation of salt covered an area from Upper Silesia to Tarnów. During that period, the oldest salts (N) of Wieliczka were deposited (Fig. 2). In cyclothem III the sedimentation of salt had the greatest extent, ranging from Upper Silesia to the area east of Tarnów. At Wieliczka, these sediments contain the following marker beds: ZP - green layered salts, SZ - shaft salt, SD - lower spiza salts. Corresponding similar sediments are found in neighbouring sections (Fig. 2). The cyclothem IV includes in Wieliczka area the upper spiza salt (SG) similar to the lower.

Results and interpretation

A total number of 25 samples were selected corresponding to three salt sections: the borehole Woszczyce IG-1 in the west (Upper Silesia), the Wieliczka salt mine in Kraków area, and the borehole Łęzkowice Z-1 in the east (Bochnia area) (Table 1, Fig. 1, 2).

The halite samples were collected in the autochthonous parts of the sections. In the Wieliczka section, additional samples numbered 6 and 7 were collected from the uppermost brecciated part of the deposit (not shown in Fig. 2), which primarily was deposited in the southern zone of the sedimentary basin. This upper unit consists of a coarse breccia composed mainly of salt clays with irregular blocks of coarse grained salt. The Chapel of Blessed Kinga (54 m long, 14.5 m wide, and 10 m high) is located in one of the largest blocks.

Petrology

In the studied samples halite is the main constituent. It is fine (150 μm) to coarse crystalline (up to 3 cm). Relics of randomly oriented hopper crystals are abundant in

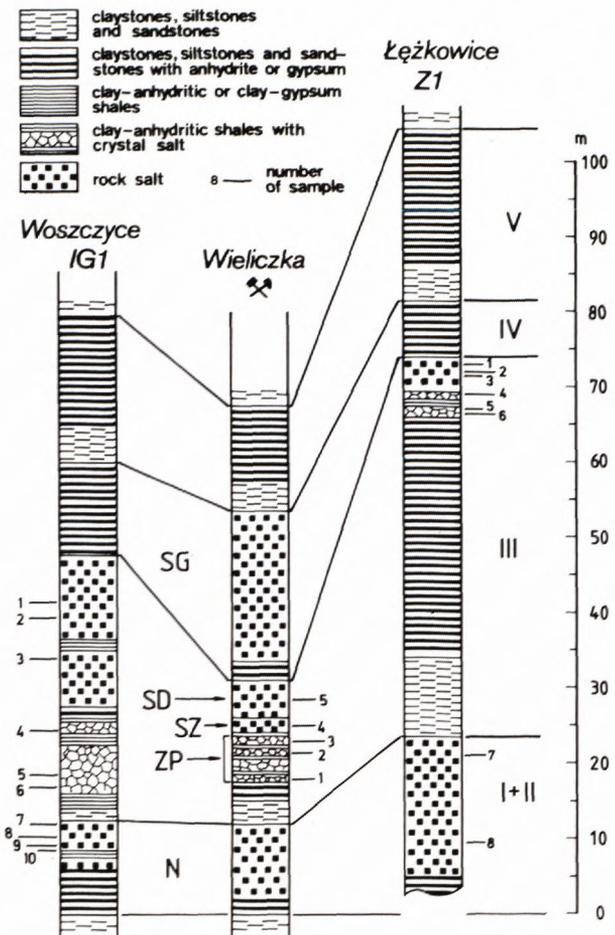


Figure 2 Lithostratigraphic correlation of salt sections Woszczyce IG-1, Wieliczka, and Łęzkowice Z-1.

samples from Woszczyce IG-1 and Łęzkowice Z-1, and scarce in samples from the autochthonous bedded deposit of Wieliczka. Neither chevron nor cornet structures were observed, although the former have been reported from Wieliczka salt mine in the literature (Czapowski, 1994).

Anhydrite and gypsum are the occurring sulphate minerals, the latter being derived from partial anhydrite rehydration. Polyhalite was neither detected by XRD nor clearly identified under microscope. Anhydrite shows different varieties: microcrystalline nodules (up to 1 cm), individual laths (up to 0.8 mm) or rectangular crystals (up to 2.4 mm) and poikilitic cements in the muddy component. Tiny euhedral gypsum crystals were observed inside some fluid inclusions; we interpret them as primary trapped crystals so that the original paragenesis was halite-gypsum (García-Veigas *et al.*, 1991).

Dolomite is scarce, but equant crystals, from 30 to 120 μm , were identified by SEM in samples from Woszczyce IG-1.

The fine-grained detrital component is scattered in general, but can occur as thin laminae up to 1.5 cm thick in

Table 1 Sampling and studies carried out in Badenian halite rocks from Poland. Facies: N - oldest salts, ZP - green salt, SZ - shaft salt, SD - lower spiza salt. Mineralogy (abundant minerals are indicated in capital letters): h - halite, g - gypsum, a - anhydrite, q - quartz, d - dolomite, c - celestite.

	Depth (m.)	Facies	Mineralogy (XRD)	Thin section study	Fluid inclusion study
WIELICZKA MINE					
	1	ZP	H-a-q-g		
	2	ZP	H-a-g	+	
	3	ZP	H-G-a-q	+	
	4	SZ	H-a	+	
	5	SD	A-a-g	+	
	6	Breccia	H-a-g	+	
	7	Breccia	H-q-g	+	
ŁĘŻKOWICE Z-1					
	1	77.0	SD-SZ	H-a	+
	2	78.0	SD-SZ	H-a	+
	3	78.5	SD-SZ	H-a	+
	4	80.9	ZP	H-g-a	+
	5	83.1	ZP	H-g-a	+
	6	83.5	ZP	H-g-a-q	+
	7	129.3	N	H	+
	8	140.7	N	H-a	+
WOSZCZYCE IG-1					
	1	291.5	SD	H-a-g-c?	+
	2	293.3	SD		+
	3	298.6	SZ	H-g-a-q	+
	4	308.8	ZP	H-a-g	+
	5	314.4	ZP	H-a-g	
	6	315.2	ZP	H-g-a-d-q	+
	7	320.5	N	H-g-a	+
	8	322.8	N	H-a-g	+
	9	324.2	N	H-a-g	+
	10	324.7	N	H-g-a	+

one sample (Łężkowice, sample 5). It is formed by carbonate minerals and clay. The former were not clearly detected by XRD except in one sample (dolomite in Wieliczka, sample 6). However, under the microscope carbonate micrite can be identified and by SEM observation calcite, and dolomite pellets were detected in some samples from Woszczyce IG-1. Opaque minerals (pyrite) are also frequent. In the Wieliczka samples muddy component contains abundant quartz grains and rock fragments.

1. Salt Mine Wieliczka

In green layered salts (ZP), halite is coarsely crystalline, with scattered fluid inclusions. It contains anhydrite as laths (from 25 to 150 μm long) and light blue nodules approximately 1 cm in diameter; they are partly hydrated to secondary gypsum. The fine-grained detrital component

is also present and contains angular quartz grains (15 to 100 μm) and rock fragments (shales, phyllites) in a clayey matrix, resembling the texture of wackes. Glauconite and hematite also occur.

In shaft salt (SZ) and lower spiza salt (SD), halite is medium to coarsely crystalline (from 200 μm to 1 cm). Crystals are anhedral and some of them are elongated. Primary fluid inclusions are scarce and only secondary fluid inclusions, caused by grain boundary migration, can be observed. Anhydrite occurs in the halite grain boundaries, inside halite crystals as prismatic/rectangular crystals (up to 1.2 mm long), and also occurs in microcrystalline (fibrous?) zones, with larger crystals around them. Some anhydrite crystals are partly hydrated to secondary gypsum. The fine-grained detrital component is scarce and contains mostly quartz grains and rock fragments.

In the brecciated deposit, one of the studied samples contains coarsely crystalline halite (1 cm across). In fine-grained detrital zones smaller euhedral halite crystals occur. Primary fluid inclusions are abundant in relics of hopper crystals. Anhydrite occurs in the halite grain boundaries and also inside the halite crystals as scattered crystals (0.4 mm long), and as rounded zones (nodules?) (1.3 mm across). Anhydrite is partly hydrated to secondary gypsum. The fine-grained detrital component is present in the halite grain boundaries and also constitutes a discontinuous lamina. The second sample studied is a large halite crystal (4 cm long) with tiny primary fluid inclusions (hopper crystal).

2. Łężkowice Z-1

In the oldest salts (N), halite is medium-to-finely crystalline. Smaller euhedral crystals (250 μm - 0.5 mm) occur associated with the fine-grained detrital component. Larger anhedral crystals are elongated and up to 8 mm long. Primary fluid inclusions are frequent in the larger halite crystals being relics of hopper crystals. Zones of clear halite are also present. Secondary fluid inclusions originated by grain boundary migration can be observed. Anhydrite forms nodules (3.5 mm across) with a microcrystalline texture. Larger prismatic anhydrite crystals arise from the periphery of these nodules. Anhydrite is also present as scattered laths (up to 0.8 mm long). These laths are absent in clear halite zones. Fine-grained detrital component occurs among the halite grain boundaries and is also lacking in clear halite zones.

In green layered salts (ZP), halite is coarse crystalline (1.5 cm) but euhedral crystals (200 μm - 1 mm) occur associated with the fine-grained detrital horizons. Primary fluid inclusions can be observed in relics of hopper crystals (8 mm - > 2 cm). Clear halite zones are also present. Secondary fluid inclusions originated by grain boundary migration also exist. Anhydrite occurs in two varieties: nodules replaced by secondary gypsum porphyroblasts

preserving anhydrite relics, and tiny anhydrite laths (80 μm long). The fine-grained detrital component occurs around the anhydrite nodules and among the halite crystals, and can also form laminae. Sample 6 is petrographically similar to the oldest salts described above.

In shaft salt (SZ) and lower spiza salt (SD), halite is medium to coarsely crystalline (up to 1 cm across). Zones of cloudy halite can be observed. Small anhydrite nodules (1-2 mm across) and scattered fine-grained detritus also occur.

3. Woszczyce IG-1 (Upper Silesia)

In the oldest salts (N), halite is mainly coarse crystalline (1 cm across) but smaller euhedral crystals (from 150 μm to 0.5 mm) are also recorded. Primary fluid inclusions are abundant corresponding to relics of hopper crystals (up to 9 mm) and secondary fluid inclusions originated by grain boundary migration also occur. Anhydrite is present in two varieties: blue coloured nodules (up to 5 mm across), often hydrated to secondary gypsum, in which larger prismatic crystals arise from the periphery of the nodules; and large rectangular crystals (up to 2.4 mm long) partly hydrated to secondary gypsum. Dolomite occurs as square ("sucrosic") crystals (from 30 to 120 μm long) that occur preferentially in the halite grain boundaries and locally are associated with fluid inclusions caused by grain boundary migration. A fine-grained detrital component is present among the halite crystals and around the anhydrite nodules. It contains tiny anhydrite crystals and opaque minerals.

In green layered salts (ZP), halite is coarsely crystalline (up to 3 cm) but smaller (less than 3 mm) euhedral crystals also exist, partly replaced by anhydrite. In some crystals primary fluid inclusions are preserved corresponding to relics of hopper crystals up to 1 cm. Anhydrite occurs as large elongated crystals associated with the fine-grained detrital component. Many of them are partly hydrated to secondary gypsum. Locally, lutecite was observed replacing anhydrite. Anhydrite also occurs as poikilitic cement in the fine-grained detrital component. This component is abundant and contains dark elongated dolomite pellets, identified by SEM-EDS, and gypsum crystals. Samples 4 and 5 contain coarse crystalline halite with relics of hopper crystals and a scattered fine-grained detrital component.

In shaft salt (SZ) and lower spiza salt (SD), halite is coarse crystalline with relics of hopper crystals and a fine-grained detrital component in variable amounts.

Bromine

All the analyzed halite samples have bromine contents between 20 and 40 ppm, in accordance with previously published data (Garlicki & Wiewiórka, 1983). These low values result from precipitation in a weakly concentrated

brine where halite recycling in slightly concentrated seawater took place (Holser *et al.*, 1972; García-Veigas *et al.*, 1995).

Fluid inclusions

The analysis of fluid inclusions was performed by the Cryo-SEM-EDS methodology described by Ayora & Fontarnau (1990) and improved by Ayora *et al.* (1994a,b) and García-Veigas (1995). This method allows quantitative analysis of the electrolytes present in fluid inclusions by direct microanalysis of frozen salt samples in SEM-EDS equipment.

In this method, a slice of halite about 1 cm^2 by 1 mm thick is placed in a sample holder with four droplets of solutions of known composition. The sample holder is then immersed in liquid N_2 and introduced in a lateral cryo-chamber of a Scanning Electron Microscope at -170°C . Inside the cryo-chamber, the mineral is broken and a flat, pristine surface is obtained, which contains a number of frozen fluid inclusions. The surfaces of the halite and the droplets are coated with aluminium in order to avoid surface electric charging. The holder is placed in the chamber of the SEM and the electron probe is focused in a few microns volume over frozen fluid inclusions or droplets and an Energy Dispersive Spectrum (EDS) in a Si-Li detector is obtained. The work conditions are established at 15 kV of probe energy, 1.5 nA of beam current and 200 s counting time. The peak-to-background ratio (I_p/I_b) of the EDS peaks for the elements present in the droplets defines a linear regression where the (I_p/I_b) of the elements in fluid inclusions are interpolated, to obtain the chemical composition of the fluid inclusions. This methodology allows the quantitative analysis of major solute chemistry (Na, Mg, K, Ca, Cl and SO_4) in natural brines trapped in primary fluid inclusions in halite.

Due to the scarcity of primary fluid inclusions in the halite from the Wieliczka salt mine, the determinations were performed in samples from the boreholes Łęzkowice Z-1 (Bochnia area) numbered 1, 7 and 8, and Woszczyce IG-1 (Upper Silesia) numbered 2, 4 and 7. The results of Cryo-SEM-EDS analysis are shown in Table 2.

The composition of the fluid inclusions corresponds to the system Na-Cl-Mg- SO_4 -K that can be considered as a marine brine. The average compositions (Table 2) are similar to the composition of concentrated seawater at the beginning of halite precipitation (McCaffrey *et al.*, 1987) (Table 3).

All the analyzed fluid inclusions have very similar compositions suggesting that the mother brines did not vary significantly from Upper Silesia to the Bochnia area. This is in agreement with the idea that the three sub-basins described in the Badenian evaporite basin had free and continuous water/brine exchange (Garlicki, 1979). Differ-

ences may be caused by minor variations in the composition of the mother brines, or due to analytical errors of the technique (less than 10%).

On the other hand, the homogeneity in the fluid inclusion compositions, from the oldest salts to the lower spiza salts suggests that the original brines reached a steady state during the deposition of the halite recorded in the studied sections. This steady state can be attained if the amounts of Na and Cl lost by halite precipitation are compensated by the inflow of a brine enriched in both elements so that a recycling mechanism of an older halite deposit is necessary.

Table 2 Average composition (in mol/l) of the components in the fluid inclusions analyzed from the Badenian salt deposit in Poland. Analyses performed by Cryo-SEM-EDS

		Na	Mg	SO ₄	Cl	K
ŁĘŻKOWICE						
Z-1						
	1	4.27	0.54	0.14	5.46	0.15
	7	4.39	0.50	0.12	5.50	0.06
	8	4.28	0.44	0.12	5.52	0.07
WOSZCZYCE						
IG1						
	2	4.14	0.57	0.15	5.52	0.13
	4	4.38	0.57	0.14	5.57	0.08
	7	4.30	0.44	0.14	5.46	0.07

Table 3 Composition of Inagua brines during the evaporation path of seawater at several stages: inflow seawater, beginning of gypsum precipitation, beginning of halite precipitation, first brine evaporated in laboratory and beginning of potassium and magnesium salts precipitation. Original data from McCaffrey *et al.* (1987).

	Na	Mg	SO ₄	Cl	K
Seawater	0.49	0.05	0.03	0.59	0.01
Gypsum	2.05	0.23	0.12	2.44	0.04
Halite	4.48	0.51	0.118	5.24	0.10
Laboratory	2.52	1.93	0.69	5.44	0.36
Potassium salts	0.63	3.53	1.19	5.91	0.67

Discussion

The geochemical study (fluid inclusion composition and bromine contents in halite) of Badenian rock salts of the Carpathian Foredeep in Poland indicates that halite is partly recycled in origin. The recycling of early halite deposits located at the basin margin is a common process at the final stage of many saline formations, as it has been reported in the Messinian salt deposits of Central Sicily basin and Lorca basin (Spain) (García-Veigas *et al.*, 1995) and in the Eocene potash basin of Navarra (Spain) (Ayora *et al.*, 1994b).

As stated above, the homogeneity in the composition of fluid inclusions (steady state) and the low bromine

contents in salt, can be achieved by the inflow of waters enriched in Na and Cl by dissolution of an older halite deposit. With the available data it is not possible to determine the source of the inflow (marine, continental or mixed) or the evaporitic formation recycled (the Zechstein salt rocks or the earlier halite deposits of the Badenian basin).

In order to maintain the halite precipitation in a steady-state condition, an inflow enriched only in Na-Cl is required but, in this case, the contents of potassium, magnesium, and sulphate would be lower than those obtained in the analyzed fluid inclusions because the mother brine would achieve the saturation in halite in an early stage of concentration. This situation is recorded in the composition of fluid inclusions in the upper section of the Messinian halite formation of Lorca basin (Spain) (Ayora *et al.* 1994a; García-Veigas, 1995) where the brine composition shows a continuous decrease in Mg and K, and an increase in Na contents.

Although the composition of the fluid inclusions studied is very similar to the composition of seawater at the beginning of halite precipitation, it could also be achieved by the evaporation of a special type of continental waters (Ayora *et al.*, 1994a). However, the connection of the Badenian Carpathian Foredeep with the open sea is accepted in the literature (Rögl & Müller, 1978; Czapowski, 1994).

The relics of hopper halite crystals that exist in the studied halite samples show some features that are in accordance with the idea that halite precipitation took place in a calm brine body that had reached a steady state composition. These crystals have an inner core where fluid inclusions are disorientated suggesting the equilibrium of the brine, without a marked salinity gradient, and with no variations and no supersaturation. This situation can be achieved in a deep brine or in a stratified brine. The orientation of fluid inclusions that can be observed in the outer part of these crystals is related to their large size: when halite crystals reach a critical size, a preferential development of cube edges over cube faces occur due to a mass transfer problem (Batchelder & Vaughan, 1967).

Polyhalite is absent or, at least, very scarce in Badenian salt deposit. This mineral grows interstitially during early diagenesis replacing initially a precursor sulphate mineral (gypsum or anhydrite) and after the halite crystals. The halite replacement starts from the grain boundaries surrounded by muddy sediment. Primary sedimentary deposits of polyhalite are unknown, as far as we know. In the predicted evaporation sequences this mineral precipitates only if potassium is abundant in the brine, and also magnesium, although in a lower degree. In the Eocene potash formation of the Navarra basin polyhalite occurs in the lower part, below the potash beds, but is lacking in the upper halite unit which formed from a K-poor brine

(Rosell, 1983; Ayora *et al.*, 1994b). In the halite samples studied from the Badenian salts, potassium contents are also very low in the fluid inclusions indicating a low concentration of this element in the mother brines.

Acknowledgements

This study has been supported by the Spanish DGICYT Project PB 94-0882. Fluid inclusions and XR analysis were performed at the Serveis Científic-Tecnic of the Universitat de Barcelona. The authors are indebted to Dr. F. Ortí by his helpful suggestions, and to Dr. T.M. Peryt for the revision of the final manuscript.

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Geochemistry of the Badenian salts from the East Slovakian Basin, Slovakia

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Abstract. The chemical composition of primary fluid inclusions in chevron halite occurring in the Badenian Zbudza evaporite formation in the East Slovakian Basin shows that the brine belonged to the Na-K-Mg-Cl-SO₄ type and that during salt accumulation the ratio of ions was close to modern seawater when saturated to the corresponding stage. A slightly decreased content of SO₄ caused by inflow of continental water into the basin was recorded. The brine concentration did not rise over the initial stages of halite precipitation. Bromine content in the halite (13-89 ppm) also indicates a marine genesis for the salt, a very low brine concentration, and the impact of continental water.

Key words: Badenian, evaporites, salts, halite, fluid inclusions, bromine, East Slovakian basin.

Introduction

Badenian evaporite deposits are widespread in the foreland basin and inner depressions of the Carpathian Mts (Sonnenfeld, 1974; Korenevsky *et al.*, 1977). They were formed in restricted basins which have been connected one with another. The marine origin of evaporites in most basins is supposed considering paleogeographic reconstructions, facies analysis, determinations of bromine content in salts, isotopic composition of sulfate sulfur, and the chemical composition of solutions in primary inclusions from chevron halite (Sonnenfeld, 1974; Korenevsky *et al.*, 1977; Claypool *et al.*, 1980; Garlicki & Wiewiórka, 1981; Petrichenko, 1988; Karoli, 1994; Kovalevich, 1990, 1994; Kovalevich & Vityk, 1995; Kovalevich & Petrichenko, 1997). The significant role of other sources of ion supply is emphasized by some authors (Dzhinoridze *et al.*, 1980; Liszkowski, 1989). Until now the geochemical study of halite deposits from the East Slovakian basin has been very limited. Specifically, inclusions in halite were studied in only a few samples (Panov *et al.*, 1989; Kovalevich & Petrichenko, 1997). Therefore the hydrochemical evolution of the brine during salt accumulation and the impact of continental water on the chemical composition of brine in basin remain uncertain. The goal of this paper is to interpret these questions by the detailed investigation of bromine content and of the chemical composition of brine inclusions in halite in the entire halite sequence.

Geological setting

The Zbudza Formation in the uppermost part of the middle Badenian deposits in the East Slovakian Basin, which is a part of the Transcarpathian Depression. Deposition of the formation reflects the beginning of the Paratethys disintegration and conspicuous paleogeographic changes. The Zbudza Formation represents the regression stage of the early to middle Badenian sea. At that time, evaporitic deposition was restricted to the deepest, tectonically restricted, basin areas. The regressive character of the formation is evident from Fig. 1 showing the paleogeologic reconstruction. After the deposition of the Zbudza Formation, deltaic sedimentation prevailed in the brackish and lacustrine environment during late Badenian. At that time the East Slovakian Basin opened toward the south Panonian Basin.

The maximum thickness of the evaporite formation is 300 m. The formation is known only from the subsurface. Predominantly, it contains halite. The layers or lenses have maximum thickness of 75 m, occasionally they are interbedded with clays. The evaporite facies of Zbudza Formation from the studied boreholes are shown in Fig. 2.

Petrography and analytical methods

Fourteen samples (each 1 kg in weight), representing the entire section of the halite sequence from borehole Ep-2

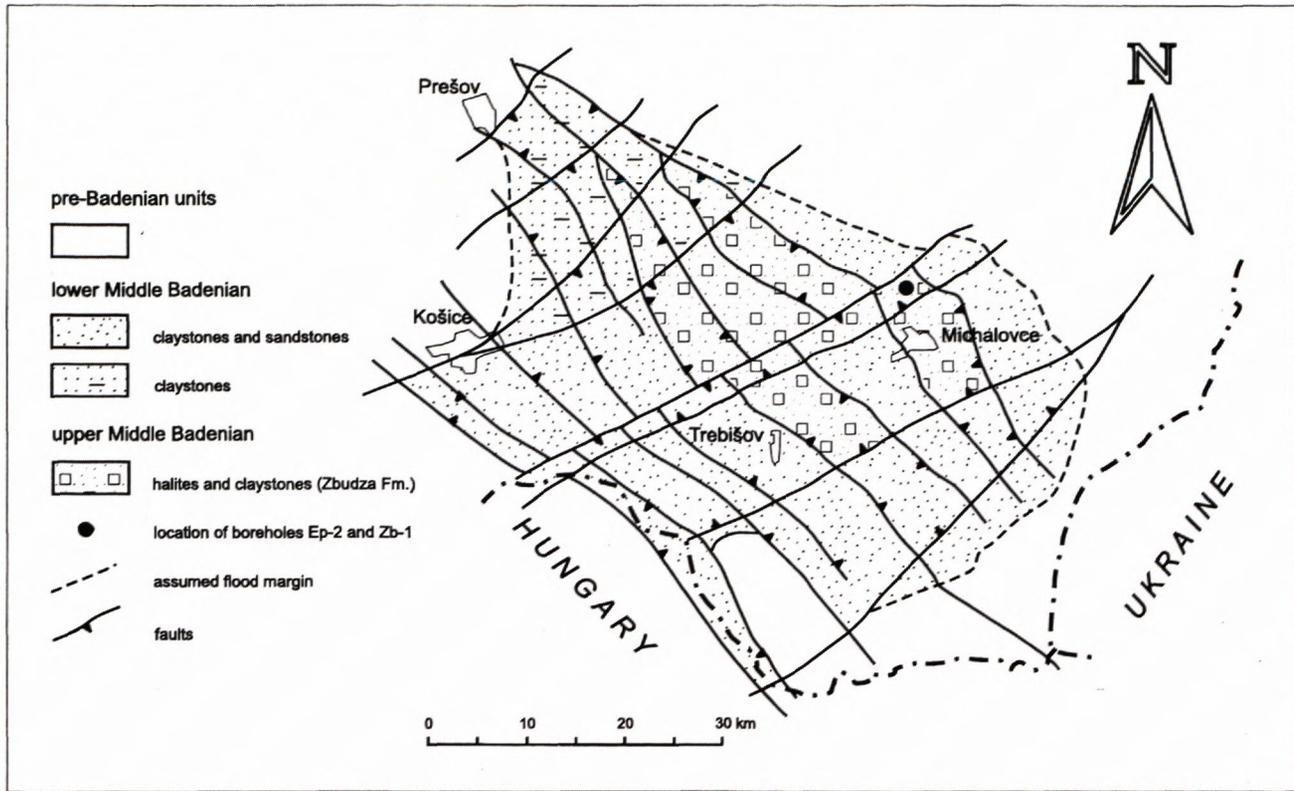


Fig. 1 Paleogeologic map of Lower and Middle Badenian

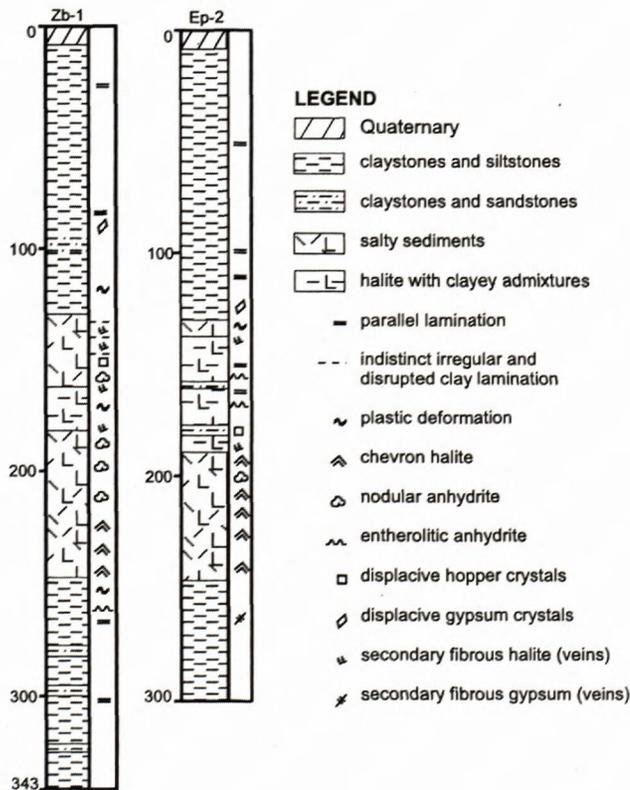


Fig. 2. Sedimentary succession in boreholes Ep-2 and Zb-1.

were investigated. Halite bedding is caused by intercalation of coarse-grained and fine-grained salt and thin layers of anhydrite with an admixture of terrigenous material (Fig. 3). Coarse-grained salt prevails in the section; its layers range in thickness from 1 to 10 cm and average 5 cm. The thickness of the layers of fine-grained salt, as a rule, does not exceed 3 cm, and of anhydrite - several mm. The dip of the beds in some samples reaches 40°.

The boundaries between the beds are crumpled, the contacts sometimes rupture evidence of intensive tectonic crumpling of the rocks. Coarse-grained rock salt is composed of halite grains of isometric (or close to cubic) shape, sometimes elongated (up to 3 cm). White spots formed by numerous fluid inclusions are observed in almost all halite grains. In elongated grains chevron structure is sometimes well developed. Accumulations of microcrystalline aggregates of white anhydrite that form nodules up to 1.5 cm across are often present around the grains. Fine-grained rock salt is composed of flattened halite grains oriented along the bedding. Their length reaches 10 mm and thickness 3-4 mm. Zoned inclusions have not been seen in this salt type. Anhydrite layers are crumpled and are mainly along the contact between coarse-grained and fine-grained rock salt. They are obvious due to the white colour of anhydrite aggregates.

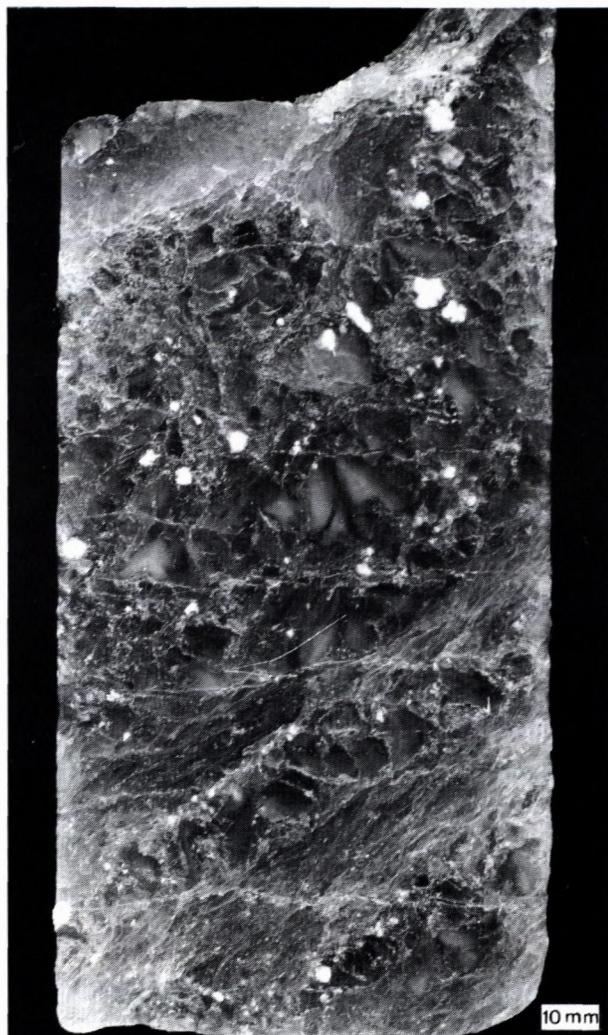


Fig. 3 Fabric of the rock salt, Ep-2, sample No. 66

In borehole Zb-1 three samples of coarse-grained rock salt, very contaminated by terrigenous material, were studied by Panov *et al.* (1989). Chevron halite crystals were observed in one of these samples.

Bromine content has been determined and the morphology, shape, phase composition of fluid inclusions and their distribution in sedimentary and recrystallized halite have been studied in the rock salt from borehole Ep-2. The determination of bromine content in salt was carried out by means of volumetric iodometric-titration method and was controlled by analyses of standard specimens. The error of analysis was 0.002 %. The ultramicrochemical analysis of brine in the individual inclusions has been carried out by method of Petrichenko (1973) by means of glass capillaries. Such compounds as K^+ , Mg^{2+} , SO_4^{2-} , Ca^{2+} (Na^+ and Cl^- contents are calculated) may be determined by this method. The error of determination for each element in case of 3 parallel replicate analyses does not exceed 17%. This method permits the investigation of inclusions 40 μm across.

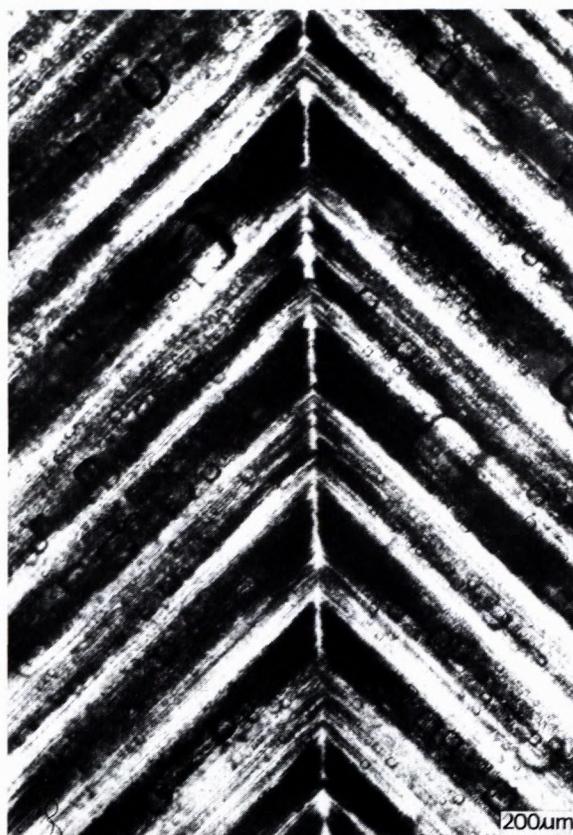


Fig. 4. Symmetric chevron crystal with definite rhythmic zonation.



Fig. 5 Asymmetric chevron crystal

Fluid inclusions in halite

Fluid inclusions are widespread only in the halite grains of coarse-grained salt. For their investigation plates of halite up to 2-5 mm thick were prepared. In the central part of the grains chevron crystals with fluid inclusions were observed. The mechanism of their growth has been studied in detail in modern as well as in ancient halite deposits (Valiashko, 1951; Dellwig, 1955; Holser, 1979; Roedder, 1984). Chevron crystals are believed to

form on the bottom of the basin due to competitive growth during the evaporation of brine. In the recrystallized transparent part of halite grains rare single inclusions are observed which are arranged without any order. Chevron crystals are symmetrical (Fig. 4) or asymmetrical (Fig. 5), obviously caused by a different orientation of halite crystals on the bottom of the basin and resulting from different rates of halite growth on separate faces. In some crystals the rhythmic alternation (see Fig. 4) is formed by intercalation of relatively wide in-

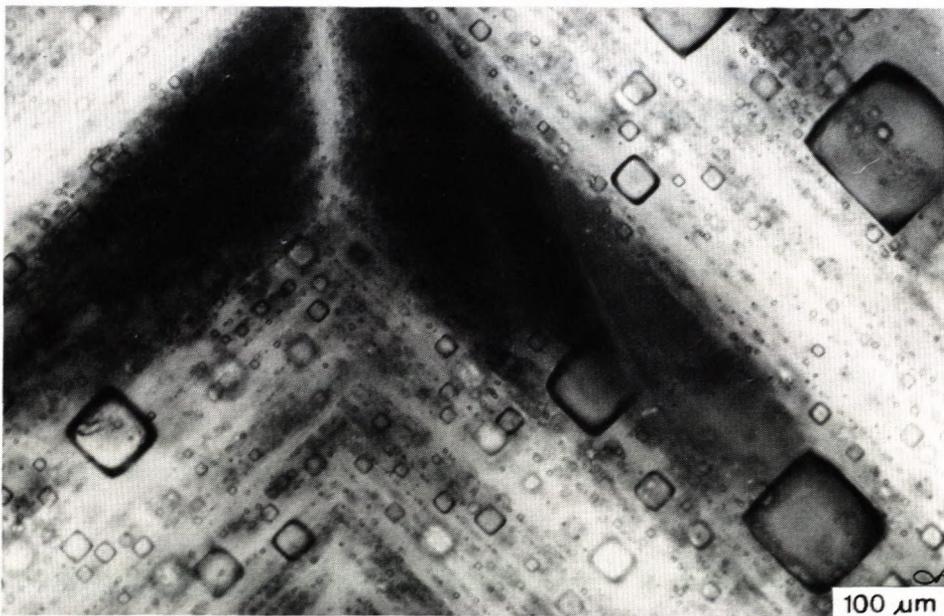


Fig. 6 Fragment of chevron crystal with large one-phase fluid inclusions

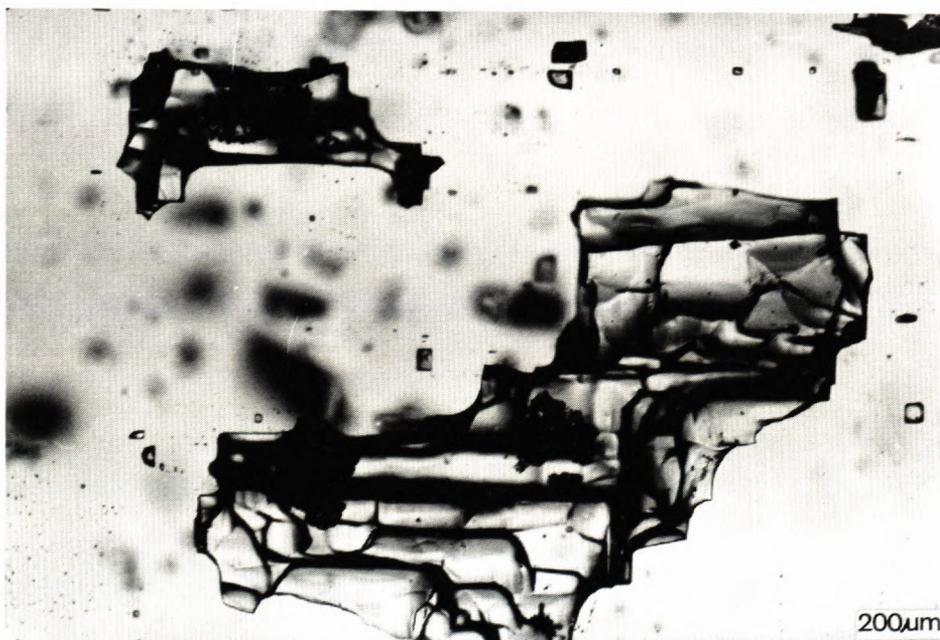


Fig. 7 Large fluid inclusions of irregular shape in recrystallized halite

clusion-rich zones and inclusion-poor zones. The zones with numerous inclusions were formed during the day (high rate of growth), and zones without inclusions during the night (slow rate of growth) (Valiashko, 1951; Holser, 1979). The inclusions in chevron crystals are one-phase, fluid, of cubic shape (Fig. 6). In large inclusions the terrigenous parts and anisotropic needle-crystals (anhydrite?) are present. Inclusions are a fraction of to 300 μm across and rarely reach 450 μm . A transparent halite that forms separate crystals or peripheral parts of chevron halite is recrystallized during a post-sedimentary stage. Inclusions in this halite are also one-phase, but they are rare and located in crystals without any order. Sizes of these inclusions, as a rule, are larger (up to 2 mm) and their shape is mainly irregular (Fig. 7). Many of them contain the terrigenous material. Thin platy crystals of anhydrite are present in peripheral parts of the transparent and chevron crystals as well as in tight cracks.

Results and interpretation of analyses

The chemical composition of inclusions in sedimentary halite is shown in Tab. 1 and Fig. 8. The content of K^+ changes from 3.3 to 5.5 g/l, of Mg^{2+} from 11.0–16.7 g/l; of SO_4^{2-} from 8.2–9.8 g/l. No sharp deviations from average values are noticed from the lower to upper part of the rock salt sequence. The previous data (Panov *et al.*, 1989) about the chemical composition of the inclusions in sedimentary halite in borehole Zb-1 are close to ours in ratio of ions as well as in total

concentration of solutions. The results indicate that the basin brine corresponds to the Na-K-Mg-Cl- SO_4 type. The concentration of brine did not exceed the initial stage of halite precipitation (see Table 1). The results of analyses were plotted in a Jänecke diagram (Fig. 9). Sample compositions are grouped on the boundary between the fields of crystallization of kainite and sylvite. That grouping is characterized by lower content of SO_4^{2-} in the basin brine, compared to that in modern seawater when saturated to the point of halite precipitation. The lower SO_4^{2-} content may be related to an increased supply of continental water to the basin. The bromine content in the medium-grained halite ranges from 13 to 33 ppm, and in coarse-crystalline halite from 27 to 89 ppm. Values characteristic for medium-grained salt are lower than normal values for initial stage of halite precipitation from seawater (Valiashko, 1962; Holser, 1966). The bromine content in both the halite varieties correlates along the vertical profile and the deviation of values from the average is not significant (Fig. 8). Accordingly, although the source of salt was marine, there was an impact of continental run-off on the composition of brine in the East Slovakian Basin. The presence of large amounts of chevron crystals and, specifically, those with rhythmic zonation evidences the shallow depth of the basin and the formation of halite sequences due to evaporation. The data on brine concentration in the basin and on bromine content in halite show the low likelihood of occurrence of potash salt deposits in the Badenian rocks.

Table 1. The chemical composition of brine inclusions in primary halite of the Badenian evaporite formation from borehole Ep-2. The number of analyses is shown in brackets. Data on modern seawater after Valiashko (1962).

Sample number	Content, g/l solution			Br in the coarse-grained halite, ppm	Br in the medium-grained halite, ppm
	K^+	Mg^{2+}	SO_4^{2-}		
71	5.1 (2)	13.9 (3)	8.7 (3)	65	
70	4.8 (2)	13.4 (3)	8.8 (2)	48	31
68	3.9 (2)	13.0 (3)	8.5 (3)	40	13
65	5.5 (2)	16.7 (3)	9.1 (3)	33	
63	5.2 (2)	12.9 (3)	9.4 (3)	33	20
61	4.5 (3)	11.4 (2)	8.3 (2)	26	13
59	4.3 (3)	13.5 (3)	8.6 (2)	66	33
57	4.8 (2)	12.8 (2)	9.0 (3)	51	20
56	5.1 (2)	12.4 (2)	8.8 (3)	40	3
55	5.2 (2)	13.0 (2)	9.8 (2)	89	
54	4.7 (2)	12.1 (3)	8.6 (3)	53	
53	4.5 (2)	13.3 (2)	9.7 (3)	33	
52	4.5 (3)	12.6 (2)	9.6 (3)	40	6
50	3.3 (2)	11.0 (2)	8.2 (2)	27	13
Modern seawater saturated to the beginning of precipitation of:					
halite	3.3	15.5	21.0		
sylvite	33.8	75.7	79.1		

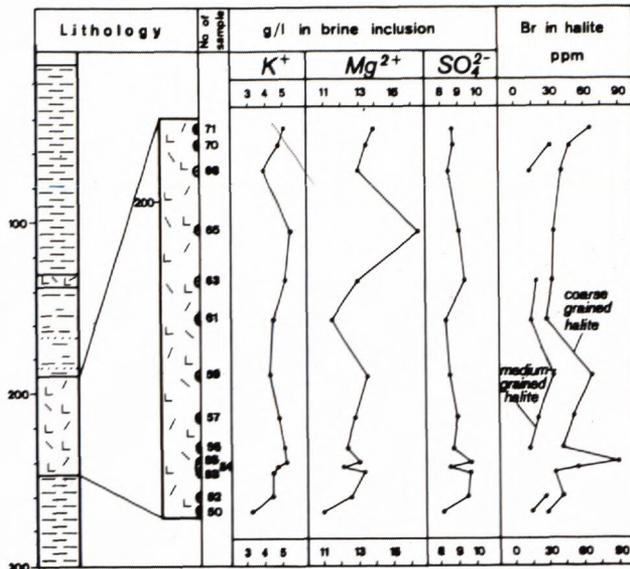


Fig. 8. Comparison of K^+ , Mg^{2+} , and SO_4^{2-} contents in brine inclusions in halite and of bromine in halite in 14 samples from borehole Ep-2.

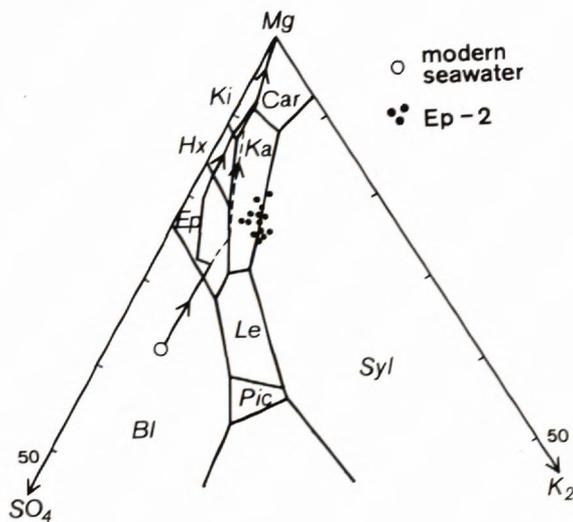


Fig. 9. Analyses of inclusion brines in primary halite from borehole Ep-2 plotted on a Jänecke projection of the quinary system $Na-K-Mg-SO_4-Cl-H_2O$ saturated with respect to halite at $25^\circ C$ (Eugster et al., 1980). The stability fields of Bl, bloedite; Car, carnallite; Ep, epsomite; Hx, hexahydrate; Ka, kainite; Ki, kieserite; Le, leonite; Pic, picromerite; Syl, sylvite, are indicated. Solid line – equilibrium path, dashed line – fractionation path.

Conclusions

Chevron structure in the samples is common. One-phase fluid inclusions with cubic shape prevail in coarse-grained varieties of halite. The sizes of inclusions vary from a fraction of to $450 \mu m$. The results show that the basin brine belonged to the $Na-K-Mg-Cl-SO_4$ type. The seawater was the main source of salt formation, and

its composition was close to the modern one. The sedimentation took place in a relatively shallow basin due to evaporation, and the brine concentration did not rise over the initial stage of halite precipitation; these conditions indicate a low likelihood for potash-bearing salts in the studied region.

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Geochemistry of Neogene evaporites of the Transcarpathian Trough in Ukraine

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Abstract. The initial brine during halite sedimentation in the Zaluzh salt-forming basin in the Chop-Mukacheve depression was of $\text{Na}^+\text{-Cl}^-\text{-Mg}^{2+}\text{-K}^+\text{-SO}_4^{2-}$ composition, and by ratio of K^+ and Mg^{2+} was close to the modern seawater saturated to the stage of halite precipitation. The progressive evaporation of the brine has led to a significant increase of the total concentration of solutions in the basin, but the halogenesis has not reached the high stages of its evolution and finished on the halite stage. During diagenesis the sediments were recrystallized under the impact of solutions, with the decreased concentration of the major compounds.

Key words: Miocene, evaporites, fluid inclusions, geochemistry, Transcarpathian basin.

Introduction

The Transcarpathian basin together with the Transylvanian and East Slovakian basins was a part of the united system of intracarpadian evaporite basins in the Middle Miocene (Kityk *et al.*, 1983). Two basins of the second order can be distinguished in the Transcarpathian basin: Zaluzh and Solotvyne, separated by Khust bar.

The distribution of salt-bearing deposits in the north-western part of the Transcarpathian trough in the Chop-Mukacheve depression is restricted to Mukacheve-Svalava region (Kityk *et al.*, 1983). Salt-bearing rocks are developed in the eastern part of the depression (Zaluzh, Irshava, Vynogradove) and other areas and sulfate-carbonate rocks occur in its southern part, in the Vynogradove area (Fig. 1). The Badenian deposits occur at a depth of 1000-1800 m. Their thicknesses range from 170 to 310 m. The deposits consist of interbedded dark grey, black, and rarely white rock salt, siliciclastic rocks and sometimes tuff-mudstones. In lower part of section the layers of gypsum and anhydrite are sometimes found. In some places (Zaluzh area), layers of tuff-sandstone and grey vitroclastic tuff were found.

The geochemical peculiarities of rock salts and the conditions of their formation have been studied mainly in the southeastern part of the trough (Solotvyne deposit). The literature data on the geochemistry of evaporites from the north-western part of trough are scarce (Kityk *et al.*, 1983; Khrushchov & Petrichenko, 1980; Petri-

chenko, 1989), and therefore the purpose of this investigation was to establish the geochemical peculiarities of formation of rock salt in this part of the trough. I have studied the core samples of rock salt from borehole 6-T in the Mukacheve region (Svalava, Health Centre "Carpathians"). During research work on thermal water at a depth of 1047-1318 m under the cover of Recent volcanic rocks of Vygortat-Gutinsk ridge where the occurrence of salt has not previously been supposed, an evaporite sequence of about 300 m thick was recorded.

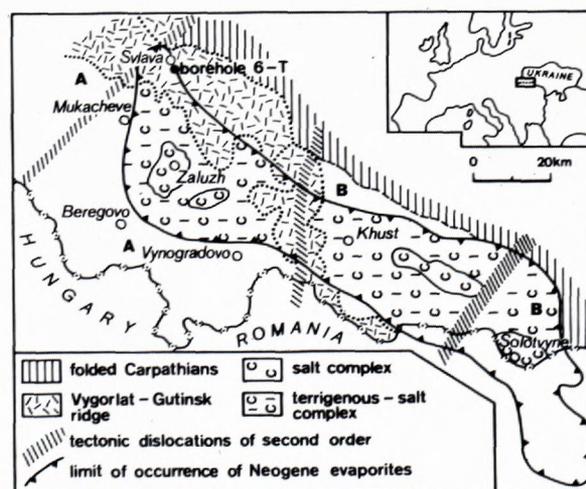


Fig. 1. Schematic map of distribution of Neogene evaporites in the Transcarpathian Trough (after Kityk *et al.*, 1983). A - Mukacheve depression, B - Solotvyne depression.

The composition of inclusion brines in halite has been determined by means of methods suggested by Petrichenko (1973) and Yermakov & Dolgov (1979). The data on Br⁻ and Br1000/Cl in halite and the composition of rock salt have been also used. The obtained information was correlated with data from the southeastern part of the trough (Solotvyne deposit).

Lithology

The studied rock salt is recrystallized. Its sedimentary origin is indicated by occasional occurrences of zonal constructions (chevrons) that have been preserved in grains and crystals and are macroscopically visible. Their diameters reach 2 cm. Under the microscope it can be seen that the zonation is caused by numerous microinclusions of brine and gas, that look like negative cubic crystals. These primary inclusions in halite indicate its primary crystallization from the brine.

The rock salt is fine- to coarse-grained and grain sizes vary from 1 mm to 2.0 cm. The structure is massive, cellular or laminated. The colour of the rock is light or dark grey and is caused by clay admixture. The clay in the salt is present in dispersed form (and the grains are grey and slightly transparent) or as thin seasonal layers, sometimes balls or chains inside the halite grains or around them. The clayey fraction in the insoluble residue of rock salt from the depth of 1075-1205 m consists of illite and mixed-layered growths of chlorite and trioctahedral montmorillonite. The amount of mixed-layered minerals decreases with depth. It should be noticed that chemical and X-ray analyses indicate that hydromica prevails and the chlorite admixture is present in the clayey fraction of the rock salt of Solotvyne deposit. My data confirm results obtained by Bilonizhka (1979) who recorded the hydromica with a significant admixture of magnesium-ferriferous chlorite in the clay fraction of salt rocks. In the same fraction from overlying terrigenous rocks the hydromica, chlorite, mixed-layered minerals (hydromica-montmorillonite), kaolinite and possibly montmorillonite are present. These facts permit the conclusion that during evaporation in the evaporite basin or during diagenesis of salt rocks, the montmorillonite and kaolinite were not stable and were transformed into illite and chlorite. It should be noted that Bilonizhka (1992) pointed out the presence of clastic magnesium-ferriferous chlorite and authigenic magnesium chlorite in the clay fraction from the rock salt of Solotvyne deposit.

The content of bromine and the value of the bromine-chlorine coefficient in halite is an important index for conditions of rock salt formation (Valiashko, 1962; Bilonizhka, 1975). Actual bromine contents in rock salt of different formations often differ from experimental and theoretically calculated contents of bromine in halite

crystallized at different stages of seawater saturation. The changes of the bromine-chlorine coefficient in halite from Chop-Mukacheve depression are shown in Fig. 2. The cleanest halite grains and crystals with the lowest amount of terrigenous admixture have been used for analyses. The sedimentary as well as recrystallized halite have been sampled. The chlorine and bromine content in halite are shown in Table 1. I compared these data with experimental and theoretically calculated contents of chlorine and bromine in the halite crystallized at different stages of seawater saturation (Table 2). The comparison shows that the studied halite is similar to that typical for a halite stage of crystallization of chlorides in marine-derived salt basin. The variation of the bromine-chlorine coefficient may be explained by the processes of postsedimentary alteration of halite that led to the bromine depletion. For Solotvyne deposit (mine 8), the average value of bromine in water-soluble part of halite (10 determinations) is 0.011% (maximum 0.020%, minimum 0.004%). The values of the Br 1000/Cl coefficient are 0.075-0.374, and the average is 0.187. These data also correspond to experimentally determined ones for the halite stage of chloride precipitation. Much lower is the content of bromine in halite, sampled in mine 9 of this deposit. The average value of bromine (22 analyses) is 0.003% (maximum 0.014%, minimum 0.001%). The Br 1000/Cl coefficient ranges from 0.016 to 0.205, and the average is 0.048. For the majority of samples from mine 9, these values are lower than in the samples from initial zones of halite crystallization from seawater. The decreased content of bromine and values of the Br 1000/Cl ratio are caused by recrystallization of halite.

Table 1. The content of chlorine and bromine in halite from the rock salt of the Chop-Mukacheve depression

Depth (m)	Content, %		Br 1000/Cl coefficient
	Cl ⁻	Br ⁻	
1047-1050	59.33	0.0055	0.093
1068-1079	59.41	0.002	0.034
1075-1078	57.13	0.007	0.122
1087-1090	58.84	0.009	0.153
1110-1114	56.35	0.004	0.071
1113-1114	55.86	0.0055	0.098
1127-1131	59.59	0.004	0.067
1135-1140	56.42	0.0025	0.044
1145-1149	55.67	0.003	0.054
1150-1154	55.67	0.003	0.054
1164-1167	55.38	0.005	0.090
1171-1174	55.22	0.008	0.145
1189-1194	57.07	0.003	0.053
1200-1205	57.08	0.006	0.105
1274-1278	56.75	0.002	0.035
1302-1306	58.30	0.0025	0.043
1314-1318	58.35	0.0035	0.060
Average	56.71	0.005	0.081

Table 2. The content of bromine (%) and the values of bromine-chlorine coefficient in chlorides of marine genesis.

Stage of chloride precipitation	After Valiashko (1962)		After Bilonizhka (1975)	
	Br ⁻	Br 1000/Cl coeff.	Br ⁻	Br 1000/Cl coeff.
Halite	0.068-0.026	0.11-0.43	0.006-0.016	0.099-0.26
Sylvite	0.027-0.037	0.44-0.61	0.016-0.025	0.26-0.41

sions in sedimentary halite have a cubic shape. They contain solutions with individual gas bubbles. The presence of this gas may be explained by overheating of inclusions after sedimentation. Sometimes a solid phase - needles of gypsum or anhydrite - is noticed. There are more variable inclusions in diagenetic halite. Except of relics of sedimentary halite, several types of inclusions are developed.

Both primary and secondary inclusions are distinguished. Secondary ones are located in healed fissures, by aggregate state they are fluid and gas-fluid with a not-

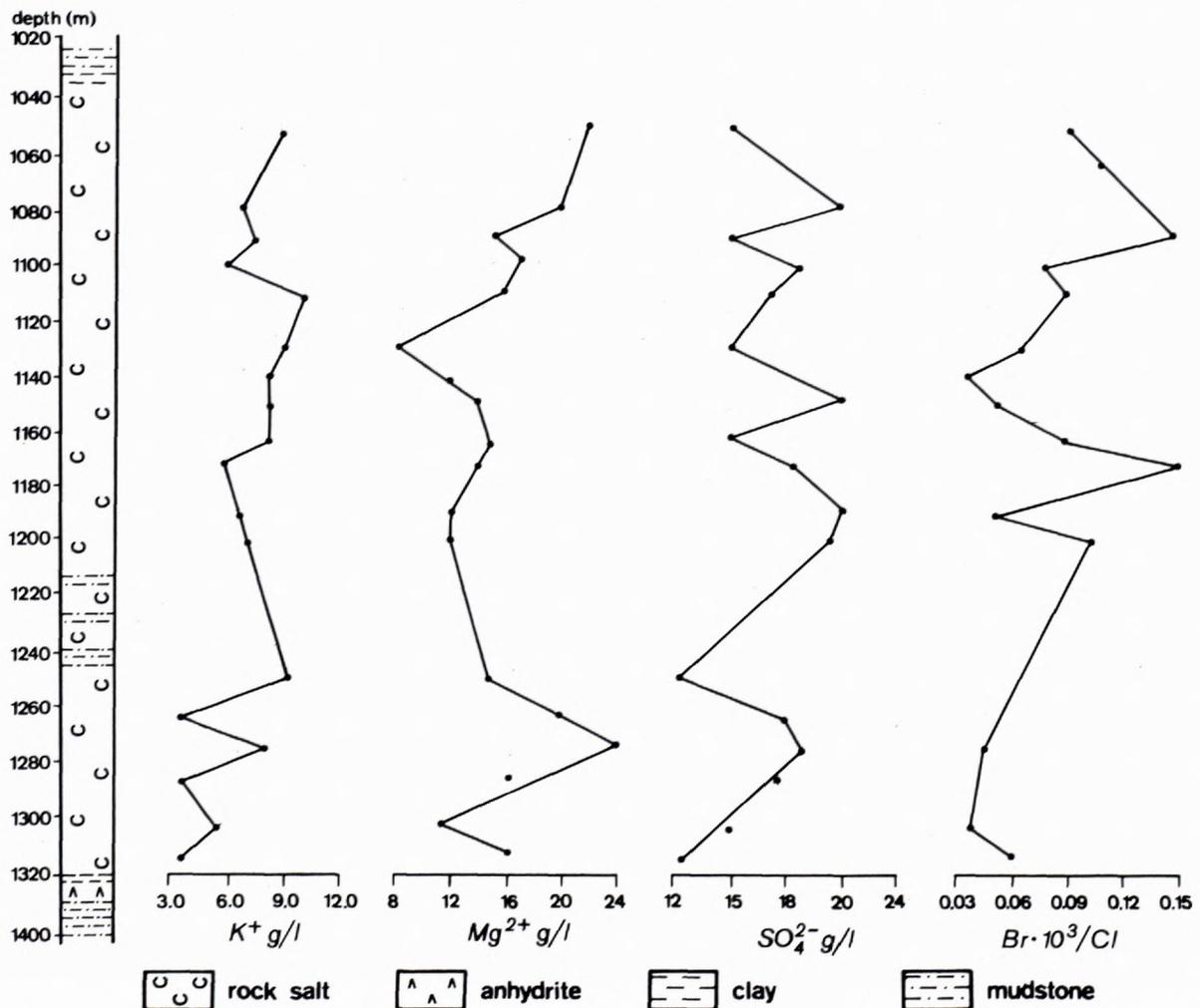


Fig. 2. The content of potassium, magnesium and sulfate ions in brine inclusions and the values of bromine-chlorine coefficient in recrystallized halite in the section of borehole 6-T (Svalava, Mukacheve region).

The results of inclusion study

Under the microscope it is seen that the rock salt consists mainly of recrystallized (diagenetic) halite with chevron relics. Often the parts of sedimentary crystals with rhythmic location of inclusions are preserved. Inclu-

constant ratio of phases. Primary inclusions by aggregate state are one-phase (solid), two-phase (gas-liquid), three-phase (gas-liquid with solid phase), multiphase (gas-liquid with several solid phases) and inclusions with hydrocarbons. Two-, three- and multiphase inclusions in recrystallized halite are distributed without any order. By

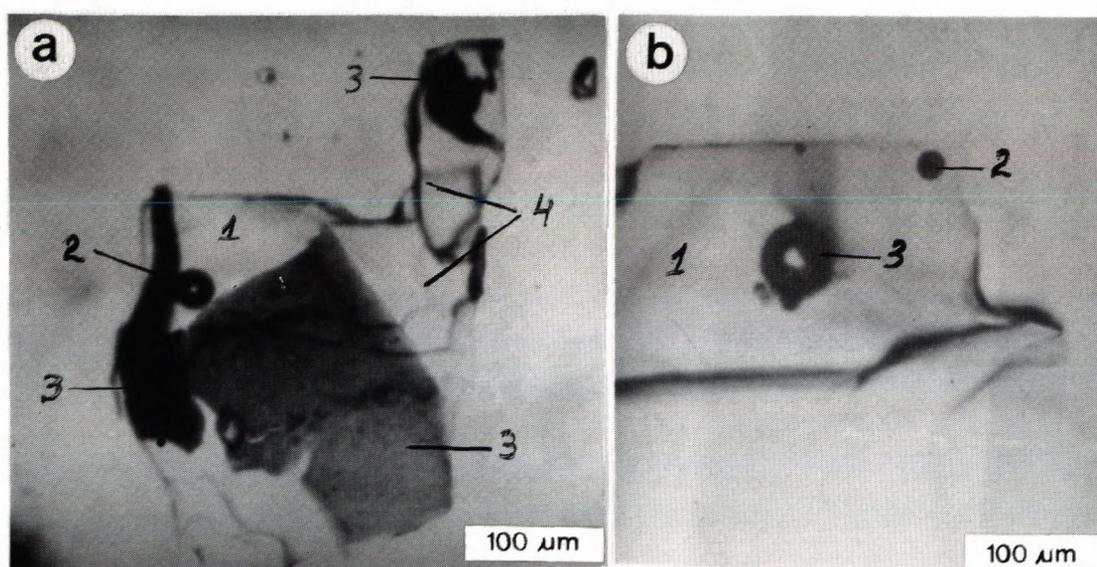


Fig. 3. Inclusions in diagenetic halite of Chop-Mukacheve depression (borehole 6-T); a - depth 1287-1291 m: 1 - water solution; 2 - gas phase, 3 - hydrocarbon crust; 4 - anhydrite; b - depth 1200-1205 m: 1 - water solution; 2 - oil; 3 - gas phase.

composition the solid phase in these inclusions is similar to the composition of solid inclusions in halite. The liquid phase is represented by water solution or oil, and gas phase - by gas mixture.

The most interesting are inclusions with hydrocarbons. In the Badenian rock salt they were discovered for the first time. They have been found in samples from depths of 1200-1205 m, 1274-1278 m, and 1287-1291 m (Fig. 3). Inclusions with hydrocarbons are mainly irregular in shape and rarely cubic. Hydrocarbons form globules or thin red-brown crusts. The aggregate state of inclusion hydrocarbons may be liquid and solid. In the first case, hydrocarbon globules are formed by light-yellow, yellow and dark-yellow fluid (in translucent light), that is immiscible with the inclusion solution. Except for fluid hydrocarbon globules and solution, the solid phase composed of black matter is often present in inclusions. Hydrocarbons make up less than 2% of inclusions. The number of globules is different. Globules have mainly homogeneous construction; however, there are globules with zonal construction, and their centre, as a rule, is darker in colour (dark brown or black) than peripheral parts which are light-brown or red-brown. Under luminiscence microscope in ultraviolet light, fluid hydrocarbon globules have yellow, brown-yellow, red-yellow luminescence, that testifies to their organic nature and is typical for oils with high content of pitch-asphaltene compounds and show the process of oxidation of hydrocarbons (see Botneva, 1979). Solid globules of hydrocarbons are brown, dark-brown and black. In reflected light they are translucent in brown colours. When the globules are extracted from the inclusion, they often divide into two parts and the droplet of yellow fluid is separated from them.

Table 3. The chemical composition of brine inclusions in sedimentary halite of the Badenian rock salt from the Chop-Mukacheve depression.

Depth m	Content of elements, g/l		
	K ⁺	Mg ²⁺	SO ₄ ²⁻
1047-1050	9.0	24.0	16.0
1068-1079	8.0	24.0	24.0
1075-1078	9.0	21.0	25.0
1087-1090	9.0	15.0	16.0
1110-1114	8.5	20.0	22.0
1113-1114	14.0	22.5	24.0
1127-1131	11.0	20.5	18.5
1135-1140	8.0	16.5	19.5
1145-1149	8.0	11.0	20.5
1150-1154	8.5	13.0	21.0
1164-1167	9.0	14.0	23.0
1171-1174	9.0	14.0	17.0
1189-1194	9.0	14.0	20.5
1200-1205	9.0	16.5	20.0
1274-1278	13.0	26.0	23.5
1302-1306	6.5	14.0	16.0
1314-1318	4.0	17.0	14.0
Average	9.5	18.0	20.0

Primary solid inclusions in diagenetic halite are disordered separations or are located on the boundary between terrigenous layers and recrystallized halite. Individual solid inclusions in the halite and the solid phase in two-, three- and multiphase inclusions are represented by authigenic minerals such as anhydrite, dolomite, quartz and pyrite, or terrigenous material. Anhydrite forms grains or crystals, fine-aggregate sepa-

rations, balls or nodules. More frequently the tabular, prismatic crystals with jagged edges and also needle crystals 0.1 to 1.5 mm long, that form bundle-like accumulations, are present. In halite plates, one can see the growth of needle anhydrite from clayey terrigenous layers towards the halite. Dolomite is located on the contacts of halite grains, along the cleavage planes, on the boundary of terrigenous layers and halite and forms aggregates, individual inclusions, randomly located in the recrystallized halite. Its sizes range from 0.1 to 0.5 mm. Crystal shapes are rhombohedral. Quartz forms transparent short-prismatic crystals with well developed rhombohedral heads, aggregates of several crystals, and rose-like growths; their sizes range from 0.5 to 1.0 mm. Pyrite looks like small black balls that often form segregations. They are located within clayey layers or are present as individual inclusions in diagenetic halite.

Composition of solutions

The data on the liquid phase in inclusions allow the reconstruction of the composition of mineral-forming solutions (Petrichenko, 1973; Yermakov & Dolgov, 1979). Specifically, the analyses of inclusions in sedimentary halite permit determination of the composition of brine during the stage of halite precipitation, and, in recrystallized ones, the composition of solutions can be determined in which the alteration of halite took place during diagenesis. It has been determined that Na^+ , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} are the major compounds in inclusion solutions of sedimentary halite (Table 3). The content of K^+ , Mg^{2+} and SO_4^{2-} in relict mineral-forming solutions significantly changes (Fig. 4). The rhythmic increase of the content of major compounds in brine inclusions from the lower to the upper part of the section was recorded. For example, in the interval of 1302–1318 m the content of potassium is 4.0–6.5 g/l; of magnesium is 14.0–17.0 g/l, and of sulfate ion is 14.0–16.0 g/l; and in interval of 1047–1079 m potassium concentration is 8.0–9.0 g/l; of magnesium is 24.0 g/l, and of sulfate ion is 16.0–24.0 g/l. The total concentration of major elements (K^+ , Mg^{2+} , SO_4^{2-}) increases from 35.0 g/l in the lower part to 49.0 g/l in the upper one.

The same chemical composition is determined in inclusions from sedimentary halite of the southeastern part of the trough (Solotvyne deposit, mines 8 and 9), but the average contents of all major compounds are significantly higher there. The average content of potassium (42 analyses) is 15.5 g/l, with the minimal concentration of 8.0 g/l and maximal one of 25 g/l. The magnesium content ranges from 19.5 to 36.5 g/l; its average concentration is 28.5 g/l (35 determinations). The content of sulfate-ion changes from 18.0 to 63.0 g/l, and averages 36.5 g/l (33 analyses).

Brine inclusions in diagenetic halite from the north-western part of the trough as well as in sedimentary ones, have Na^+ - Mg^{2+} - K^+ - Cl^- - SO_4^{2-} -composition (Table 4). When compared to sedimentary halite, the brine inclusions in diagenetic halite are characterized by decreased concentration of major elements. In the interval 1302–1318 m the potassium content is 4.0–5.0 g/l; of magnesium 11.0–16.5 g/l; of sulfate ion 12.5–15.0 g/l; and in the interval 1074–1079 m the potassium content is 5.0–9.0 g/l; of magnesium 20.5–22.0 g/l; of sulfate ion 15.0–20.0 g/l (Fig. 2). The same composition is typical for brine inclusions in recrystallized halite from the Solotvyne deposit. The average content of potassium (22 determinations) is 10.0 g/l, maximum 19.5 g/l, minimum 4.0 g/l. The magnesium content ranges from 9.5 g/l to 26.5 g/l, averaging 18.0 g/l. Sulfate ion is present in amounts from 15.0 to 56.0 g/l; the average of 20 analyses is 27.5 g/l.

Table 4. The chemical composition of brine inclusions in recrystallized halite of the Badenian rock salt from the Chop-Mukacheve depression

Depth m	Content of elements, g/l		
	K^+	Mg^{2+}	SO_4^{2-}
1047-1050	9.0	22.0	15.0
1068-1079	5.0	20.5	21.0
1075-1078	8.0	17.0	20.0
1087-1090	7.0	16.0	15.0
1110-1114	5.5	17.0	19.0
1113-1114	10.0	20.0	22.0
1127-1131	9.0	19.0	18.0
1135-1140	8.0	16.0	17.5
1145-1149	8.0	8.0	15.0
1150-1154	8.5	12.0	19.0
1164-1167	8.0	14.0	21.0
1171-1174	6.0	15.5	15.0
1184-1189	7.0	14.0	19.0
1189-1194	7.0	12.0	21.0
1200-1205	7.0	12.0	20.0
1250-1254	9.5	15.0	12.5
1265-1269	3.5	20.5	18.0
1274-1278	8.0	24.0	19.0
1287-1291	4.0	16.0	17.0
1302-1306	5.0	11.0	15.0
1314-1318	4.0	16.5	12.5
Average	7.0	16.0	17.5

The composition and changes of the major element contents in brine inclusions from sedimentary halite show that during the stage of halite precipitation the brine of the Transcarpathian basin in its northwestern part (Zaluzh salt-bearing subbasin) had contents of potassium (4.0 g/l) and magnesium (17.0 g/l) and by ratio of these elements was close to the modern seawater saturated to

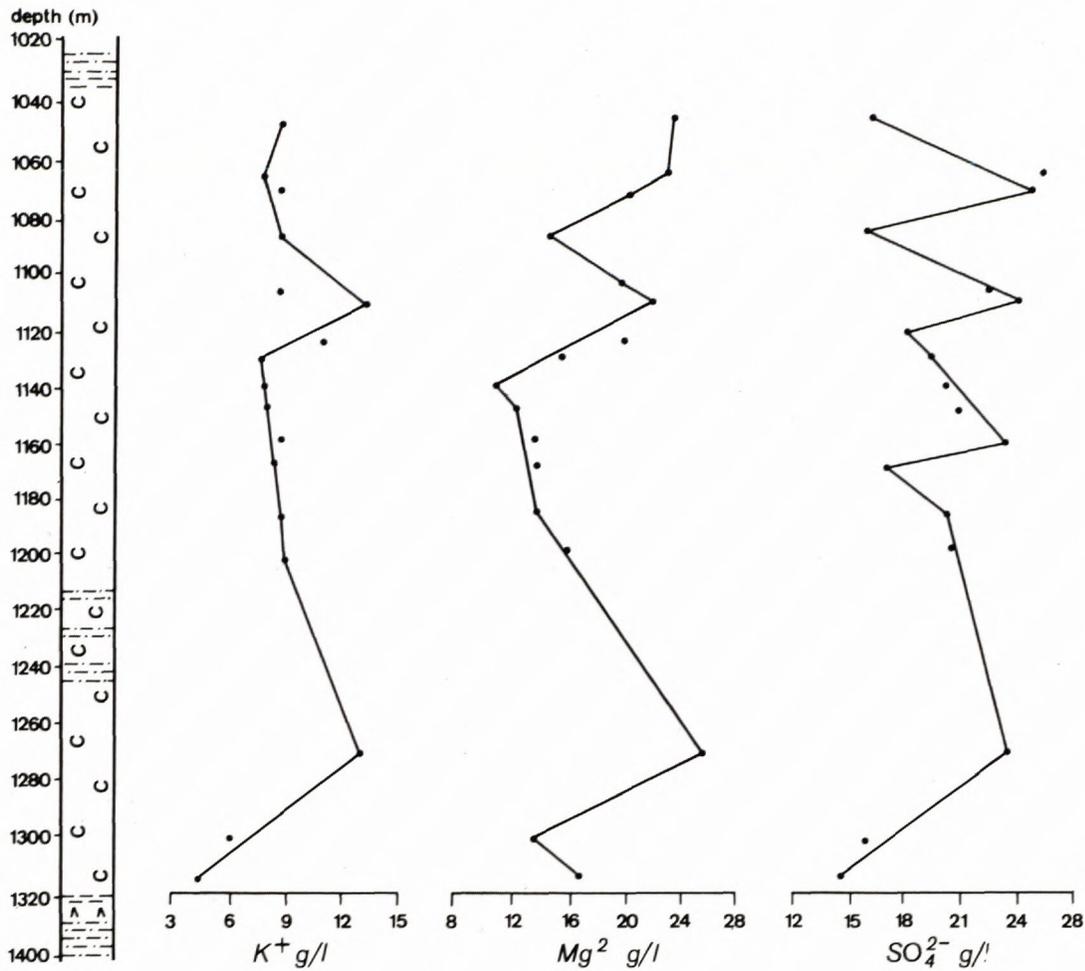


Fig. 4. The content of potassium, magnesium and sulfate ions in brine inclusions of sedimentary halite in the section of borehole 6-T. For explanation see Fig. 2.

halite stage. Concerning the sulfate ion, its content was somewhat lower (14.0 g/l) than in recent seawater. During halogenesis, the concentration of major elements gradually increased and during some stage of basin evaporation the potassium content in the brine reached 14.0 g/l, of magnesium 28.0 g/l, and of sulfate ion 24.0 g/l. The process of progressive evaporation was periodically broken by dilution of the brine by water of low concentration.

The location of the composition points in the diagram (Fig. 5) shows that the ratio of major elements in the brine did not actually differ from their ratio in modern seawater. The majority of the points is situated near the line of composition of directly metamorphosed seawater (Valiashko, 1962). Halite precipitation terminated from the brine of higher concentration compared to the initial one, but the evaporation process did not reach the high stages and finished at halite stage. This is indicated by

results of the determination of bromine and the bromine-chlorine coefficient, which correspond to the halite stage of basin evolution and are close to experimentally determined for the normal halite zone. The temperature of the brine of the Zaluzh salt-bearing basin at the halite stage was below 40°C, and its depth was from 7 to 18 m (Petrichenko, 1988).

The Solotvyne subbasin was also characterized by the sulfate type of brine during stage of halite precipitation. However, as sometimes the content of all major elements at halite stage reached much more higher values than in Zaluzh subbasin (potassium - 25.0 g/l; magnesium - 36.5 g/l; sulfate ion - 63.0 g/l), it may be concluded that the evolution of this salt-forming basin reached the later stages. The depth of the basin was 10-15 m, temperature of the brine did not exceed 40°C. Halite sedimentation took place in oxidizing conditions.

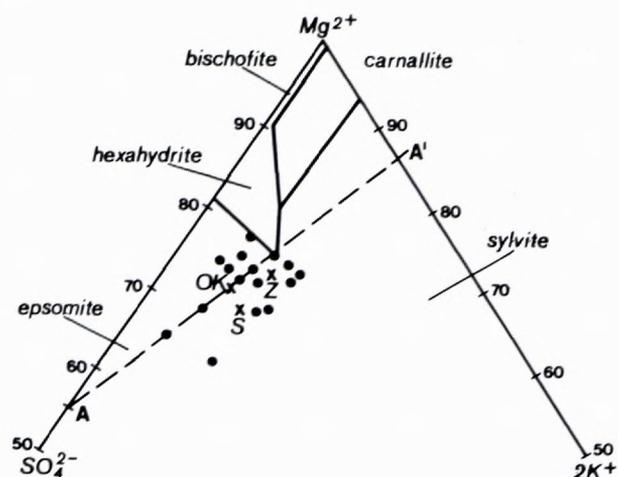


Fig. 5. Location of data points characterizing the chemical composition in salt-forming basin on stage of halite precipitation on the Valiashko (1962) diagram. OK - modern seawater composition; A-A' - the line of metamorphism of seawater (Valiashko, 1962); Z and S - average composition of solutions on halite stage of evolution of the Zaluzh and Sotolvyno subbasins, accordingly.

Halite changes in diagenesis

The rock salts of the Chop-Mukacheve depression are significantly recrystallized. Rock structures and the composition of solid and individual fluid inclusions in diagenetic halite are evidence that the alteration of physico-chemical conditions took place during rock formation. Due to tectonic subsidence the salt sediments were subject to the pressure and temperature impacts. Taking into account the maximum present depth of studied rock salt (1314–1318 m), it may be supposed that the pressure during recrystallization reached 33,000–35,000 kPa. The temperature rose to 75–83°C (Petrichenko, 1989).

The mineral-forming solutions during diagenesis as well as sedimentation were of $\text{Na}^+\text{-K}^+\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$ -composition. The concentration of major elements became lower than during the sedimentation stage explainable by processes of cation exchange and metamorphism of the brine. The composition of solid inclusions in diagenetic halite represented by anhydrite, dolomite, quartz, and pyrite indicate that the mineral-forming environment during the postsedimentary stage changed from oxidizing to reducing conditions, and pH from acid to alkaline conditions. Specifically, pyrite crystallization needs strongly reducing conditions and an alkaline environment. Inclusions with oil hydrocarbons in recrystallized halite indicate strongly reducing mineral-forming conditions in salt deposits. The migration of oil hydrocarbons that were the source of feeding for sulfate-reduction bacteria producing H_2S , caused a significant decrease in the oxidation-reduction potential of the

environment and increase in the alkalinity of solutions. During the local recrystallization of salts it led to the preservation of hydrocarbons separately or together with solutions in inclusions.

The rock salt of the Sotolvyno deposit has also been recrystallized under the increased pressure during diapirism. The solutions had a sulfate composition but their total concentration decreased and the content of some elements changed in comparison to the precipitation stage. The recrystallization of halite occurred during oxidizing conditions and acid environment: pH of solutions measured after the opening of inclusions in halite ranges from 5.0 to 5.4 ± 0.2 . Eh changes from 0 to +100mv (Kityk *et al.*, 1983).

Conclusions

Studies of relict mineral-forming solutions in sedimentary halite show that the brine in Neogene Transcarpathian salt-forming basin (Zaluzh as well as Sotolvyno subbasins), on the basis of composition belonged to a sulfate type, and were close to the brines from which modern marine evaporites precipitate. It has been found that the initial brine of the Zaluzh basin was depleted in SO_4^{2-} in comparison to modern seawater. Salt precipitation in basins terminated at the halite stage, but in the Sotolvyno basin it reached a higher stage that was close to potash precipitation. The brine temperature did not exceed 40°C. Primary sedimentary deposits were significantly changed during postsedimentary time. Recrystallization occurred under increased pressure and temperature. Mineral-forming conditions changed from oxidizing to strongly reducing, and the pH of the environment from alkaline to acid. The recrystallization of primary sediments took place under the impact of solutions that have inherited the type, chemical composition and particularities of the behaviour of the main elements from brine of the salt-forming basin. They differed from solutions of sedimentary basins by a decreased concentration of major elements. In local parts of a salt deposit during recrystallization, hydrocarbons penetrated into burial solutions and, together with mineral-forming solutions or independently, were preserved in halite as inclusions.

Acknowledgments.

I thank the International Science Foundation (Grant No. UCM000) for the support and T. Dobroszycka for the drawings.

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Sedimentology of Karpatian evaporites in the East-Slovakian Neogene basin (Slovakia)

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Abstract: After a deep-water sedimentation during the Lower Karpatian the communication between the East-Slovakian Neogene Basin and the Carpathian Foredeep was interrupted. This period is recorded by deposits of Sofná Baňa Formation containing high amount of evaporites. The Sofná Baňa Formation is subdivided into five lithofacies units. Unit I represents the period of gypsum precipitation on the coastal plain and its subsequent redeposition as well as the period of nodular anhydrite precipitation in the subaqueous environment. Halite, occurring in the unit II, has been most likely originated in salt pans. Unit III was a period of increased subsidence controlling a deposition of coarse-grained sediments. During this period the halite of unit II had been dissolved along NW-SE faults giving rise to solution-collapse breccias. Unit IV represents a typical salt-pan cycle with desiccation rip-up breccias. Unit V, lithofacially resembling unit I, marked a gradual retreat to a normal, open-marine regime. The deposition of Sofná Baňa Formation, and especially of evaporites, reflects a function of a tectonic sill between the East Slovakian Basin and Carpathian Foredeep. This sill was most likely located in the outer flysch area.

Key Words: halite, solution-collapse breccias, desiccation breccias, tectonic sill

Introduction

The East Slovakian Neogene Basin is the only basin of the Inner West Carpathians comprising economically important Miocene evaporites. The opening of the basin, located south-west of the Klippen Belt (Fig. 1), reflected the subduction of the flysch externides (European platform) below the Carpathian - Pannonian Block (Royden et al., 1983; Tomek, 1993) and the crust extension resulting from the uplift of the Pannonian asthenolite (Horváth, 1993). From the Eggenburgian to the Pliocene more than 6 000 m of mollasse sediments have been deposited in the basin. The style, time and spatial distribution of deposits has been controlled by global palaeogeographic and palaeoclimatic changes as well as by tectonic regime of the basin during its evolution. Two etapes, differing by palaeogeographic evolution and depositional character, are divided in the sedimentary history of the basin. During the first phase (Eggenburgian - Middle Badenian) the deposition has been restricted to the relatively narrow WNW - ESE oriented graben opened to the Carpathian Foredeep in the northeast. The graben was separated to the Pannonian Basin in the south.

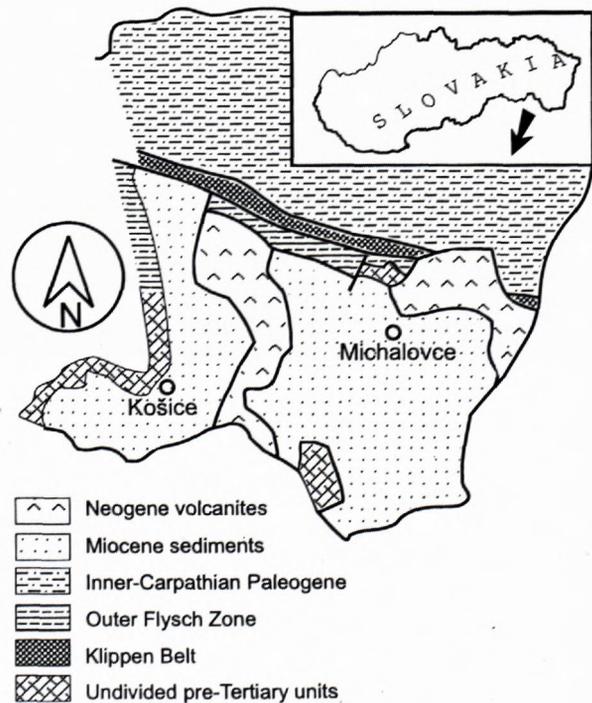


Fig. 1 Location of the East Slovakian Neogene Basin

Marine, mainly pelitic deposition prevailed during this phase. Deltaic deposition and shallow shelf deposition in the brackish-lacustrine environment dominated in the second phase (Upper Badenian - Pontian). It was established a communication to the Pannonian Basin in the south and the Mukachevo Basin in the southeast.

The sedimentary fill of the East Slovakian Neogene Basin comprises two evaporitic, halite-dominated formations. They were deposited during the middle part of the Karpatian and Middle Badenian. The deposit of the Badenian salt in the Zbudza Formation has been prepared for exploitation in 1997. The existing knowledge about its origin has been summarized by Galamay and Karoli (1997). The salt from the Karpatian Soľná Baňa (Salt Mine) Formation has been exploited since the 13th century. Until 1572, when the Leopold shaft was opened, salt was obtained by boiling of natural brine coming from a salt spring. After a construction of the shaft the underground exploitation lasted until 1752, when the shaft has been flooded. From this time the salt was again obtained by the boiling of natural brine getting from the former shaft (Butkovič, 1978). After 1950 the brine has been exploited by salt dissolution by a system of drillings.

Geological setting

After a hiatus in the Oligocene, the commencement of the Karpatian deposition in the East Slovakian Neogene Basin is the time of marine transgression. The communication to the Carpathian Foredeep was in the northeast, the deposition occurred in the elongated, transversely segmented WNW-ESE graben (Fig. 2). The ocean transgressed over the Eggenburgian and Paleogene deposits in the north and pre-Tertiary basement in the south. The graben originated by a simple NE-SW extension in the Lower Karpatian, from the Upper Karpatian the pull-apart mechanism in the transtension regime controlled the opening of the basin (Kováč *et al.*, 1995).

Three formations are being distinguished in the Karpatian (Vass & Čverčko, 1985): the evaporite bearing Soľná Baňa Formation is sandwiched by the lower Teriakovce and upper Kladzany Formations.

The lower **Teriakovce Formation** has a distinct coarse-detrinitic base evidencing a Karpatian transgression. The lower part of formation is 100 - 150 m thick and consists of conglomerates on the base passing upward to fine sandstones and siltstones. The upper part of formation is mainly composed of alternation of siltstones and claystones. Along the northern margin of the basin montmorillonitic products of the former volcanism and schlier occur. A rich foraminiferal fauna, often with pyritized tests, occur in the formation. The foraminifera indicate an environment of deeper neritic zone and

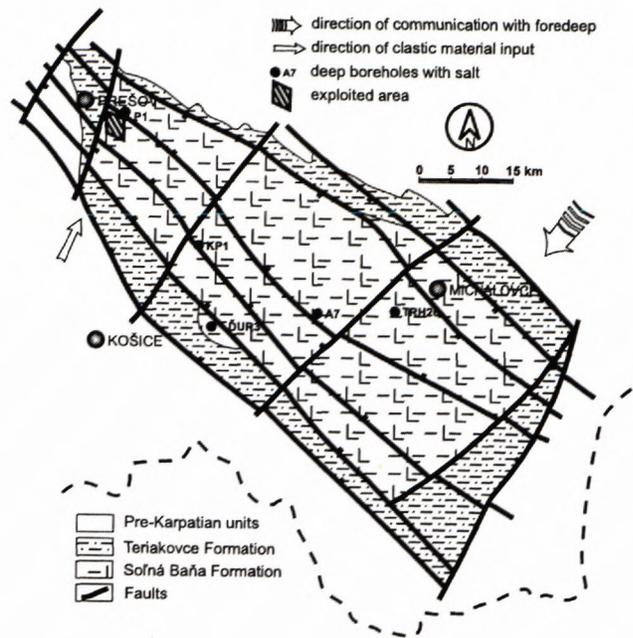


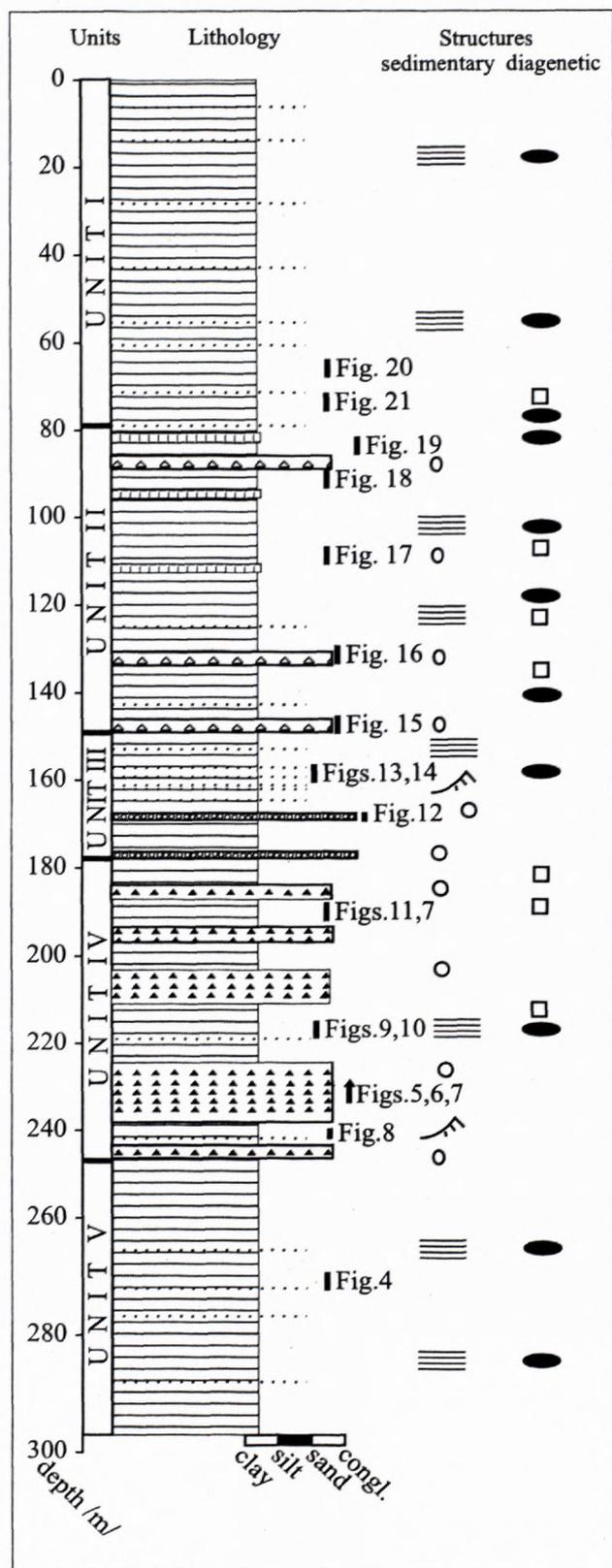
Fig. 2 Palaeogeographic reconstruction of the Lower (Teriakovce Fm.) and Middle (Soľná Baňa Fm.) Karpatian.

shallow bathyal zone (Cícha & Kheil, 1962; Zlinská, 1992). The thickness of the formation is 500 m.

The upper **Kladzany Formation**, representing the uppermost part of Karpatian deposits, is lithologically monotonous complex of silty claystones and clayey siltstones with thin, only occasionally up to 1 m thick, beds of fine sandstones. Typically, the deposits are violetish-red smudged in the lower part and yellowish-brown in the upper part. They contain scarce microfauna. Microscopic gypsum and anhydrite frequently occur in the lower part of the formation. The secondary fibrous gypsum sometimes fills interbed spaces and fissures; veins are mm to cm in thickness. The thickness of the formation is up to 1,300 m.

The **Soľná Baňa Formation** represents the middle part of the Karpatian deposits. After a long period of presumption that the salt occurrence is only restricted to the northeastern part of the East Slovakian basin, the deep boreholes during hydrocarbon prospection revealed the Karpatian deposits containing brine even in the southern and central part of the basin (Janáček *et al.*, 1975; Rudinec, 1978). The palaeogeographic reconstruction (Fig. 2), based on the stratigraphic and tectonic analysis of the area, shows the occurrence of evaporites in the entire basin. Contrary to the underlying Teriakovce Formation, the sediments of Soľná Baňa Formation were deposited during a regression.

Laminated and thin-bedded gypsum and anhydrites occur in the lowermost part of the 230 - 340 m thick Soľná Baňa Formation. There is typical an abrupt disappearance of a rich microfauna of the underlying formation (Cícha & Kheil, 1962). Very scarce is *Uvigerina*



graciliformis, *Uvigerina semiornata*, *Bulimina elongata*, *Bulimina dilatata*, *Robulus inornatus*, *Globigerina bulloides* in claystone and siltstone layers (Beroušek in Polák *et al.*, 1955). The overlying deposits comprises salt breccias with matrix-supported structure. The matrix consists of halite, clasts are composed of claystone, siltstone and occasionally of sandstone. In the uppermost part of the formation laminae and beds of gypsum and anhydrite in the pelitic and siliciclastic sediments occur again. Pollen are very scarce and non-significant; pollen association indicating cold and arid climate are known from the underlying formation (Planderová, 1988).

Solná Baňa Formation is typical by a lithofacies variability, especially in salt breccias. Tens of prospecting and exploitation boreholes have been drilled in the exploited area nearby Prešov town (Fig. 2). Although there are not preserved cores showing a continuous profile of the formation, the description of cores from many boreholes and archive samples enabled to subdivide the formation into five lithologic units on the basis of evaporite facies (Fig. 3).

Description of Solná Baňa Formation

Unit I

Unit I is 40 - 100 m thick. Its thickness increases toward north. The deposits consist of alternating siltstones and claystones and thin layers of fine sandstones. They

Fig. 3 Composite log showing the deposits of Solná Baňa Fm. in the exploitation area. Note the location of close-up figures.

contain 0.5 - 2 mm thick laminae and beds of gypsum. They occur as either individual laminae in claystones and siltstones or laminae set formed by alternation of gypsum siltstone and gypsum sandstone. The deposits consist of prismatic crystals of gypsum and their fragments without preferred orientation. The longest axis of larger selenite crystals is sometimes elongated with lamination. Siliciclastics, mainly quartz, feldspar, mica, and glauconite grains, are very common as accessories. In some boreholes the frequency of evaporite laminae increases toward the top of the unit. If the laminae occur in thicker intervals, the surrounding deposit is often gypsum- or mixed gypsum-siliciclastic siltstone (Fig. 4). The siltstones are cross-laminated occasionally. A nodular anhydrite of cm size occurs irregularly in the entire unit.



Fig. 4 Alternation of laminated gypsum (lighter laminae) and gypsum siltstone (darker laminae) of unit I. The bar for a scale is 1 cm long.

Unit II

The deposits of unit II are being exploited today. They contain the maximum accumulation of salt. The unit is from 30 to 100 m thick, it is separated by sandstone dominated unit III from overlying, another salt-bearing unit IV. Salt breccias are dominant deposits in this unit, they are separated from each other by a few metres thick claystones, siltstones and thin beds of sandstones. They are lenticular, very irregular bodies which are concentrated in horizons schematically shown in Fig. 3. The individual lenses pinch out after tens or hundreds of metres and it is almost impossible to correlate them between individual boreholes. The thickness of the breccias usually range from 3 to 7 m, occasionally it is up to 25 m. The maximum thickness of salt breccias is according to Barkáč and Grech (1988) about 40 m. The

clast size of breccias varies from gravelites to boulders. The halite matrix, forming 20 - 80 per cent of deposits, consists of grey, transparent grains. The 1 to 5 mm big angular halite grains are dispersed in the halite matrix. The basis of breccias is sharp. Deposits overlying salt breccias are fissured. The fissures are filled by fibrous salt (Figs. 6, 7 and 8). The character of the breccias is best documented by archive photos from the Leopold shaft (Figs. 5, 6 and 7) which has been flooded (and conserved) a long time ago.

The sandstones most frequently form thin interlayers in claystones and siltstones. Sometimes, if they immediately underlie salt breccias, they have thickness of several metres. Sandstones are massive, rarely cross-laminated (Fig. 8), occasionally contain laminae of gypsum and anhydrite. Claystones and siltstones are laminated, rarely massive, especially if they immediately underlie breccias. Gypsum and anhydrite laminae are common throughout the entire unit. They have the same features as in unit I (see above). Intrasedimentary cubic halite laminae of several mm size occur often in siltstones and claystones. Halite crystals are rarely 1 - 1.5 cm across (Fig. 9). This type of halite is often restricted to laminae and thin beds of sandstone (Fig. 10). Individual anhydrite nodules are very sporadic in the unit. They form 5 - 7 cm thick beds, more common in the upper part of the unit. Nodules several mm across, arranged in laminae, often occur together with salt beds. Individual nodules 6 cm across are found in association with gypsum laminae. Occasional cavernous beds of kidney-shaped anhydrite are typical for this unit (Fig. 11).

Unit III

The unit is typical by beds of medium and coarse-grained sandstone interfingering with claystone and siltstone. The occurrence of sandstone decreases upward in the unit. Thick beds of conglomerate with clasts of gravelite size occur in the lower, basal part of the unit, which is ca. 25 - 45 m thick. The conglomerate is mostly matrix-supported, only occasionally clast-supported conglomerate occurs (Fig. 12). The conglomerate is fining upward to fine-grained sandstone and siltstone in some beds (Fig. 13). Beds of gypsum identical to those described in unit I are common. Usually they are from 1 to 2 cm thick and they are associated with 5 - 15 cm thick beds of medium and coarse sandstone (Fig. 13). The sandstones are occasionally flaser bedded (Fig. 14). Gypsum selenites or their fragments are very common in these beds. The basal part is overlain by massive siltstones containing gypsum laminae. The upper part of the unit is characteristic by a decrease in number of sandstone beds and anhydrite laminae frequency. The thickness of the whole unit as well as the occurrence of coarse-grained deposits decrease toward the north.



Fig. 5 Salt breccias of unit II containing irregular claystone and siltstone clasts in claystone matrix. The length of the corridor is ca. 1.8 m. Photo by Kalvoda in Polak et al., 1955.

Unit IV

Unit IV consists of alternating claystone and siltstone beds. Occasionally thin beds of fine and medium-grained sandstone occur. The deposits comprise salt breccias and halite layers 0.1 - 0.6 m thick, occasionally they form beds with thickness 1- 2 m (Fig. 16). Salt breccias are more common in the lower part of the unit. They contain claystone and siltstone clasts or fragments of their laminae (Fig. 15). Only rarely they are underlain by halite beds alternating with siltstone and claystone. Halite occurs more frequently in the upper part of the unit. Grey, transparent, cubic halite crystals are from 2 to 15 mm long. For both halite and salt breccias are typical milky-clouded crystals of halite, which are often concentrated on the top of beds (Fig. 17). Milky-clouded center zones of halite crystals occur occasionally in layers with extreme accumulation of these crystals. Gypsum and nodular anhydrite are also common in the unit. The nodular anhydrite is often arranged in laminae (Fig. 16) and thin enterolithic beds (Figs. 18 and 19). In the upper part of the unit these laminae are sometimes sandwiching halite layers.

Unit V

Unit V is composed of alternating claystones and siltstones. The difference between this unit and unit IV is in absence of salt and salt breccias. Gypsum laminae are common (Fig. 20) and nodular anhydrite similar like in the underlying units. The nodular anhydrites are prevalingly in the lower part of the unit concentrated into enterolithic beds with tightly-packed nodules (Fig. 21). The frequency of nodules and sulphates decreases upward. The thickness of the unit is from 60 to 110 m; the unit overlain by the Kladzany Formation formed by claystones with redish-violet smudges.

Interpretation of depositional environment

The sediment description shows that all the described units but unit III consist mostly of alternation of massive and laminated claystones and siltstones. Occasionally, they comprise thin beds of massive and flaser bedded sandstone. The facies association indicates fluctuation of sediment input into the basin and prevailing deposition from suspension clouds. Thin beds of flaser bedded



Fig. 6 Contact of salt breccias and overlying deposits, unit II. The deformed parts are filled by white fibrous salt. The length of the mine adit is ca. 1 m. Photo by Kalvoda in Polak et al., 1955.

sandstone probably represent a deposition by traction current. The dominance of sandstone in unit III may be related to a higher input of coarser sediment. A more detailed interpretation of depositional environment is rendered by evaporite facies.

Horizontal laminae and beds of gypsum, occurring in all units, originated by a redeposition of a primary gypsum. The deposits forming these laminae and beds may be termed as fine- and medium-grained gypsarenites and gypslutites. Regularly laminated evaporites are thought to be deposited in a shallow water in a low-energy shelf environment. Described laminated and thin-bedded gypsum has probably originated by suspension fall-out. There is only scarce information about the source of primary gypsum. An irregular and sometimes deformed gypsum laminae have been only recovered in 0.7 m thick interval (Fig. 22) in the borehole at the margin of the basin southerly from Prešov town. The gypsum

is composed of 2 - 5 mm large selenite crystals without preferred orientation. This facies, representing the entire range of Sol'ná Baňa Formation, is not known from another boreholes and probably represents a relic of primary gypsum precipitating mostly in subaqueous environment on a coastal plain.

Nodular anhydrites, especially from recent and ancient deposits of supratidal and intertidal zones, were described by many authors (e.g. Kendall, 1984; Warren, 1991). Their formation in this environment requires short-time sea level oscillation governing the type of deposition on shelf (laminated gypsum) and evaporite mud flats. The character of nodular anhydrites in Sol'ná Baňa Formation suggests a different genesis explained by an intrasedimentary grow of nodules by a coalescence from residual brine in subaqueous environment. The heavier, sulphate brine probably entered the basin together with clastic gypsum and it was accumulated in non-lithified sediments.

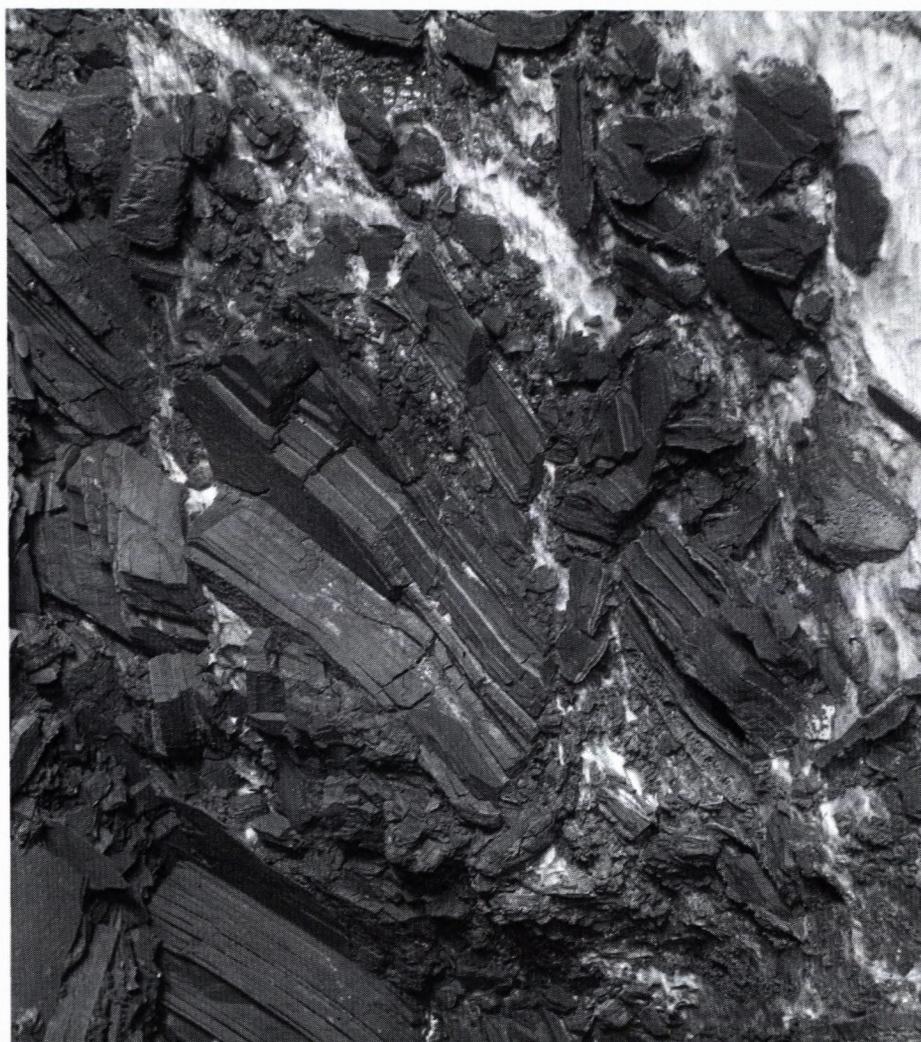


Fig. 7 Brecciated claystones and siltstones containing gypsum laminae overlying salt breccias, unit II. The fissures are filled by secondary fibrous salt. The length of the corridor is ca. 1 m.

Enterolithic layers of anhydrite (Figs. 18 and 19) with tightly packed nodules (Fig. 21) suggest short-period emergence of deposits and precipitation of nodules in salina mud flats (*sensu* Kendall, 1992). The origin of anhydrite enterolith, underlain and overlain by siltstone or claystone containing gypsum laminae without desiccation features, is explained by intrasedimentary, early diagenetic growth in extremely sulphate brine-soaked host sediments in subaqueous conditions. Both enterolithic layers of anhydrite immediately overlying halites from unit IV (Figs. 18 and 19) and laminae of small nodules are thought to be originated by an abrupt sea flooding. Sea water contained high amount of clay and silt in suspension. Their fast deposition formed a basal layer. The basal layer contained low-concentrated sulphate brine giving a rise to anhydrite nodules. This mechanism could operate during the precipitation of halite in both subaqueous and terrestrial environments.

Anhydrite in cavernous layers (Fig. 11) of unit II has a replacive character. Nodules are irregular and kidney-shaped. They were precipitated epigenetically after a dissolution of former evaporites, most likely halite.

Halite, which comprises individual layers and matrix of salt breccias, contains primary features (*sensu* Hardie et al., 1983). These features are represented by hopper crystals of halite (milky-clouded centres of crystals) precipitating on the brine - air interface (Arthuron, 1973). The crystals originate during the fast precipitation, best produced in wind-free days (Sonnenfeld, 1984). Thin salt layers overlying and underlying salt breccias of unit IV are interpreted as originated in the saline mud flat environment. Halite, containing claystone relics, probably precipitated intrasedimentary as salt crust.

Salt breccias of unit II are interpreted as solution-collapse breccias. This is supported by undisturbed bases, deformed overlying beds with fissures filled by



Fig. 8

Fig. 9

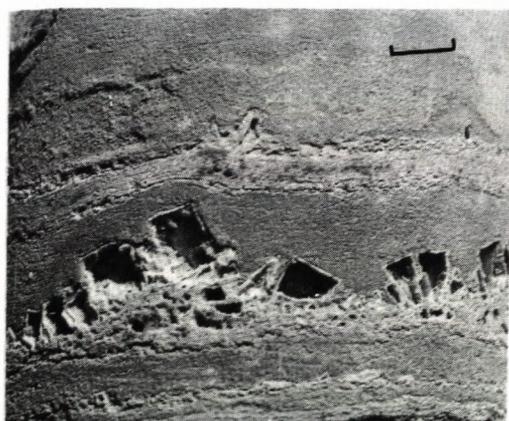


Fig. 10



Fig. 11



Fig. 12



Fig. 13



Fig. 14

fibrous salt and an absence of primary sedimentary features of halite. All these suggest to the origin of breccias by halite dissolution and collapse of non-evaporitic deposits. The dissolution by undersaturated water, which is confirmed by bromine content (14 to 32) ppm, began after the lithification of overlying beds or after the lithification of all unit II. During the collapse, the overlying beds sunk and were disturbed. As a result of lithostatic pressure the brine has been pressed into fissures, where it precipitated in form of fibrous halite oriented perpendicular to fissures. An equigranular structure of halite reflects its precipitation or crystallization during the condition of a fast mass grow. In case of more intensive sinking, the overlying beds have a character of after-collapse breccias with fissures filled by fibrous salt (Fig. 7). This type of breccias and mechanism of dissolution is also known from the Permian evaporates in the southwestern part of USA (Anderson, 1978; Johnson, 1981).

The character of breccias, the development of irregular lenses and a high lateral and vertical variability suggests that the original depositional environments were smaller coastal basins, most likely of salt pans type (*sensu* Kendall, 1992). The alternation of halite and non-evaporitic layers reflects a polycyclic development. One cycle includes a phase of flood, evaporation and most likely also a phase of desiccation as described Lowenstein and Hardie (1985).

Salt breccias of unit IV, containing fragments of siltstone and claystone laminae, are interpreted as desiccation breccias (rip-up breccias) forming in the last stage of salt-pan cycle (Lowenstein & Hardie, 1985).

Discussion and conclusion

The sedimentation of Soľná Baňa Formation in the East Slovakian Negene Basin represented a phase of regression following transgression in the Lower Karpatian (Teriakovce Formation). The formation is subdivided into five lithofacies units in the NW margin of the basin. The units reflect different depositional environments.

During the deposition of unit I, a continual communication with the Carpathian Foredeep was interrupted. A

semiclosed shallow basin with smaller depressions on coastal plain has been established. In this, climatically cool and arid, environment, a precipitation of gypsum occurred. The gypsum was mostly eroded and redeposited off the coast. Sulphate brine was also redeposited which made a source for a growth of nodular anhydrite by coalescence.

During the deposition of unit II, repeated interruptions of communication with the Carpathian Foredeep caused the precipitation of halite in salt pans. The repeated phases of floods, evaporation and most likely also desiccation of these depressions controlled the origin of typical lithofacies associations comprising halite, siltstone and claystone, occasionally also sandstone.

Halite and nodular anhydrite precipitated in surrounding salina mud flats. After a lithification of overlying beds or the entire unit II, the halite was dissolved giving a rise to solution-collapse breccias.

Unit III is the phase of deposition in a semiclosed basin controlling the gypsum precipitation. Sandstone and occasional conglomerates were deposited during events of higher sediment input.

The deposition of unit IV was again determined by partial restriction of communication between the East Slovakian Basin and Carpathian Foredeep. The character of deposits is result of a typical salt-pan cycle. Halite interfingered with claystone and siltstone originated by repeated phases of floods and evaporation. These deposits were destructed when emerged and they give rise to desiccation (rip-up) breccias. Nodular anhydrites precipitated mostly in subaerial environment of saline mud flat.

In unit V, precipitation of sulphates and their redeposition continued. The deposition in the basin retreated back to a normal marine regime as indicated by a decreasing amount of syndepositional sulphates and finely their disappearance.

Salt deposition in the Karpatian is extraordinary in the Carpathian belt (both in Internides and Externides) (*e.g.* Seneš, 1989). The reasons of this sedimentation type are specific palaeogeographic conditions. Salt deposition has not been restricted to the marginal, coastal

←
Fig. 8 Cross-laminated medium-grained sandstone overlying salt breccias, unit II. The fissure is filled by fibrous halite. The bar for a scale is 1 cm long.

Fig. 9 Intrasedimentary cubic halite (dark) in siltstone, unit II. The bar for a scale is 1 cm long.

Fig. 10 Originally displacive, now replacive halite growing from sandstone laminae and deforming overlying deposits, unit II. The inner walls of halite crystals are coated by a white anhydrite. On the right-hand side of the photo corneal crystals occur. In the sandstone lamina overlying halite originally gypsum crystals are replaced by anhydrite (the middle part of the photo). The bar for a scale is 1 cm long.

Fig. 11 The layer of cavernous, kidney-shaped nodular anhydrite, unit II. The bar for a scale is 1 cm long.

Fig. 12 Matrix-supported gravelite of unit III. Note the erosive base. The bar for a scale is 1 cm long.

Fig. 13 The upward-fining conglomerate passing into fine-grained sandstone overlain by siltstone, unit III. Gypsum laminae occur in the upper part of the siltstone bed. The bar for a scale is 1 cm long.

Fig. 14 Flaser bedded, upward-fining sandstone. The bar for a scale is 1 cm long.



Fig. 15



Fig. 16

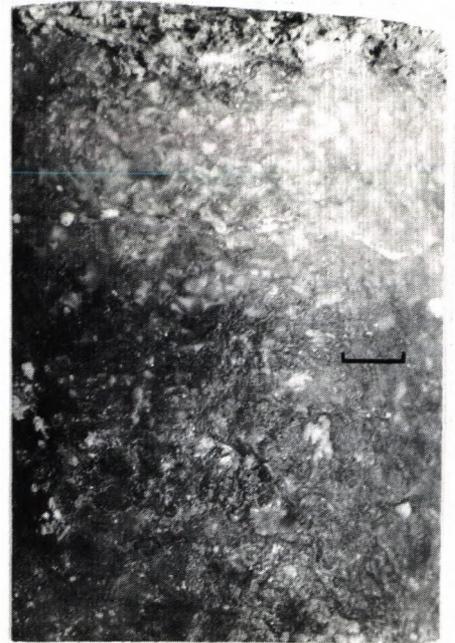


Fig. 17

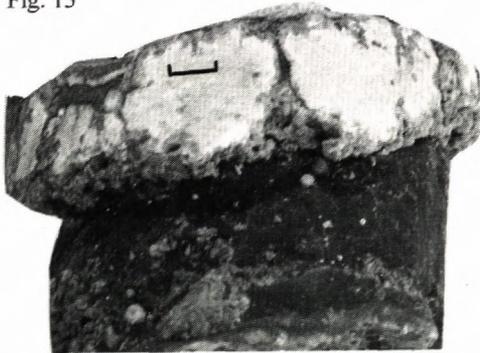


Fig. 18



Fig. 19

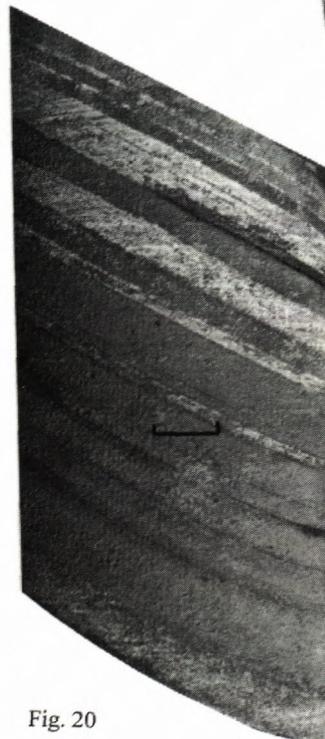


Fig. 20

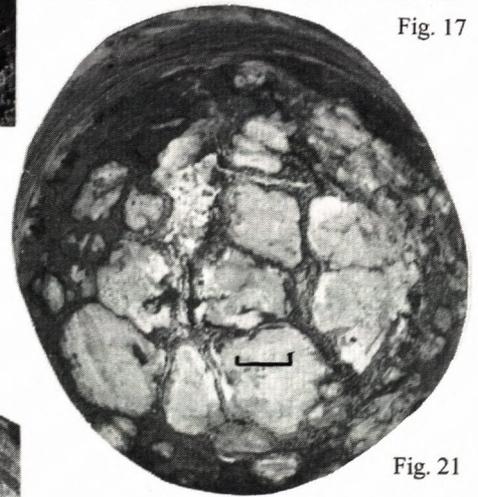


Fig. 21

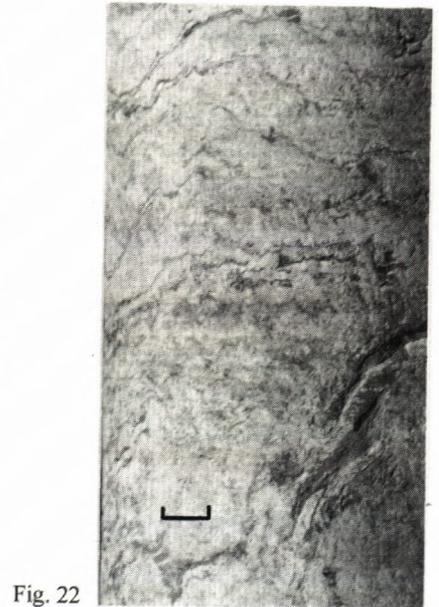


Fig. 22

plain areas of the basin; on the contrary, the boreholes in the centre of the basin show that salt occurs in the whole basin area (Fig. 2). Unfortunately, even if salt occurrence is proved in the central areas, there are not enough of recovered sediment for sedimentological study. Thin layers of halite, described by Rudinec (1978) from the borehole Trhovište 26, may have been precipitated from both surface brine of deeper basin and brine in smaller depressions of salt pan type. The cause of evaporitic deposition was the existence of a barrier, which restricted a communication between East Slovakian Neogene Basin and Carpathian Foredeep. This barrier was most probably a tectonic sill located in the area of the outer flysch zone. We assume the partial restriction of communication (gypsum and anhydrite sedimentation) or entire isolation of the basin (halite precipitation) giving a shallow-water-deep-basin type (Kendall, 1992, Fig. 35). The origin of solution-collapse breccias is related to the unit III. Coarse-grained deposits of this unit and their spatial distribution indicate an uplift of the SW basin margin and a subsidence along NW-SE faults. Undersaturated sea water or brackish water (caused by a drop in salinity due to fresh water input by flows distributing coarse-grained sediments) migrated along the system of these faults and caused the dissolution of halite from the underlying unit II.

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Fig. 15 Salt breccias composed of halite matrix, clasts and laminae fragments of claystone and siltstone, unit IV. The bar for a scale is 1 cm long.

Fig. 16 Salt breccias and halite sandwiched by laminated siltstone, unit IV. On the base and top of halite light nodules of anhydrite. The siltstone on the base contains a conspicuous displacive and replacive halite.

Fig. 17 Halite with accumulation of milky-clouded crystals, unit IV. The bar for a scale is 1 cm long.

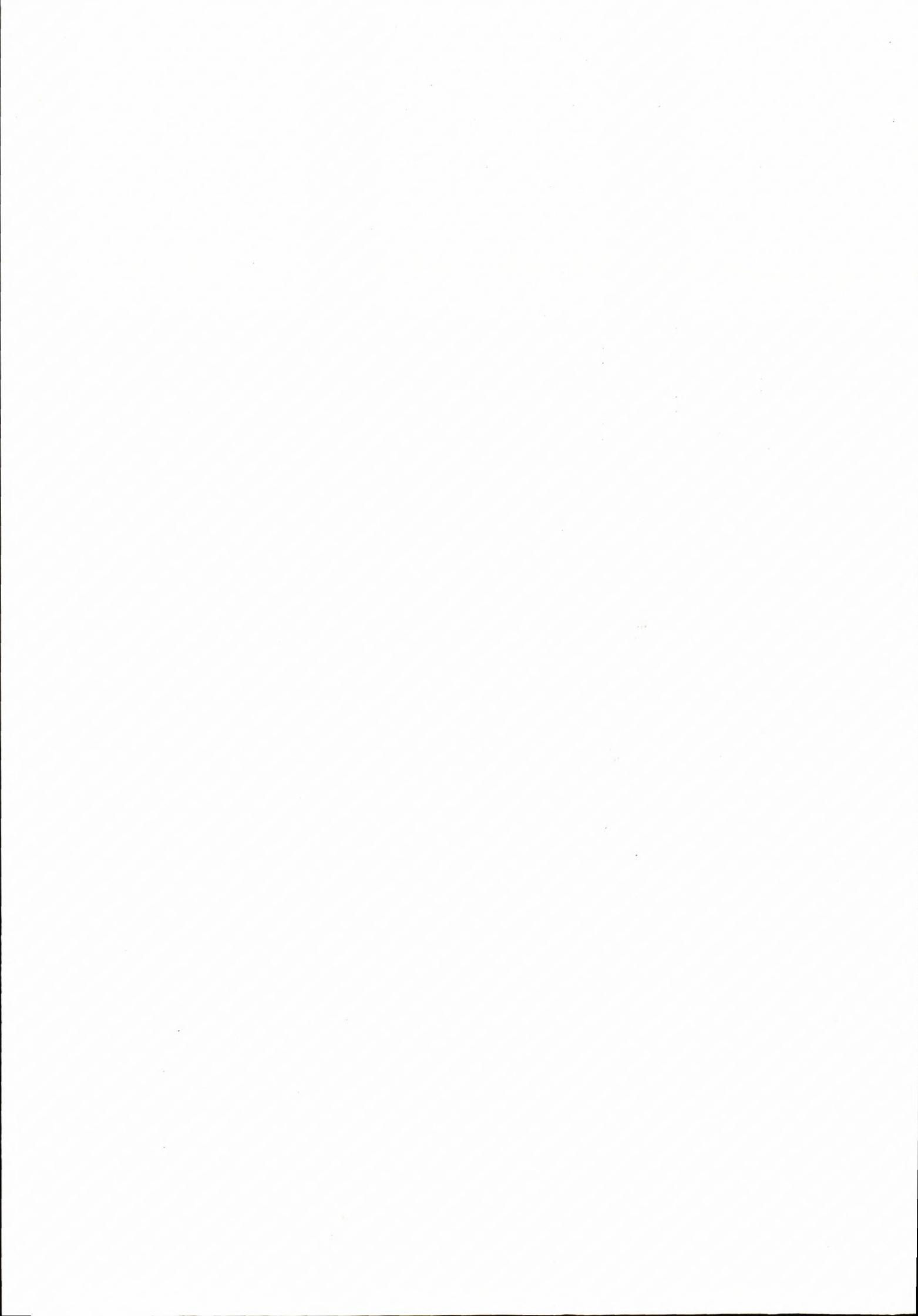
Fig. 18 Halite overlain by enterolithic layer of nodular anhydrite, unit IV. Space between nodules filled by siltstone. The bar for horizontal scale is 1 cm.

Fig. 19 Paramorphosis of a clear halite cement after original displacive halite in the middle part of the photo, unit IV. The overlying and underlying beds are composed of light, enterolithic nodular anhydrite. The overlying bed is deformed by displacive halite. The bar for a scale is 1 cm long.

Fig. 20 Laminated siltstone composed of gypsum and siltstone laminae, unit IV. The bar for a scale is 1 cm long.

Fig. 21 Enterolithic layer of nodular anhydrite, bird-eye view. Unit V. The bar for horizontal scale is 1 cm.

Fig. 22 Irregularly laminated and soft-deformed gypsum as a relic of primary precipitating gypsum. The bar for a scale is 1 cm long.



Upper Jurassic evaporites of the southwestern slope of East European Platform

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Abstract. Upper Jurassic evaporite sequences along the southwestern slopes of East European Platform consist of interbedded dolomites, dolomitic limestones, anhydrite and siliciclastic rocks, and in Predobrogea also of gypsum and rock salt. The rock salt contains chevron and recrystallized halite with specific fluid inclusions in each type. The inclusions have a chloride chemical composition, with the ratios of sodium, potassium and magnesium chlorides similar to those in the modern seawater saturated to the corresponding stage, and differed only by CaCl_2 content. Maximum potassium content in brine inclusions in halite is 15.5 g/l and indicates that the concentration of brine in the basin did not reach the stage of potash sedimentation.

Key words: Jurassic, evaporites, rock salt, brine, inclusion, East European Platform.

Introduction

Upper Jurassic evaporite deposits are widespread along the southwestern slope of the East European Platform in Poland, Ukraine, Moldova and Romania (Fig. 1). They consist of interbedded dolomites, dolomitic limestones, anhydrite and siliciclastic rocks, and in Predobrogea also of gypsum and rock salt. In south-eastern Poland these deposits belong to the Ruda Lubycka series of Kimmeridgian age and are subdivided into two parts. The lower one is 140 m thick and the upper one is 100 m thick (Niemczycka, 1976). In the Fore-Carpathian region of Ukraine sulfate-carbonate deposits are distinguished in the Rava Russka series that is 20 to 250 m thick. The thickness of dolomite layers ranges from 1 to 40 m and of anhydrites from several cm to 7 m (Dulub *et al.*, 1986). In Predobrogea region (in Ukraine and Moldova) Kimmeridgian evaporites in the Kongazsky series have a total thickness of 15-445 m (Garetski, 1985). The series contains terrigenous rocks, limestones, dolomites, anhydrite, gypsum and rock salt.

Dolomites and sulfates

Sulfate and carbonate rocks all over the region are characterized by similar features. Dolomites are grey, light-grey, or brown fine-grained massive rocks. They are composed of dolomite crystals with average sizes of 0.01-0.02 mm, and many dolomites contain silt-sized quartz, plagioclase and muscovite and clay-sized mica and

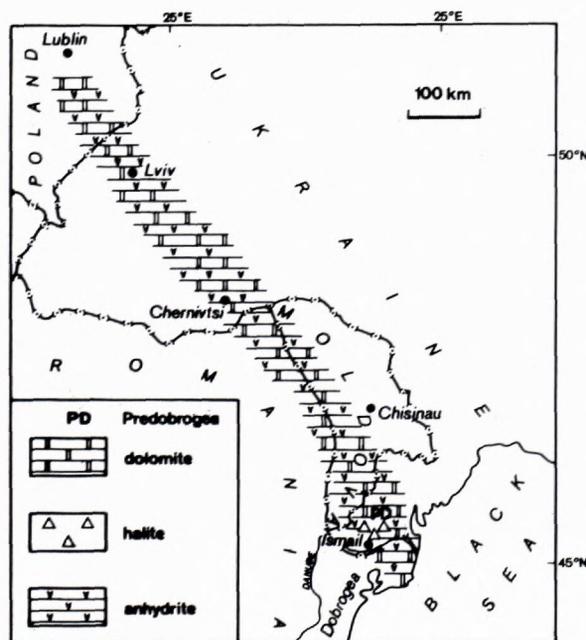


Fig. 1 Schematic map of distribution of Upper Jurassic evaporites, south-western slope of East European Platform.

chlorite. The authigenic minerals in dolomites are pyrite, anhydrite and celestite. The latter often forms thin layers in dolomites, where the content of Sr reaches 3% (Khmelevska, 1988). Anhydrites are white, light- and dark-grey, brown and commonly multicoloured, fine-grained,

massive rocks. They contain 97-99% of calcium sulfate. Among the admixtures are terrigenous and authigenic quartz, authigenic pyrite, dolomite, calcite, magnesite, and hematite. In the upper part of the Ruda Lubycka series crystals of fluorite were found (Radlicz, 1975). Many anhydrites in Predobrogea contain large inclusions (up to 3-4 cm) of carbonized detrital organic matter. In addition to anhydrite, anhydrite breccia and mixed dolomite-anhydrite and gypsum-anhydrite rocks are also present in the section. Gypsum in the Fore-Carpathian region has been described by Anastasieva (1958) in the Rawa Russka series, developed on Volyn' and Podolia at the depth of 600-1000 m. They have a restricted distribution in carbonate deposits and form the layers up to 1 m thick. In the rest of West Ukraine and in Poland gypsum rocks have not been found. In Predobrogea, gypsum is widespread in the Kongazsky series. It is fine-grained and coarsely-crystalline, blue, grey, brown and yellow in colours and forms of pods, veins and layers in anhydrites (Khmelevska, 1990).

Rock salt

Rock salt occurs only in Predobrogea near Izmail and is represented by white, grey, or pink medium- and coarse-grained halite. Its thickness is about 78 m (Tiuremina & Khmelevska, 1990). The NaCl content in rock salt ranges from 93 to 98% and contains authigenic anhydrite, calcite, dolomite, quartz, celestite, fluorite, and pyrite. Bromine content in the rock salt ranges from 0.0027% to 0.0063% and averages 0.0035%. In comparison to experimentally established content of this element (0.0068%) during the initial stage of halite precipitation (Valiashko, 1962), it is depleted. The value of Br 1000/Cl coefficient ranges from 0.038 to 0.10 and in average is 0.058. The decreased content of bromine and a low value of Br 1000/Cl coefficient may be caused by a specific chemical composition of the salt-forming solutions. Valiashko *et al.* (1976) showed that the presence of CaCl₂ and MgCl₂ in brine could significantly decrease the ability of bromine to enter into the crystalline lattice of halite.

Fluid inclusions

Thermobarogeochemical investigation showed that the rock salt is composed of sedimentary and recrystallized halite. The first contains chevron and hopper crystals with primary fluid inclusions 5-10 to 100-120 μm across. Inclusions have a cubic shape; locally they contain a solid phase represented by anhydrite or pyrite. Ultramicrochemical analysis of fluid inclusions revealed that they have a Na⁺-K⁺-Ca²⁺-Mg²⁺-Cl⁻-composition (Fig. 2). The potassium content ranges from 5.8 to 15.5

g/l (average is 7.9 g/l). Seawater was the main source of this element in the evaporite-forming process. At the initial stage of halite crystallization the concentration of potassium in the salt-forming basin of Predobrogea was 5-6 g/l. These values correspond to those experimentally established in seawater saturated to the stage of halite precipitation (Valiashko, 1962). During salt crystallization in the basin the concentration of potassium increased to 15 g/l, but such an increase was not gradual. Probably, periodic dilution of the brine led to decrease of potassium content and prevented it from reaching high levels. The concentration of calcium in the brine ranged from 8.5 to 11.8 g/l (average was 10.5 g/l); and of magnesium from 7.9 to 30.5 g/l (average was 13.0 g/l). The total dissolved solid content of the brine was 320-350 g/l.

I have determined the composition of brine inclusions in halite from the lowest part of the salt deposit in Predobrogea. This composition was, on whole, very close to that of modern seawater saturated to the stage of halite precipitation (Table 1). The main difference was in the presence of CaCl₂ and in the absence of MgSO₄ in salt-forming brine of Predobrogea, that, possibly, was caused by the evolution of the chemical composition of seawater during the Phanerozoic (Kovalevich, 1990). Recrystallized halite is widespread in the salt deposit. It fills the space between relics of zoned grains of sedimentary halite and occurs as separate grains or thin layers. It contains fluid and solid inclusions, rarely two-phase ones (with solid+fluid; fluid+solid phase). Inclusions have different shapes, their sizes range from 20 to 1300 μm. The solid phase in two-phase inclusions consists mainly of xenogenic anhydrite. Solid inclusions are anhydrite, carbonates, quartz and pyrite. Ultramicrochemical analysis of brine inclusions in recrystallized halite shows that they also have a Na⁺-K⁺-Mg²⁺-Ca²⁺-Cl⁻-composition (Fig. 2). The content of major elements differs from those in sedimentary halite. The concentration of potassium ranges from 1.0 to 12.5 g/l (average 4.6 g/l); of calcium from 8.3-36.0 (average 20.6 g/l); and of magnesium from 13.0-39.5 g/l (average 26.9 g/l) (Khmelevska, 1993). Thus, the recrystallization of salt took place under the influence of residual chloride solutions that were buried in soft sediment. The subordinate role of recrystallized halite in salt deposit and the insignificant difference in chemical composition of solutions in fluid inclusions from sedimentary and recrystallized halite suggest that fast postsedimentary alteration of salt sediment was terminated during early diagenesis.

The studied halite does not contain gas inclusions; the gases are dissolved in brine inclusions. The total gas saturation of solutions has been determined by method of Petrichenko (1973). Its value ranges from 1.5 to 9.0 ml/l and in the samples from the bottom of the salt layer is 4.0 ml/l. Such a quantity of dissolved gases could be caused

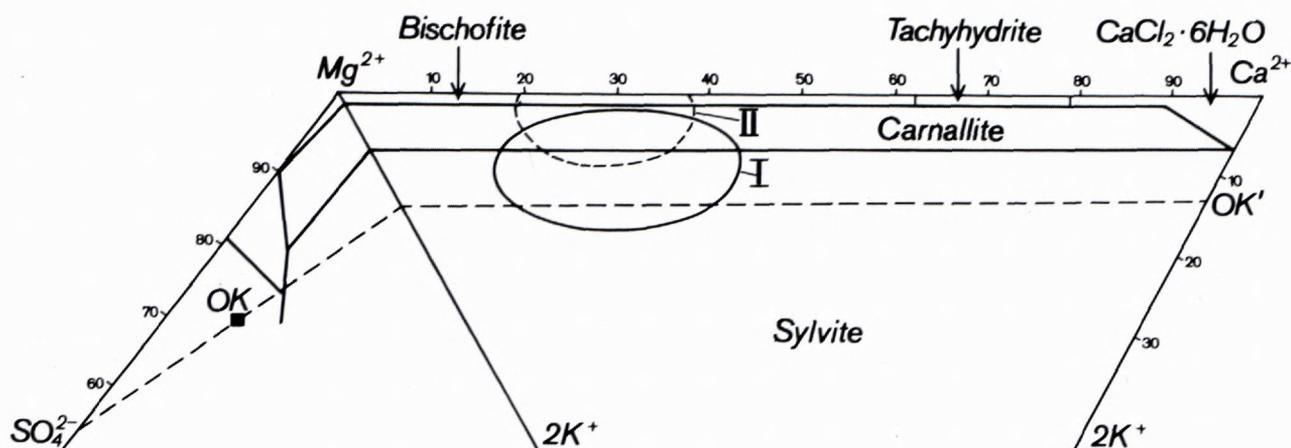


Fig. 2 The brine composition in the Predobrogean evaporite basin on the Valiashko (1962) diagram; I - the field of brine composition during halite sedimentation; II - the field of brine composition during diagenesis. OK - the composition of salt-forming solutions of marine origin; OK-OK' - the line of metamorphism of marine solution.

Table 1. The content of major ions and salts in sea water of different saturations (after Valiashko, 1962) and in brine inclusions of sedimentary halite from the lower part of Predobrogean salt series

Type of seawater	Content of ions and salts, g/l										
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	CaCl ₂	MgCl ₂	NaCl	KCl	MgSO ₄
Normal seawater	0.43	1.3	11.3	0.4	20.1	2.9	-	3.385	27.6	0.76	2.305
At the beginning of halite precipitation	0.42	15.5	104.3	3.3	191.2	21.0	-	33.4	214.1	5.2	21.0
At the beginning of halite precipitation in the Predobrogean basin	9.7	13.0	90.0	5.2	166.6	0.5	26.8	59.0	214.5	9.3	-

by low pressure, that occurred in the salt-forming basin at the depth of 16-20 m. The presence of only one-phase fluid inclusions (without daughter crystal and gas bubble) suggest that the temperature of brine in the basin did not exceed 40°C. The gas mixture consists of N₂ (72.7 - 83.3 vol%), CO₂ (10.0 - 18.2 vol%), and CH₄ (4.4 - 9.1 vol%). The absence of solid hydrocarbons in the gas mixture shows a low possibility for oil discoveries in underlying deposits.

Conclusions

The analyses of brine inclusions in halite show the marine origin of this rock salt. The chloride composition of solutions and the absence of significant amounts of SO₄ and HCO₃ demonstrate that the salt deposits do not contain sulfate salts and soda. The maximum content of potassium in brine inclusions in sedimentary halite is 15.5 g/l and according to Petrichenko *et al.* (1976) is typical for deposits that do not contain potash salts. The

maximum concentration of KCl in solutions (29.6 g/l) is only 30% of what is necessary for precipitation of KCl as a solid phase. The calculations show that the Predobrogea rock salt has no potash-bearing indications. This is also confirmed by mineralogical and geochemical data which show that the rock salt is composed of NaCl (up to 98%) and the amount of KCl is less than 0.6%. Among the authigenic minerals in the water-insoluble part of rock salt anhydrite prevails, dolomite is common, but magnesite is completely lacking. As the latter is the indicator of higher stages of evaporation, the brine, obviously, did not reach them during its evolution. Also the bromine content in the rock salt corresponds to the initial stage of halite precipitation. Thus the economic interest in these deposits may be related only to the rock salt itself.

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New information on the Markušovce - Šafárka gypsum and anhydrite deposit (Eastern Slovakia)

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Abstract. Results of new geological researches on the evaporite deposit Šafárka (Eastern Slovakia) enable a substantial re-evaluation of its economical significance. Within the deposit, gypsum and anhydrite form regular and qualitatively distinguishable technological subtypes of raw material that fulfil different industrial requirements.

Key words: Permian-Triassic, gypsum, anhydrite, Northern Gemicum

Introduction

The deposit Markušovce - Šafárka is a part of the Spis deposit belt of anhydrite and gypsum. Nowadays it is known under the name Spišská Nová Ves - Nová štôlna (New adit) (Michalko, 1994).

The deposit has been known since its finding in thirties of this century as well as on the basis of more geological-prospection works performed later. The latest data about the deposit were obtained in the frame of the project "Šafárka - prospection and assesment of open casting gypsum, prospection etape (Jančura et al., 1997)."

Location, position and shape of the deposit

The deposit Markušovce - Šafárka is located in the area between Zadna dolina valley, Rysovec, Nova stolna adit and a mountain crest Gretla - Trubačovec southerly of Spišská Nová Ves and northerly of Hnilčík. It is a part of the north gemeric evaporite formation. The deposit is formed in the stratigraphic horizon of sedimentary sulphides identical with sulphides occurring in the anhydrite - gypsum deposit of Novoveská Huta.

The deposit Markušovce - Šafárka is bound by a fault systems governing the characteristic block structure of the area. The southern margin of the area is formed by Muráň or Gretel (Daniel et al., 1985) E - W fault having a character of an oblique thrust. From the south the deposit is bound by a system of oblique normal faults of NNW - SSE direction along the mountain crest Zompy. The system of normal faults, extended in the line from Teplička to Bindt, makes the eastern boundary of the deposit.

The shape of the deposit is fully determined by the spatial distribution of the above mentioned faults. The tectonic structure renders a possibility to divide a block of open casted resources in the area of Zadná dolina valley, which is uplifted to the level 15 - 20 m under the surface.

Lithostratigraphic characteristics of evaporite horizon

The evaporite horizon is associated with the uppermost sequences of Nová Ves Formation (Novotný et al., 1987) belonging to the Kropachy Group (Bajaník et al., 1981). The upper boundary between the evaporite horizon and the Lower Triassic rocks is not exactly given because of different interpretation of conglomerates overlying shales containing evaporites in the larger surroundings of Novoveská Huta.

Nová Ves Formation is dated to the Upper Permian on the basis of palynologic assemblage (Planderová in Václav et al., 1980). The isotopic analysis performed on the sulphur from evaporitic horizons mostly approximates to the Upper Permian - Lower Triassic age (Kantor, 1982).

Nová Ves Formation contains deposits with a conspicuous fining up grain size trend (Vozárová et al., 1988). Novotný et al. (1987) divided the formation to the Strážany and Biela Voda Beds. Strážany Bed commences by polymict conglomerates having a gradual transition to sandstones, shales and aleurites upward. Vojtechovce horizon, bearing Cu and U mineralization, is divided separately. Strážany Beds pass to evaporite lithofacies of Biela Voda Beds. These beds are typical by

occurrence of gypsum, anhydrite and locally also halite and sylvine (Mahel' et al., 1973). Fragments of complementary claystones and siltstones are typical too. A part of the evaporite lithofacies are layers of intraformational breccias containing clasts consisting of sediments or

dolomites (Karlovi, 1992; Turanová et al., 1993; Michalko, 1994). Evaporites pass to porous yellowish brown massive carbonates (termed as rauwacks) upward. The carbonates contain raddles of green or redd clayey rocks and grey dolomites. (Fig. 1).

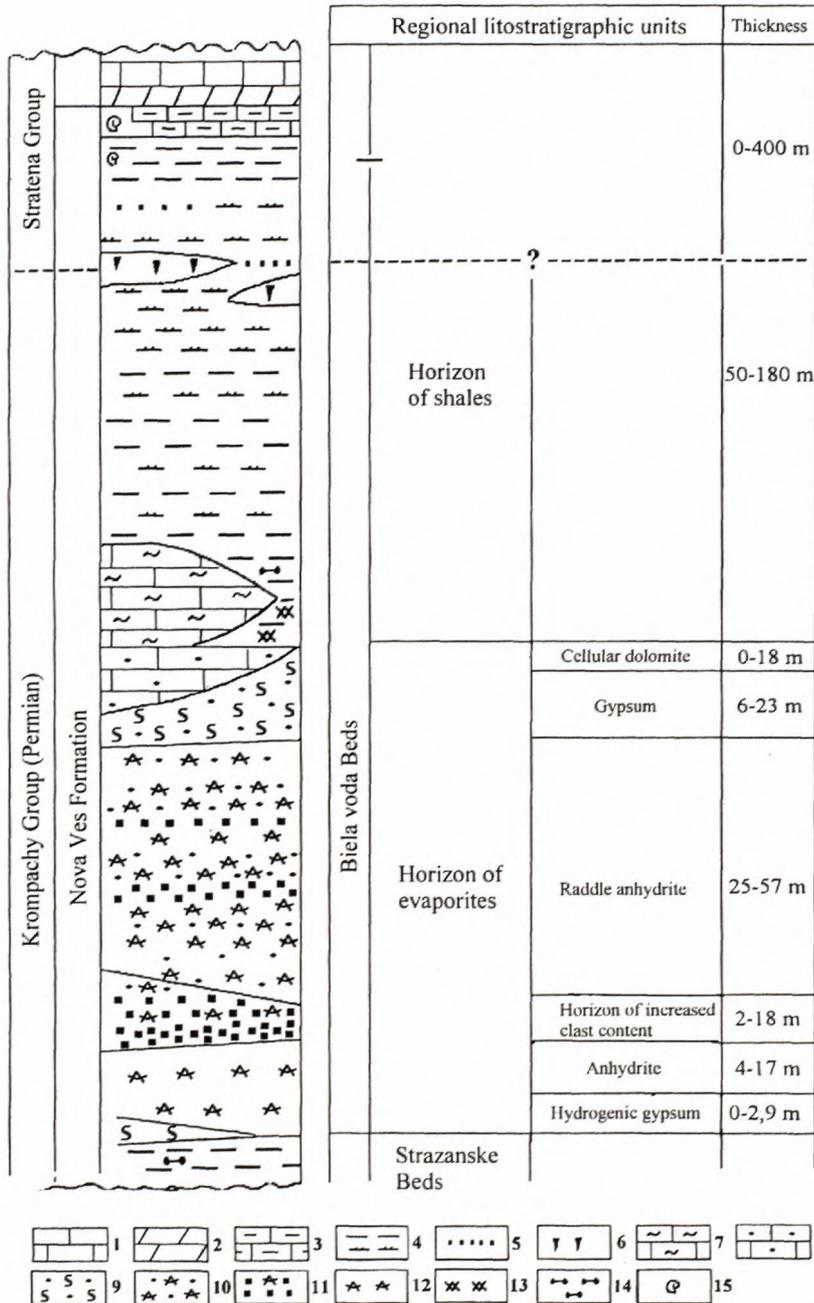


Fig.1 Schematic lithostratigraphy string of Evaporites horizon from Markušovce - Šafárka deposit.

1 - limestones, 2 - dolomites, 3 - marly limestones, 4 - shales, aleurolitics, 5 - sandstones, 6 - quartzose sandstones, 7 - marly limestones and shales, 8 -- cellelar dolomites (rauwackies), 9 - gypsum with clastic admixture, 10 - anhydrite with clastic admixture, 11 -- horizon with higher abundance of clasts, cemented with anhydrite, 12 - anhydrite, 13 - gypsum (veinlets), 14 -- nodules of dolomite, 15 - occurrence of fossils.

A genetic connection between the occurrence of evaporites and cellular carbonates is assumed on the basis of the spatial relationship (Maheľ et al., 1956). The transition of cellular carbonates to overlying marl phyl-lites is gradual. The bedding with constant bed thickness is well developed in the Nová Huta Formation deposits, especially in evaporite facies. The deposits are characteristic by the development of small cycles in the range from 1 to 10 m and mesocycles in the range from 10 to 50 m (Vozárová et al., 1988).

The formation belonging to the Lower Triassic, which occurs in the deposit area, crops out as erosive relics especially in the northern part of the area. The lowermost members are rhythmically alternated beds of violet, green and grey slates, sandy slates and sandstones. The facies changes upward where marls, marl limestones and slates of grey to greyish green colour appear (Campanian). The upper part of the formation consists of bedded limestones of Campanian (Biely et al. in Fusan et al., 1967). The Lower Triassic formation underlies erosive blocks of Middle Triassic carbonates forming peaks of more conspicuous hills (Okruhlovec and others). The carbonates are represented by underlying dark dolomites and limestones of Anisian age and pale limestones of Anisian - Ladinian age (Novotný et al., 1985).

Evaporite horizon of the part of the deposit Markušovce - Šafárka was recently petrographically described (Faryad in Jančura et al., 1997) in the borehole Sa-1 (depth 126 m) located in the Zadná dolina valley. The gypsum and anhydrite occur as formation containing quantitatively variable clast admixture consisting of slates without or with organic matter content, dolomites, quartz and sandstone. Clasts have various shapes, size and they are irregularly distributed. The fragments up to the size of 1 cm prevail, occasionally fragments up to 5 cm occur too. More important concentrations of NaCl or KCl have not been confirmed in evaporites and there has not been found a dolomite having a form of massive layer. The occurrence of anhydrite and magnesite inclusions suggests the origin of a part of anhydrite by chemical alteration from dolomite. Magnesite, which includes anhydrite in gypsum, shows the origin of gypsum by anhydrite gypsification in zones overlying and underlying evaporites. Anhydrite crystals are clear, without admixture of other components, which may suggest their recrystallization from sedimentary anhydrite during the diagenetic process.

Preserved sedimentary structures, clast character, hints of graded bedding and erosive bases of individual depositional rhythms point to depositional conditions. The evaporite deposition occurred most likely on a shallow, tectonically active basin margin with periods of tectonic activity and stable depositional conditions. The

near-base anhydrites are the product of more quiet development, the so called raddle anhydrite and/or anhydrite conglomerates and breccias having anhydrite matrix are the product of the development during partial tectonic movements (Karlovi, 1993).

The correlation between stratigraphic horizons and mineralogic composition of evaporite formation between individual prospection workings implies the greatest depth of the raddle type of evaporite formation in the area of Zadná dolina valley. It is possible to observe here more than three times repeated rhythms of graded bedding containing more massive basal layer with prevailing clastic part in the bed overlying anhydrite. The raddle horizon diminishes toward north and west. The evaporites form a compact layer of anhydrite with gypsum in the borehole GR-5. Evaporites do not have clastic admixture here. The overlying rocks locally contain gypsum in veins, aggregates and hems.

The evaporite characteristics differs in the only confirmed occurrence in the Markušovce valley at the locality Slivníky (borehole 229), easterly from the prospection area. Under the slates, interfingering by gypsum, the evaporite horizon commences in the 232.1 - 244.2 depth interval by a compact anhydrite having weakly hydrated zone in the upper part. In depth 244.2 - 268.1 anhydrite interfingering by slates is developed. In the depth interval 268.1 - 276.0 anhydrite contains fragments of greenish slates. In the depth 276.0 - 279.7 compact anhydrite occurs.

The correlation of evaporites at the locality Markušovce - Šafárka and more distant deposits in the area of Novoveská Huta, Biele Vody, Poráčska dolina valley and the area northerly of Rudňany and Smizany reveals facies originated in different depositional environments.

Distribution of evaporite minerals

The evaporite formation in the area of Nová stôlna adit - Šafárka - Zadná dolina valley may be characterized from the base upward as follows:

a) Chemogenous anhydrite layer, locally hydrated to gypsum on the base of evaporite formation. The admixture, irregularly impregnated in anhydrite, is mostly represented by dolomites. The boundary between anhydrite and dolomite is transitional, anhydrite grains contain fine dolomite inclusions on their hem.

b) The middle bed of raddle anhydrites, represented by graded and rhythmically bedded conglomerate- and breccias-evaporites, commences by the prevailing clast abundance comparing to anhydrite matrix in the lower part. The boundary between the chemogenous layer and anhydrite bed with prevailing clast content is sharp, suggesting an abrupt change of depositional conditions.

The size of conglomerate clasts varies, the largest ones are up to 5 cm. The clasts are variably rounded. Between lithotypes, better rounded slate clasts prevail above the less rounded carbonates comprising mainly dolomite. In the upper part of the section quartz occasionally occurs. The anhydrite matrix consists of anhydrite grains having marmor structure. Diagenesis is indicated by secondary anhydrite in the form of veins, aggregates, metacrystals, redeposited quartz in the form of veins and hexagonal metacrystals and magnesite (Faryad in Jančura et al., 1997).

Conspicuous indication of redeposition in the form of chaotic structures and irregular bedding has not been observed in the layer of raddle anhydrite. In boreholes Sa-1, Sa-2 and Sa-3 primary bed structures are preserved without discordance, even on the erosive bases (?) of individual depositional cycles with graded bedding. The changes in measured values of foliation cleavage in one section are gradual and they are consistent with plikatives deformation of evaporite formation. The special phenomenon is the preferred clast orientation.

c) The gypsum horizon is locally developed in the upper part of evaporites. The gypsum is analogous to raddle type of evaporites comprising fine-grained clasts. It occurs along a hydrated zone parallel to muran (gretel) fault. It extends from Zadna dolina valley to Nova stolna adit and further on to the west.

d) The evaporite formation ends by an irregularly developed bed of cellular dolomites which is assumed to be a part of Biela Voda Beds. This horizon almost always directly overlies evaporites. Locally the horizon individually occurs in the overlying slates and sandstones (borehole Gr-4).

Tectonic structures characterized on the basis of geophysical investigation

Ten NE-SW profiles were performed during the geophysical investigation (Komon in Jančura et al., 1997). The geophysical map of rock resistivity has been made. Except of surface resistivity map, three subsurface horizontal sections were made in depths 10 - 15 m, 30 - 40 m and 80 m. Resistivity isolines show conspicuous zones of different resistivity. The low resistivity zones point to a strong watering, of tectonic structures and it is possible to compare them with azimuths of dislocations founded on the surface.

Active springs, swamps and peats were found on the surface during the mapping in the area of deposit Sa-farka. They point to the outcrops of water-bearing structures. The communication between above mentioned water sources can be confirmed by correlation of directionally most frequent geophysical structure zones of re-

sistivity and founded dislocation in the surroundings of the deposit (Sasvári in Jančura et al., 1997).

Geophysical resistivity profiles, made on the basis of horizontal geophysical sections, show important subvertical fault structures coinciding with main structures of tectonic deformation.

Model of structural pattern of the Šafárka deposit

The comparison of geophysical resistivity measurements (Fig. 2a-d) at evaporite economy deposit Sa-farka, tectonic structures of dislocated character in the northern part of the area, outside the deposit area, and water-bearing structures cropping out on the economy deposit area (Fig. 2e) show that:

- The economy deposit is deformed at least by three systems of subvertical dislocations of NW-SE, NE-SW and NWW-SEE direction. The azimuth variance of these directions is in the range of 10 - 25 degrees. The reason of this variance is probably caused by mutual rotation of individual blocks.
- The deposit is deformed at least by one subhorizontal, resp. slightly inclined tectonic zone in the depth level under 50 m. Mylonite zone has been recovered by the borehole Sa-1 in the depth 49 - 50 m. The horizontal geophysical section in the depth 80 m shows substantially more conspicuous NNE-SSW and NE-SW zones of lower resistivity, other directions are less conspicuous. It indicates two subhorizontal blocks separated by a mylonite zone in the distance of ca. 50 depth meters.
- The more essential deformation of the deposit with the occurrence of more dense dislocation structures is in the southern part nearby the Muráň Fault. This area is most conspicuous watered.
- Subhorizontal and subvertical dislocation results in high amount of blocks in the deposit. This suggests the mutual rotation of blocks respectively sinking of some structural blocks of the deposit.

The model of above mentioned structural pattern deposit probably originated by sinistral shear of the shear zone of Muráň Fault. Incompetent rocks in the area of anhydrite deposit Šafárka got sigmoidal course of foliation. More competent anhydrite layer has been formed to asymmetric megaboudin -shear lense as a result of higher values of shear strain. This megaboudin - shear lense represents the deposit Šafárka.

Sinistral orientation of the shear shows model conditions of a simple shear and a formation of extension and compression structures. Directions of these structures are consistent with geophysical structures with low resistivity, the occurrence of surface springs, karst sinks and swamp zones.

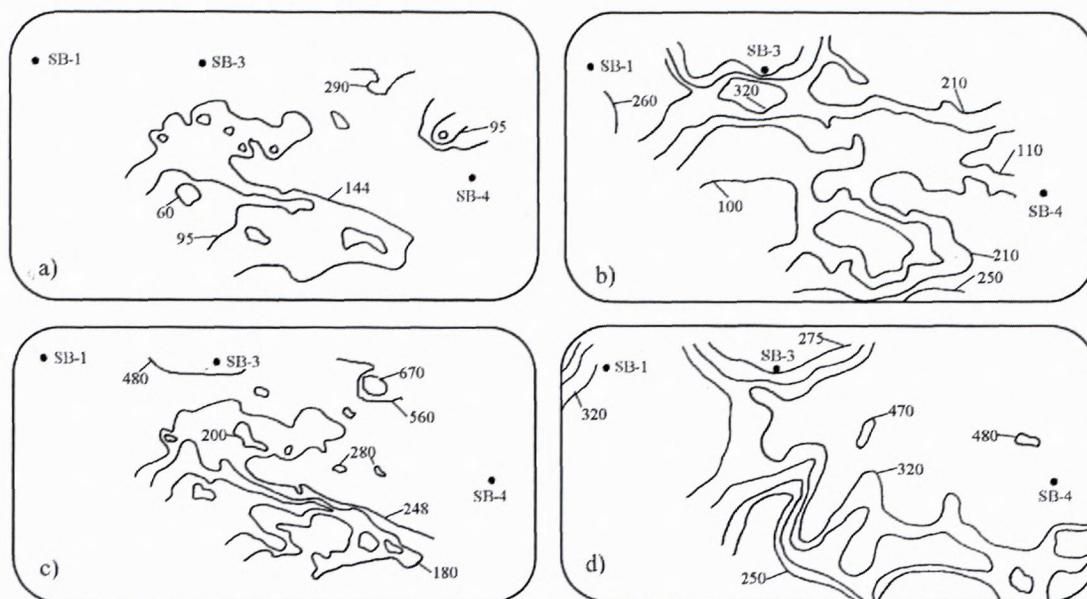


Fig. 2a-d Šafárka deposit. Geophysical sketches of izolines of low resistivity. a-surface (335-60 OHM_M), b-horizon 10-15 m (576-100 OHM_M), c-horizon 30-40 m (676-100 OHM_M), d-horizon below 80 m (487-250 OHM_M). SB-1, SB-3, SB-4 are boreholes.

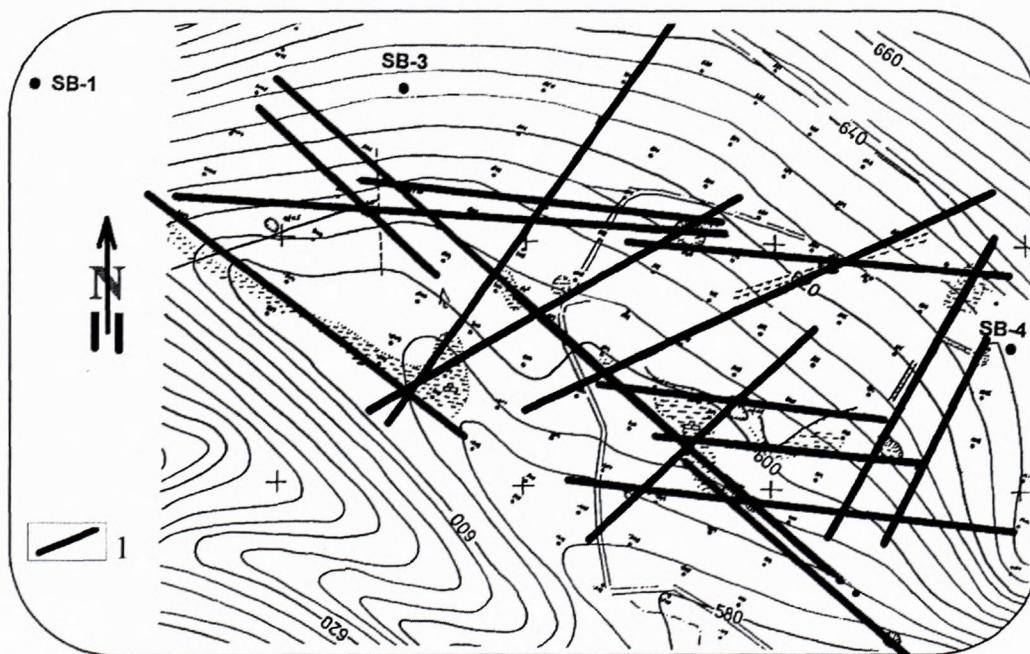


Fig. 2e Šafárka deposit. Coincidence of geophysical structures with low resistivity (by fig. 2a-d) with surface springs, karst sinkhole and zones of sloughs.

Conclusion

New geologic-prospection works at gypsum and anhydrite deposit Markušovce - Šafárka enabled reevaluation of economic importance of the deposit. The gypsum and anhydrite form regularly distributed and qualitatively

discerned technological subtypes of the raw material. The raw material fulfill the requirements for more possibilities of industry use. Specially interesting type of raw material is open casted gypsum at locality Zadná dolina valley.

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Upper Permian - Lower Triassic evaporites in the Western Carpathians (Slovakia)

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Abstract. The Upper Permian - Lower Triassic Western Carpathians evaporite basins formed in a semiarid climate, generally in non-marine and marine depositional setting. The origin and time/space distribution of marine evaporite basins was connected with transgression, which reflected the beginning of Alpine orogenic cycle. All these marine evaporite basins were rimmed by shallow shelves that became covered by sulphate and in more rapidly deepening part by chloride precipitation. Sedimentary structures indicate that part of the anhydrite and even halite sediments was deposited through the action of gravity currents. Semiarid flash floods were the major suppliers of siliciclastic sediments. Non-marine evaporites (carbonates, sulphates, albitolites) originated in endorheic basins and alkaline lakes as well as by groundwater precipitation.

Key words: Western Carpathians, Upper Permian/Lower Triassic, evaporites, S isotope composition

Introduction

On the territory of the Western Carpathians Upper Permian - Lower Triassic evaporites are found in several tectonic units (Fig. 1). They, however, differ from one another not only in their stratigraphic position, but mainly in structural features and the depositional setting, partly also in mineral composition. In sedimentological analysis of these sequences the main problem is their occurrence in the complicated Alpine structure when extension and original shape of sedimentation basins were reduced to a considerable extent with Alpine orogeny. Moreover, evaporite formations are not cropping out and for this reason they can be studied on the basis of materials obtained from borehole profiles or mine workings only.

From the genetic point of view, the Upper Permian - Lower Triassic evaporites were formed in three fundamental types of sedimentation environment - continental lakes; - groundwater precipitations; - subtropical marine bays and lagoons (Fig. 2). These fundamental genetic types of evaporites were practically established in all main Alpine tectonic units of the Central and Inner Western Carpathians; i.e. in the Tatricum, Veporicum, Zemplinicum, Hronicum, Northern and Southern Gemericum, Turnaicum and Silicicum. Of course, in each of them not all three types are found together or not each of them is represented in more significant amount. As to the

amount and variety of development most significant occurrences are in the Northern Gemericum and in units of the Turnaicum and Silicicum.

Geological setting

In Alpine nappe edifice of the Western Carpathians Upper Permian - Lower Triassic evaporite formations are represented in the inner structural zone, which is mainly formed by a complex of pre-Gosau nappe units. A part of them, besides identical Mesozoic formations, also contains an own crystalline basement, the second group of nappes mainly consists of Mesozoic sequences, at most with relics of tectonically reduced Carboniferous-Permian formations in their lower part.

The lowermost tectonic unit, Tatricum, contains medium - to high-grade crystalline complexes associated with deep-seated migmatites and magmatites, which were covered by Permian continental sediments with angular unconformity. Lower Triassic sediments of the Mesozoic cycle are lying parallelly disconformably on both structure stages. An identical geological situation is in the Northern Veporicum, the main differences from the Tatric unit are in lithofacial development of the Mesozoic sequences. (Maheľ 1986, Biely et al., 1996). The superficial, Križna nappe, as the home area of which the unit of the Northern Veporicum is considered, does not contain sediments older than the Lower Triassic (with the exception of the

Tectonic sketch of the Slovak part of Western Carpathians (after Biely et al. 1996)

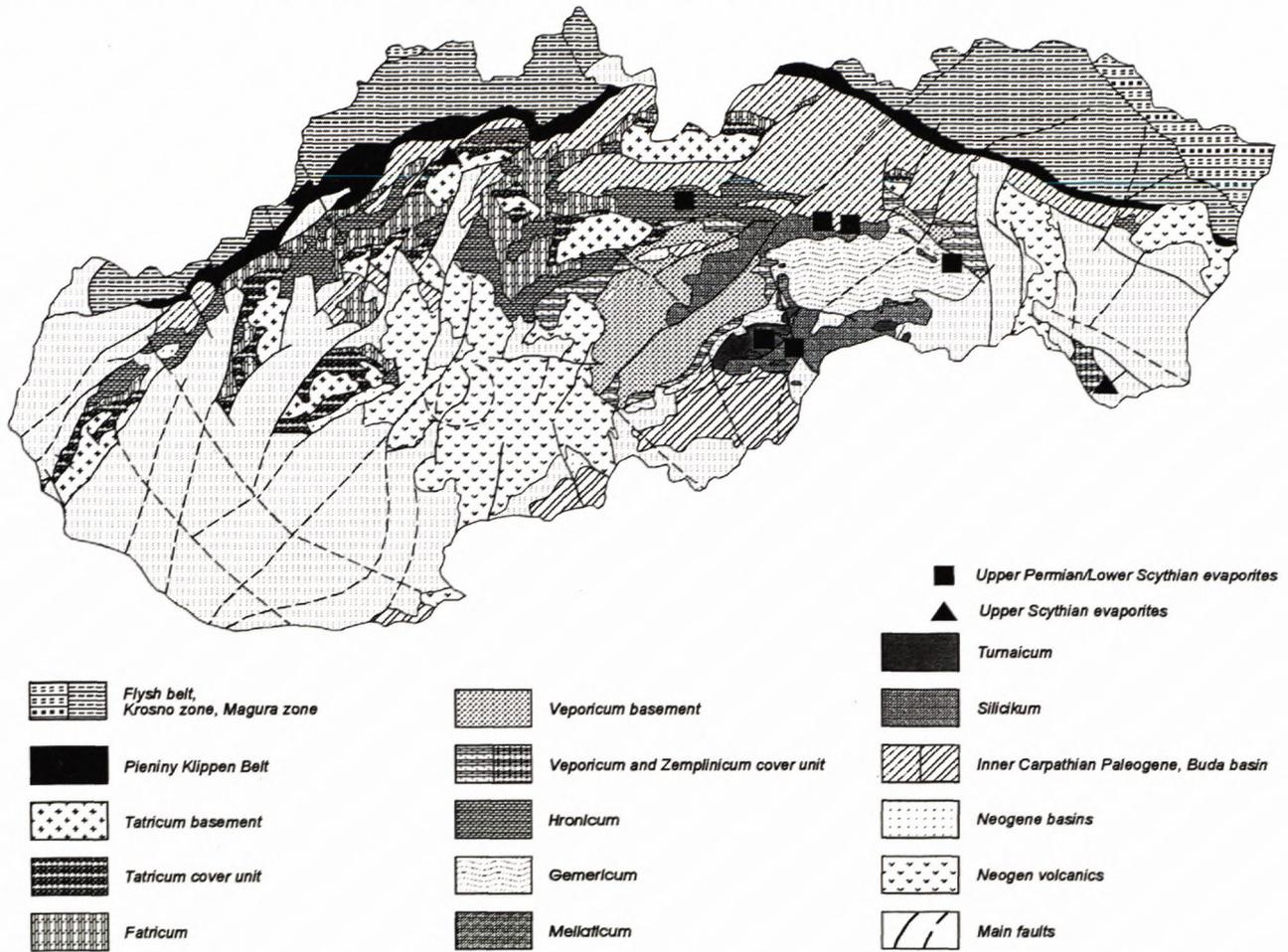


Fig. 1 Distribution of the Upper Permian - Lower Triassic evaporite formations on the territory of the Central and Inner Western Carpathians. Based on the geological map of the Slovakia 1 : 500 000 (Biely et al., 1996)

		CENTRAL WESTERN CARPATHIANS					INNER WESTERN CARPATHIANS				
		T	NV	SV	Z	H	NG	SG	M	TU	S
main paleo-Alpine Western Carpathians units											
depositional setting											
Upper Permian - Lower Scythian	non-marine: groundwater precipitation	■			■	■	■	■		■	
	endorheic basin					■	■			■	
	alkaline lake						■	■			
	paralic sebkha						■			■	
Upper Scythian	marine: lagoon, restricted sea, connected with sebkha						■				
	wide shelf marginal closed sea									■	■
primary precipitation		sulphates + carbonates					carb. sulph. + chlor.	carb.	sulphates + carbonates		
Permian/Lower Triassic boundary		disconformity					gradual		continuation		

N ←-----→ S
direction of marine transgression

Fig. 2 Scheme of sedimentary evolution of the Western Carpathians Upper Permian - Lower Triassic evaporite basins. Explanation to symbols: T - Tatricum; NV - Northern Veporicum; SV - Southern Veporicum; Z - Zemplinicum; H - Hronicum; NG - Northern Gemicum; SG - Southern Gemicum; M - Meliaticum; TU - Tornaicum; S - Silicikum

occurrence of Permian sediments at a small area in the Starohorské vrchy Mts.). From the point of view of the crystalline basement, but also Triassic development, with the Tatricum and Northern Veporicum units also the Zemplinicum unit (Vozárová, 1991), originally delimited as an independent tectonic unit in the southern part of the East Slovakian lowland, is identical (Slávik, 1976). In it only the stratigraphic range of the Late Variscan envelope, which is represented by the continental Upper Carboniferous and Permian in the Zemplinicum, is different. The Mesozoic cycle starts again with Lower Triassic sediments, which are separated from Variscan post-orogenic sediments by a hiatus and parallel disconformity.

A different type of the crystalline basement and also envelope sequences has the unit of the Southern Veporicum. Crystalline complexes are represented by medium - to low-grade metamorphosed complexes, which are highly Alpine-reworked and penetrated by Alpine granitoids. The Late Paleozoic envelope of the Southern Veporicum is represented again by the Upper Carboniferous and Permian rocks, which are parallelly disconformably covered by Lower Triassic clastics.

The whole group of the above mentioned basement nappes including the Krížna nappe is overthrust by the Hronicum nappes (Subtratic nappes *sensu* Andrusov, 1968). They belong to rootless nappes, mainly consisting of Mesozoic sequences, which are underlain by remnants of Upper Carboniferous-Permian sediments reduced tectonically, preserved in places only.

The southernmost nappe units, in which the crystalline basement is preserved, are the Northern and Southern Gemicum. Rock sequences of the basement of the Northern Gemicum are composed of high-grade and low-grade metamorphosed complexes of oceanic and/or lower crust affinity, mutual tectonic contact of which is overstepped by Westphalian conglomerates. Syn- and post-orogenic Variscan formations are represented by Lower Carboniferous flysch, Westphalian marine and continental, Permian molasse. Characteristic of this tectonic unit is the Upper Permian - Lower Scythian evaporite formation, which is continuously linked to Upper Scythian carbonate-siliciclastic sediments. The basement of the South Gemicum unit consists of low-grade metamorphosed Early Paleozoic flysch, which is covered with angular unconformity by continental Permian sediments, continuously replaced by lagoonal near-shore Lower Triassic sediments.

The nappe units of the Turnaicum and Silicicum mainly consist of Mesozoic sequences, only in a partly of the Turnaicum the Middle Carboniferous flysch formation is preserved at its base. After a stratigraphic hiatus this is covered by continental sediments with angular unconformity and by lagoonal - evaporite formations of Upper Permian age continuously evolved from them.

Depositional setting

Groundwater precipitations

Minerals forming by precipitation from groundwaters mainly occur as crusts or pedogenic nodules. They were associated with relatively little yielding (poor) regime of groundwaters under continental, semiarid climatic conditions. Calcite nodules and calcretes (often pink-coloured from the present Fe pigment) are known from Permian sediments in the Hronicum (Malužiná Formation), Northern Gemicum (Petrova hora and Novoveská Huta Formations) and Turnaicum (Brusník Formation). Distinct cyclic fluvial sediments, with intermittently developed discharge lakes in the flood plain, contain besides calcite nodules also Fe-dolomite concretions, testifying to slightly reductional conditions at the floor of shallow, stagnant reservoirs. In the Permian of the Hronicum also horizons of caliche or cohesive crusts (calcite, dolomite) are known, attaining several dcm to 1 m on an average, laterally linked to calcretes scattered in surrounding sandy and clayey sediments.

Continental sebkhas (endorheic basins)

Evaporite sediments belong here, which are formed by precipitation in closed basins, accumulation and evaporation of fluvial inundation waters in semiarid areas. This type of environment is represented by small gypsum lenticles established in upper parts of megacycles of the Permian sequence in the Hronicum (Ďurovič, 1971, Novotný & Badár, 1971). They usually contain clayey admixture associated with a variable amount of grains of aleuritic and sandy size. This type of continental evaporites is bordered by horizons of gypsum and/or carbonate sandstones.

Alkaline lakes

Sediments of alkaline lakes were interpreted in Permian sediments of the Northern and Southern Gemicum (Čurlík et al., 1984, Vozárová & Vozár, 1988). They are represented by horizontally laminated, fine grained sediments, originally claystones, aleurolites, less fine grained sandstones with carbonate cement and a high content of authigenic to anchimetamorphic albite. We suppose that albite formed by subsequent alteration of zeolites, which were linked genetically with decomposition of acid volcanoclastic material in highly alkalic environment of lakes. With these sediments horizons enriched in Ca and Ca-Mg carbonates are associated laterally, also with sediments having higher content of siliceous cement.

Paralic sebkhas and subtropical marine environments

They are evaporite sediments linked genetically with the environment of supratidal flat, connected with marine



environment spatially and in time, with separated lagoons, bays or shallower or deeper parts of shallow sea basins.

Upper Permian - Lower Scythian horizon: The largest accumulations of such evaporite sediments are preserved amidst Upper Permian - Lower Scythian sediments of the Northern Gemic (NG), Turnaic (T) and Silicic (S) units. All these occurrences of evaporites (NG - Novoveská Huta Formation, S and T - Perkupa Formation) belong to transgressive formations, reflecting the transgressive phase of salinity. In the Northern Gemicum and Turnaicum evaporite sediments occur amidst a sequence, which starts with continental red-beds and terminates with deposits of open sea. In the Silicicum unit the substratum of the evaporite formation on the territory of Slovakia is not documented. The main evaporite minerals are sulphates, associated with less amount of dolomite, which occurs underlying the whole evaporite formation or also at the base of partial cycles inside the evaporite formation. In the Northern Gemicum, besides that, in the frame of evaporite breccias halite and in mineralogical amounts also potassium salts - sylvite and carnallite are present (Ďurkovičová in Maheľ & Vozár 1973).

Two fundamental sedimentation models are characteristic of this sedimentation area: 1. Clastic facies of red-beds type prograding into arid sabkha-lagoonal and near-barrier environments, with intermittent connection to open sea; 2. Evaporite aride coasts linked to a mobile, highly subsidentially sinking basin, with well developed slope and basin facies.

Northern Gemicum: In this zone evaporite facies were established in mine workings (Rudňany, Poráč, Gretľa, Novoveská Huta, latest Markuška - Šafárka) and were attested in numerous boreholes in the areas of Spišská Nová Ves, Krompachy and Košická Belá. The variegated red-beds and evaporite sequences of the Northern Gemicum are part of the Novoveská Huta Formation. The age of the evaporite horizon was established as Upper Permian - Lower Triassic however, not later than the Smithian as proved on the basis of its occurrence underlying the zone with *Claraia claraia* already in the sense of older data from boreholes SM-1 and SM-2 (Maheľ & Vozár, 1971) and also confirmed again by newer stratigraphic data of Salaj (in Vozárová et al. 1993) from borehole RHV-25 on the basis of microfauna *Meandrosira cheni* (Ho) and *Mendrosira pusilla* (Ho). Characteristic of lithological development of the Novoveská Huta Formation is a clastic basal sequence, which is developed regionally. This horizon consisting of sediments of psephitic and psammitic grade (Strážany Member), is typical in relatively mature detritus with prevalence of quartz grains (60-70 % and in places also more) and relatively abundant intraformational clasts,

mainly of volcanics coming from the underlying, Petrova hora Formation. These areal sheet floods of alluvial sediments at profiles alternate with deposits of continental sabkha and/or alkalic lakes (last documented by horizons of carbonatic sandstones and aleurolites alternated with layers of albitolites).

Overlying basal clastic sediments evaporite horizons are developed, containing also wedges of red-beds type clastic continental sediments, indicating on the whole a marginal position of evaporite facies sedimentation in the zone, of paralic sabkha and lagoon. The precondition of great facial differentiation in the frame of evaporite sediments is the existence of an areally extensive supratidal flat and lagoon, which was gradually linked to marine environment. The layers of evaporites, several tens of metres thick (also in order of hundreds of metres and more as a consequence of tectonic boudinage) alternate with greengreyish or variegated clastic sediments. In evaporite sediments are in places well preserved sedimentary structures, mainly horizontal lamination, nodular structures, ripplemarks and an amount of structures proving redeposition of evaporite precipitates by gravity currents and slumps and/or cohesive flows similar to turbidity currents. A part of horizons of re-sedimented evaporites are beds of graded-bedded and massive anhydritearenites, pebbly anhydritestones (also described by Karoli 1993) and also halite breccia (described from borehole SM-1; Maheľ & Vozár, 1973).

Pebbly anhydritestones have matrix supported structure and most probably represent high density debris flow deposits. Thickness of beds most often attains 1 to 2 m, rarely more. The detritus in them consists of fragments of light- and dark-grey dolomites, grey dolomitic shales, green, grey, very scarcely red claystones and siltstones, rarely fine-grained sandstones and also fragments of fine-grained acid volcanoclastics. Clastic grains of psammitic grade are formed by quartz, feldspar and clastic micas. The size of psephitic grains varies from 2 to 35 mm, only a small part attains 50 mm to 70 mm. They are angular and/or subangular. The matrix is formed by grained anhydrite with admixture of originally clayey fraction, in which diagenetic new forms of albite, dolomite, scarcely of quartz are scattered.

Anhydritearenites are associated with pebbly anhydritestones and also non-evaporite sediments, mainly with dolomitic shales and clayey aleurolites. These form thin beds of massive, indistinctly horizontally laminated, rarely graded-bedded structures. The clasts of psammitic grade are concentrated in laminae or are of chaotic distribution within the bed, less often ordered graded positively.

Halite breccias are composed of greyishwhite or slightly pinkish halite, in which subangular, less angular fragments of greenishgrey claystones and shales are en-

closed. The fragments of shales are most often of ellipsoidal, oval shape. In horizons with content of halite are often marks of dissolution and reprecipitation. Halite breccias, however, may be considered as primary, with regard to the fact that at profiles they are alternating with laminae or thin beds of claystones. Mahel' & Vozár, (1973) mention the content of halite in breccias in the extent of 40 to 90 %. In fragments of claystones contents of sulphate and halite are mentioned in the extent of 10 to 30 % and carbonates up to 15 %. Ďurkovičová (in Mahel' & Vozár 1973) also identified in this horizon sylvite, in concentrations of 6,5 and 8,5 %.

Besides the above mentioned types of evaporite sediments thin layers of light-grey, crystalline anhydrites, in places with fine laminae of yellowishgrey dolomite are associated in these horizons. Dolomites, which in places occur with anhydrites are mostly fine-grained, of dolmicrite character, without fauna and with gypsum crystals locally only. Yellowishgrey fine-grained dolomites of cellular structure, with galls of greenishgrey or red shales, which are found in the upper part of and overlying the anhydrite horizon, were described at the new evaporite deposit Markušovce - Šafárka (Jančura & Šašvári, in this volume).

Besides primary evaporites several generations of epigenetic sulphates are present, which are a reflection of dissolution and mobilization of primary evaporite minerals as a consequence of post-sedimentary diagenetic to anchimetamorphic alterations and mainly of tectonic reworking of evaporite facies along a system of faults and/or subvertical tectonic zones (plastic deformation and polyphase dissolution and recrystallization in the system of circulating fluids).

Turnaicum and Silicicum: Upper Permian - Lower Scythian evaporites of the Turnaic and Silicium units are of equal lithological character. They were described under the uniform term Perkupa Formation (Mello et al., 1996) with the main occurrences in the Slovak Karst and northern Hungary in the Aggtelek Karst near the locality Perkupa (Kovács et al., 1989). In the Turnaic unit on the territory of Slovakia to this formation evaporites from borehole DRŽ-1 studied in detail lithologically by Karoli (in Mello et al. 1994), may be ranged. Underlying the classical Werfen Formation of the Silica nappe, evaporites are known from many boreholes in the area of Rožňava (G-1, G-1/2), Gemerská Ves (Š-7 to 49; VŠ-1), Bohúňovo (VB-20; SA-2 to 8; SA-12 to 16; VPS-4 to 12) and further (Bystrický & ORAVCOVÁ 1962; Dianiška et al., 1984 and others).

Primary facies of evaporites of the Perkupa Formation similarly as in the Northern Gemericum include clastic facies of evaporites - pebbly anhydritestones (described by Karoli, 1993 as anhydriterudites) and anhydritearenites. On the contrary to the Northern Gemeric

Novoveská Huta Formation, however, in pebbly anhydritestones among clasts, fragments of shales of violet and/or red colour, even fragments of sandstones are not found. Besides grey and greenishgrey claystones and aleurolites among fragments dark-grey to black dolomites, fine-laminated dolomites, in irregular horizons scattered fragments of acid volcanoclastics and in small amount fragments of fine-laminated anhydrites are present. The content of clasts in pebbly anhydritestones is not exceeding 40 %. Thick beds of these paraconglomerates have a massive and/or slightly graded-bedded structure. The roundness of clasts is mostly subangular. The matrix is anhydrite, highly gypsified.

In anhydritearenites clastic grains are formed by anhydrite, dolomite and dolomite shales. Grains of authigenic quartz and feldspars are scarce. The structure of anhydritearenites is massive or horizontally laminated. Lamination is caused by fine laminae of greenishgrey clays and/or yellow and yellowishgrey and black dolomites, alternating with thick layers of anhydritearenites. A part of evaporite horizons are layers of fine laminated sediments, in which laminae of anhydrite and light-coloured and dark dolomite are alternating.

Upper Scythian horizon (Röt): Evaporites of this stratigraphic range were recorded by borehole MGF-1 in the Malá Fatra Mts. (Vozárová & Vozár, 1986). The evaporite horizon is evolving gradually from a variegated, siliciclastic formation, characteristic of the Lower Scythian of the Tatric unit in the Western Carpathians (Lužná Formation). In the basal part (about 30 m) this consists of a horizon with cyclical alternation of fine-grained oligomict conglomerates, quartz arenites and subarkoses and/or wackes of adequate mineral composition. The middle part (40-50 m) is formed by a complex of thin- and medium-bedded (thicknesses 5-20 cm) light-violetishgrey and violet sandstones and shales, into which thin interbeds of oligomict conglomerates are wedging in. From structural features ripplemarks, horizontal lamination, load casts, bioturbation structures and erosional wash-outs at the base of coarse clastic layers are typical in these sediments. The associated shales contain nodules and concretions of carbonates.

In the upper part of the Lužná Formation in borehole MGF-1 layers of marly shales and intramicrites were established, in which a poorly preserved foraminifer microfauna was found, determined by dr. Salaj as the species *Glomospirella* sp. With regard to the small size they are generally considered by the author as Lower Triassic. The layers of intramicrite and dolosparite alternate first with violet and greenishgrey shales and aleurolites and in overlying direction are gradually replaced by a horizon of anhydrite breccias (thickness 30 m). The breccias with supporting matrix structure contain fragments of dolomite and claystones, which are cemented by anhy-

drite, in places secondary-gypsified anhydrite matrix. Besides that small amounts of baryte and new forms of quartz and albite were established. Overlying the anhydrite breccias, a horizon of black shales with interbeds of anhydrite, gypsum and argillaceous dolomite occur. The remaining part of the evaporite formation is reduced tectonically at the borehole profile.

The similar sedimentary environment is assumed for the Upper Scythian anhydrites of the Zemplincium (borehole near Ladmovce vill.).

Isotopic composition of anhydrites

Isotopic composition of O and S was studied in anhydrites of the Turnaic unit in borehole DRŽ-1 and particularly only isotopic composition of S in anhydrites of the Northern Gemeric, Turnaic and Silicic units as well as in Upper Scythian evaporites in the Tatric unit in the Malá Fatra Mts. (Fig. 3).

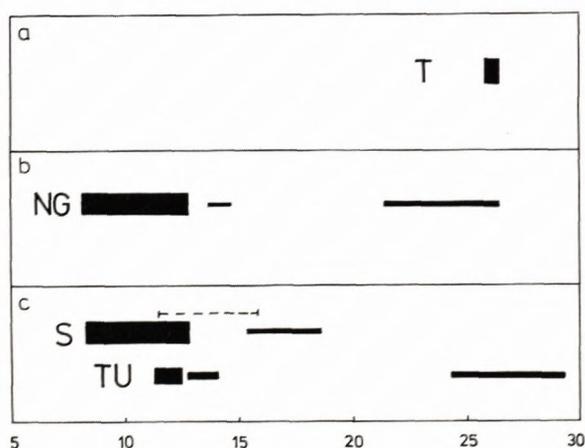


Fig. 3 Spread of isotope sulphur data for anhydrite from the Upper Scythian of the Tatric Unit (a.), the Upper Permian-Lower Scythian of the Northern Gemeric unit (b.) and the Turnaic and Silicic units (c.). Thickness of lines corresponds to frequency of data. Dashed line (diagram a.) belongs to isotope sulphur data for pyrite.

The results of isotopic analyses of S in the Turnaic unit (borehole DRŽ-1; Ďurkovičová & Repčok in Mello et al., 1994) point to the occurrence of two groups of anhydrites, with different content of S heavy isotope. The majority of samples have $\delta^{34}\text{S}$ values within the range of 11.4 to 12.3 ‰ (from the total amount of 19 samples 11). In four samples somewhat higher values were recorded - within the range of 12.8 and 14.1 $\delta^{34}\text{S}$ ‰. Extremely high values were established in further four samples - within the range of 24.4 to 29.3 $\delta^{34}\text{S}$ ‰. S isotopic analysis document the marine origin of evaporites, the contents of heavy sulphur

isotope correspond to composition of marine evaporites from the time section of the Upper Permian - lowermost Triassic (NIELSEN 1965, Holser et al., 1977, Claypool et al., 1980). Ďurkovičová & Repčok (l.c.) interpreted samples with extremely high content of sulphur heavy isotope in two ways: they either correspond to conditions of precipitation in a stratigraphically younger period (Upper Scythian = Röt) and were tectonically folded in the whole complex or their isotopic composition was influenced by activity of sulphate-reducing bacteria. We tend to the latter interpretation, because horizons of these anhydrites are not only reduced in thickness, but also secondary contain magnesite and a high amount of organic substance. Isotopic composition of sulphate ion oxygen was established at the borehole DRŽ-1 profile only in 7 samples and varies within the range of 10.6 to 14.9 ‰ $\delta^{18}\text{O}$, indicating considerable variability. All these values, however, correspond to or are little different from the diapason Upper Permian - Lower Triassic at the age curve of oxygen isotopic composition of marine evaporites (Claypool et al. 1980).

In the Silicic unit, in the area of Strelnice in the Slovak Karst, Kantor (1972) established S isotopic composition from anhydrites. Isotopic composition of S from the bulk of anhydrites (26 samples) in borehole G-26 is relatively homogeneous. It varies within the range of $\delta^{34}\text{S}$ from 8.3 to 12.8 ‰, corresponding to the values mentioned for Upper Permian marine evaporites. Only three samples escape from the mentioned range ($\delta^{34}\text{S}$ = 15.5 and 18.6 ‰). Kantor (l.c.) interprets this enrichment of anhydrites in sulphur heavy isotope by the activity of sulphate-reducing bacteria. The author confirmed his statement by data of sulphur isotopes composition from associated pyrites, in which $\delta^{34}\text{S}$ values varied within the range of 11.5 to 15.9 ‰ (Fig. 3).

Most isotope analyses of S were performed at anhydrite occurrences in the Northern Gemeric (worked out comprehensively by Kantor et al., 1982). From borehole SM-1 13 samples were elaborated, with isotope values $\delta^{34}\text{S}$ varying within the range of 10.1 to 12.7 ‰. These values, highly enriched in light sulphur, are comparable with data mentioned from the Zechstein in Western Europe. In borehole SM-2, situated in the equal area (loc. Smižany), from 21 samples the majority are also showing low contents of heavy sulphur - $\delta^{34}\text{S}$ within the range of 9.1 to 12.7 ‰. Four samples contained higher $\delta^{34}\text{S}$ values, within the range of 14.3 to 14.7 ‰. Even 7 samples from the given complex, however, displayed extreme enrichment in isotopes of heavy sulphur, with $\delta^{34}\text{S}$ values within the range of 21.4 to 26.6 ‰. Kantor compared these anhydrites with extreme contents of heavy sulphur with Upper Scythian marine evaporites (saline Röt in western Europe). This interpretation corresponds to the geological situation of Mahel' & Vozár

(1971, 1973), according to which the evaporite horizon occurs in the frame of a complicated fold/upthrust structure, in the core of which Middle Triassic carbonates are preserved. In the deposit area of Tolstein and Grétla, south of Spišská Nová Ves, 14 samples from mine workings and further 18 samples from boreholes in the area of the locality Teplička (borehole Š-866, SB-4) were analysed. From 14 samples coming from mine working in 8 samples $\delta^{34}\text{S}$ contents varied within the range of 10.1 to 11.4 ‰, with values lower in two samples (8.7 and 7.8 ‰) and, vice versa, higher in further two samples (13.7 and 14.3 ‰). Only in one layer extremely high contents of heavy sulphur were found ($\delta^{34}\text{S} = 26.1$ ‰). Thus the overwhelming majority of samples are characterized by low contents of heavy sulphur isotope, what is typical of marine evaporites of Upper Permian age. The values around 13 to 14 ‰ $\delta^{34}\text{S}$ most likely correspond to younger, Lower Triassic horizons of the evaporite formation. The sample with extreme contents of heavy sulphur isotope, according to data of Kantor (l.c.), was taken in close proximity of tectonic borders of the deposit, what could be influenced by this fact. All other anhydrite samples, obtained from the mentioned boreholes, have $\delta^{34}\text{S}$ contents in the extent of 9.2 to 10.7 ‰ (11 samples) or 9.6 to 12.5 ‰ (7 samples), fully corresponding to marine evaporites of Upper Permian/Lower Scythian age. Similarly also $\delta^{34}\text{S}$ values from anhydrites obtained from boreholes in the area of Rudňany (borehole RG-3) and Biele vody (borehole SB-10) are varying in this extent. From 11 samples $\delta^{34}\text{S}$ values in the extent of 8.1 to 12.8 ‰ were obtained.

From Upper Scythian evaporites of the envelope group in the Malá Fatra Mts. (borehole MFG-1; Kantor, 1988) 3 samples were analysed, which are characterized by relatively stable isotope composition. Values of $\delta^{34}\text{S}$ are varying within the range of 25.82 to 26.33 ‰ and correspond to the grades of enrichment in heavy sulphur by marine sulphate from the time section of the upper part of the Lower Triassic, in the sense of data according to the time scale of Claypool et al. (1980) as well as data from the germanic Röt (Nielsen 1965) and from some localities in Austria (Pak, 1974; Klaus & Pak, 1974).

Discussion and conclusion

In the Central and Inner Western Carpathians, in the Upper Permian - Lower Triassic interval evaporite sediments of different genesis, as well as chemical and isotope composition and of course, also different as to the amount of occurrence and their economic importance occur. In the Central Western Carpathians only evaporites of non-marine origin formed in the Upper Permian and Lower Scythian, either as groundwater precipitates or as deposits of endorheic basins and alkaline lakes.

In equal time interval marine evaporites originated in Inner Western Carpathians. From the point of view of the lithological character and spatial linking to the associated non-evaporite sequences in lateral as well as vertical direction a genesis in two subenvironments may be taken into consideration.

i) The evaporites, which originated in separated lagoons or marginal parts of the sea and were associated with deposits of paralic sabkha or in the fore shore part with deposits of semiarid playa and alluvial fans on the one hand and with open sea on the other hand. A representative of this environment are evaporite sediments of the Northern Gemicum. The proximity of semiarid continental flat is well documented by interlayers of red beds type sediments or redeposited fragments of variegated shales, sandstones or ash rhyolite tuffs directly in evaporite clastic sediments. The prevalence of redeposited evaporites (anhydritearenites, pebbly anhydritearenites), their structural features and distinct cyclity or intercalations of continental detritus document considerable synsedimentary tectonic activity and repeated subsidence of the sedimentation basin. Laminated and graded anhydritearenites have sedimentary structures characteristic of transport in turbidity flows and debris flow, structureless, thick beds deposited earliest as grain flow (so interpreted by Karoli, 1993) or fluxoturbidites. The matrix supported conglomerates correspond to deposits of high-density debris flow, which in parts with distinct content of continental detritus were influenced by storm activity. The existence of these sediments is conditioned by a bathymetrically considerably dissected, also generally shallow-water, unequally subsiding marine sedimentation basin. Bathymetric inequality resulted from tectonic breaking of sedimentation basin floor by faults of different activity in space and time. Alternation of relatively shallower and deeper parts is also documented by occurrences of halite-claystone breccias. We suppose that they originated in an area near to the depocentre, from highly saturated, subtropical salt brines in relatively calm periods, interrupted by rushes of rain freshwater, as represented by interbeds of claystones and also admixture of clay in halite. Precipitation of a small amount of sylvite associated sporadically with halite could have been brought forth by overlapping of salt brines with rain waters, making possible oxidation of organic compounds, which reduce solubility of sylvite in salt brine (Steinike, 1962). In times of higher tectonic activity claystone-halite sediments were redeposited into relatively deeper parts of the depocentre. The original admixture of clay in places gives halite a grey colour. A part of salt breccias is linked genetically to post-depositional leaching and consequently to plastic deformation and pressing of claystone material in the halite matrix (evaporite solution breccia). The marginal deposition,

under conditions of paralic sabkha, is documented by nodular anhydrites.

ii) Evaporites, which originated in marine basin with wide shelf of extensive surface. Evaporite sequences of the Turňa and Silica nappe units belong here. According to Karolí (1993) these sediments may be interpreted as a result of intense precipitation on platform and their subsequent destruction at water level and contingent re-deposition into relatively deeper and in places more reductional parts of the original basin. The sediments have sedimentary structures indicating redeposition in an environment of thin non-cohesive currents as also testified by missing or only little represented clay in anhydrite matrix. When compared with the preceding type, the continental source area provided essentially less amount of siliciclastic detritus, wedges of continental red-beds are completely missing.

Upper Scythian evaporites belong to marine evaporites of the first type, originating at a coast dissected tectonically, with hypersaline lagoon, linked to paralic sabkha in direction to the continent.

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