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-SO$_4$ 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 SO$_4$ 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
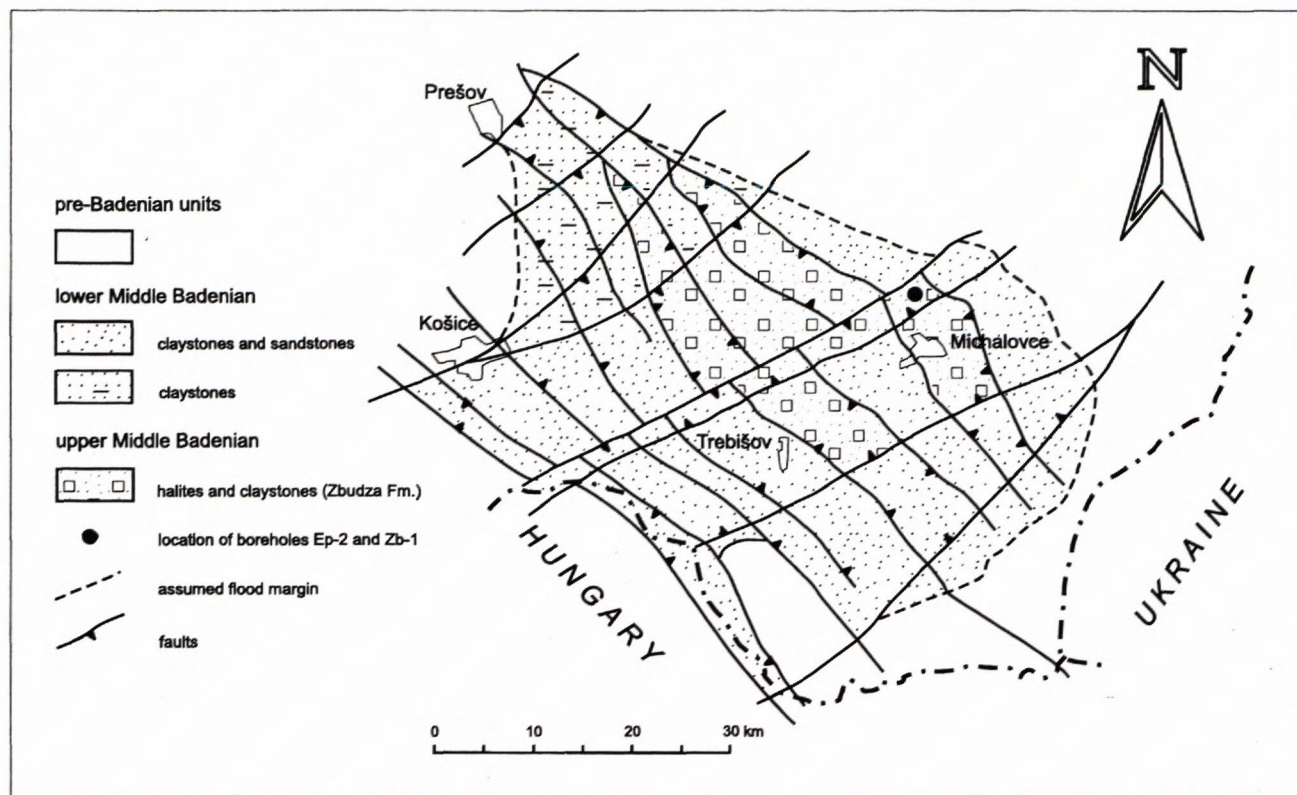
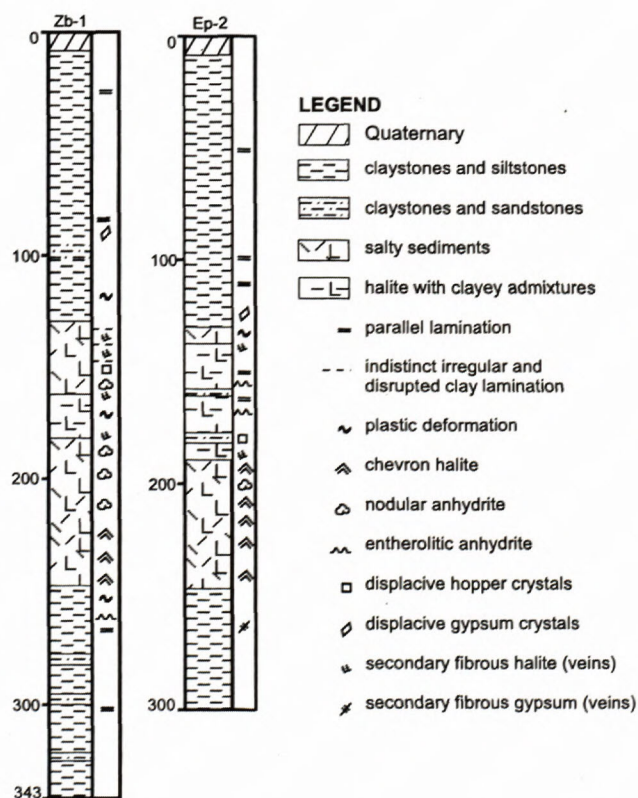Fig. 1 Paleogeologic map of Lower and Middle Badenian

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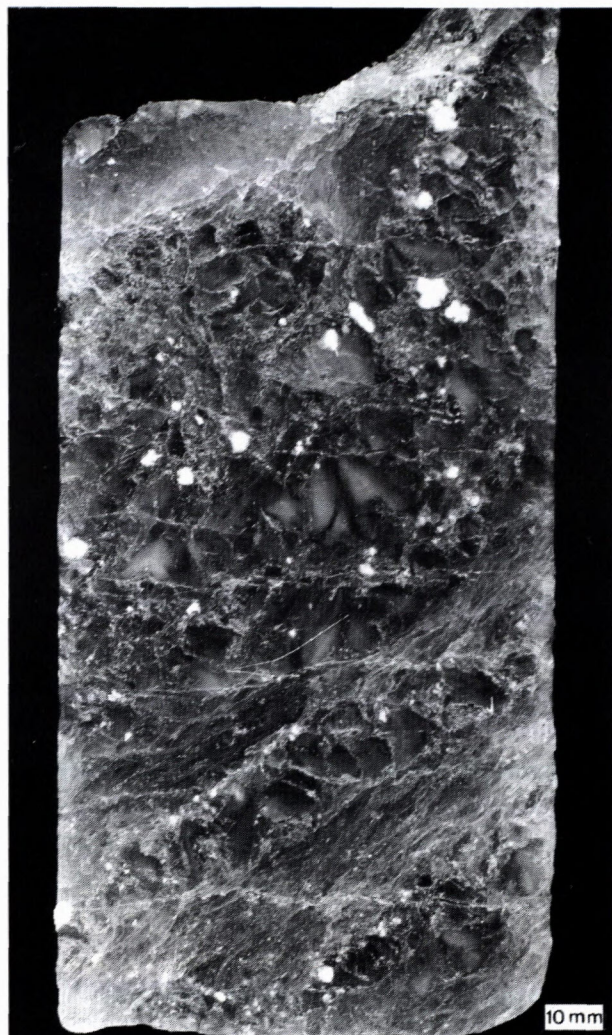
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Fig. 3 Fabric of the rock salt, Ep-2, sample No. 66

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

Fig. 5 Asymmetric chevron crystal

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 by 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.
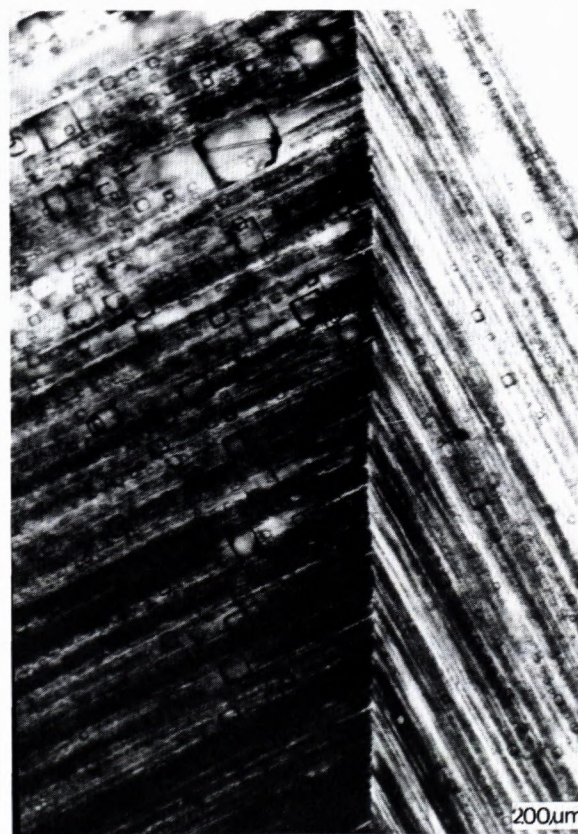
Fluid inclusions in halite

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-
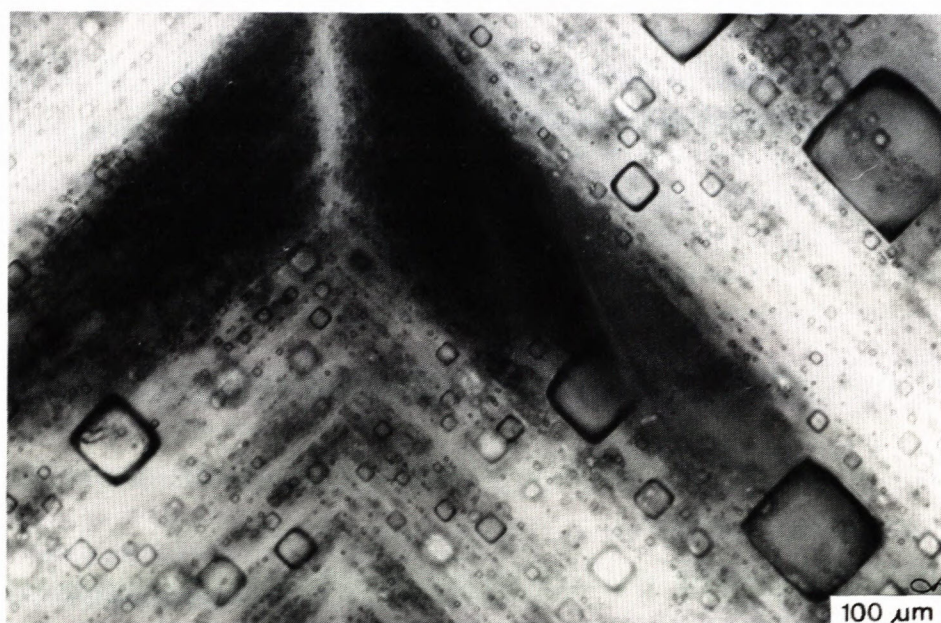

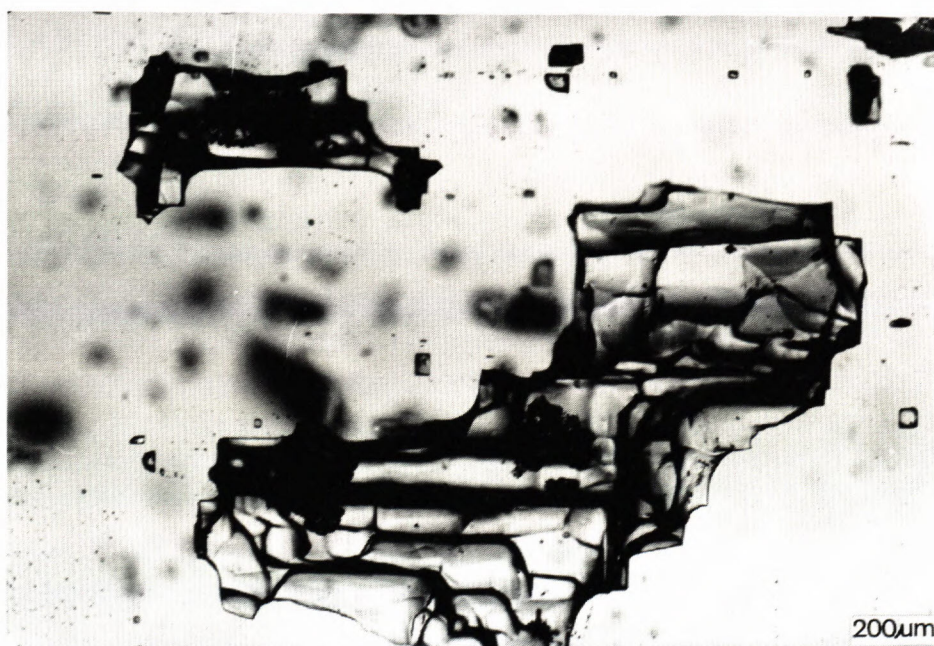*Fig. 6 Fragment of chevron crystal with large one-phase fluid inclusions*

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

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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 11.0-16.7g/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:

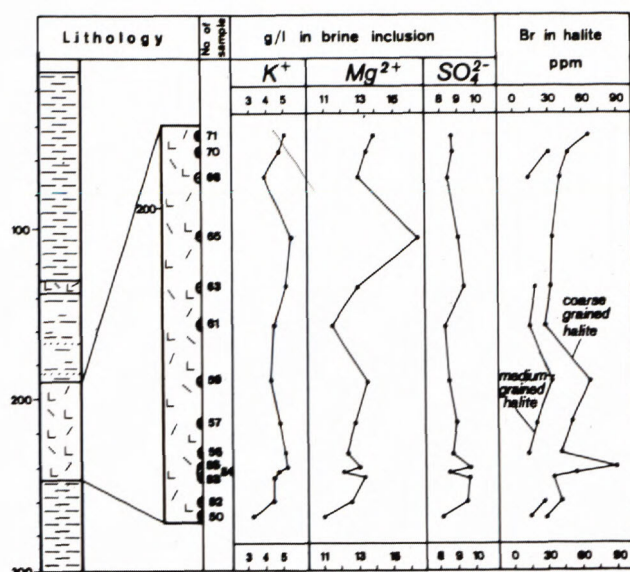|			
halite	3.3	15.5	21.0
sylvite	33.8	75.7	79.1

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.
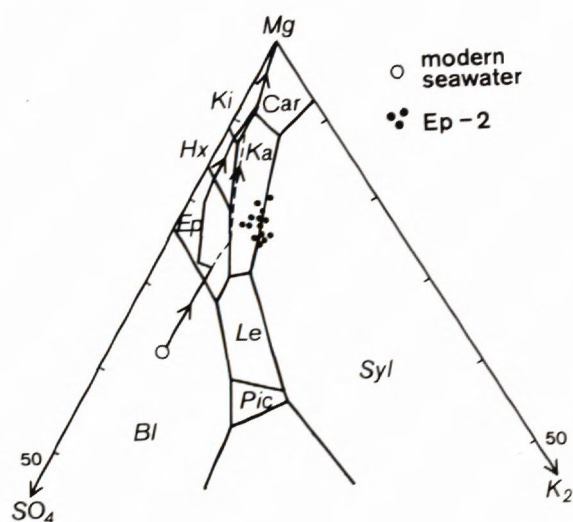

Fig. 9. Analyses of inclusion brines in primary halite from borehole Ep-2 plotted on a Jänecke projection of the quinary system $Na-K-Mg-SO_4-Cl-H_2O$ saturated with respect to halite at 25^oC (Eugster et al., 1980). The stability fields of Bl, bloedite; Car, carnallite; Ep, epsomite; Hx, hexahydrite; 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 μm. 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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