

## Chemical composition and origin of brines in the Badenian evaporite basin of the Carpathian Foredeep: fluid inclusion data from Wieliczka (Poland).

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**Abstract.** The chemical composition of brine inclusions in chevron halite from all stratified parts of the Wieliczka deposit (Badenian salt formation, Polish Carpathian Foredeep basin) has been determined for the first time. This deposit is unique considering the amount, sizes, and preservation of chevron structures in halite crystals. Some of these crystals reach 15 cm. Inclusion sizes range from fractions of to 600  $\mu\text{m}$ . Cubic, one-phase fluid inclusions are the most common. The data show that brines belonged to Na-K-Mg-Cl-SO<sub>4</sub> type. Seawater was the main source of salt formation, and its composition was close to modern water. The sedimentation occurred in relatively shallow basin by evaporation, and brine concentration did not proceed beyond the initial and middle stages of halite precipitation.

**Key words:** Badenian, halite, fluid inclusion, chevron, brines, ultramicrochemical analysis

### Introduction

Fluid inclusions in halite are a unique source of information about the composition of ancient salt-forming basins, conditions of sedimentation, and recrystallization of evaporite deposits (Petrichenko, 1973). For determination of sedimentary conditions, chevron and hopper crystals are used, as their origin is well studied in modern and ancient salts (Valiashko, 1951; Dellwig, 1955; Røedder, 1984; Raup, 1970). The bromine content in halite is also often used as an important criterion for salt genesis elucidation (Valiashko, 1962; Herrmann, 1972). The investigation of fluid inclusions in single samples of halite from the Wieliczka mine has been done earlier by Petrichenko (1988), and the bromine distribution in halite was studied by Garlicki & Wiewiórka (1981). These studies indicated the marine genesis of salt deposit, but until now, the changes in the composition and concentration of brine inclusions in halite in a section of the salt series have been not studied yet.

### Geological setting and lithology

The evaporite deposits (rock salt, gypsum and anhydrite) that precipitated at Wieliczka in the middle Miocene (Badenian) are the part of a long and narrow band stretching along the border of Carpathians from outskirts of Kraków through Ukraine to Romania (Fig. 1). In

Ukraine the analogues of Wieliczka deposits are the deposits of Tyras Suite (Petrychenko *et al.*, 1994).

The sequence of Badenian salt precipitation in Wieliczka remains uncertain yet because of the complicated and unusual geological structure of the deposit which results from facies changes within the basin, subaqueous flows and creepings that have changed the initial sequence of layers (Kolasa & Ślęczka, 1985), and strong tectonic movements in the Carpathians during Late Miocene. As the Carpathian nappes moved from the south, the salt deposits were folded and displaced to the north. Such a tectonic rebuilding caused the conglomeration of salt rocks in a relatively narrow band, the maximum width of which in the Wieliczka region was about 1500 m. The deposit has two parts (Fig. 2). In the lower, bedded part the salt rocks are layered and form the elongated structures similar to scales and asymmetrical folds (Fig. 3). In the upper part (called boulder) the clayey-salt deposits are developed that include the boulders and blocks of rock salt (Gaweł, 1962). The boulder sizes are different and range from 1 m<sup>3</sup> to giant blocks of volume about 100,000 m<sup>3</sup>. All lithological types of salt are shown in Fig. 4.

The lowest horizon of the deposit contains the oldest salts. At this level the strongest changes in formation of salts are characteristic. The thickness of the oldest salts ranges from 2 to 20 m, and in average is about 10 m. They consist of several layers of fine- and medium-grain

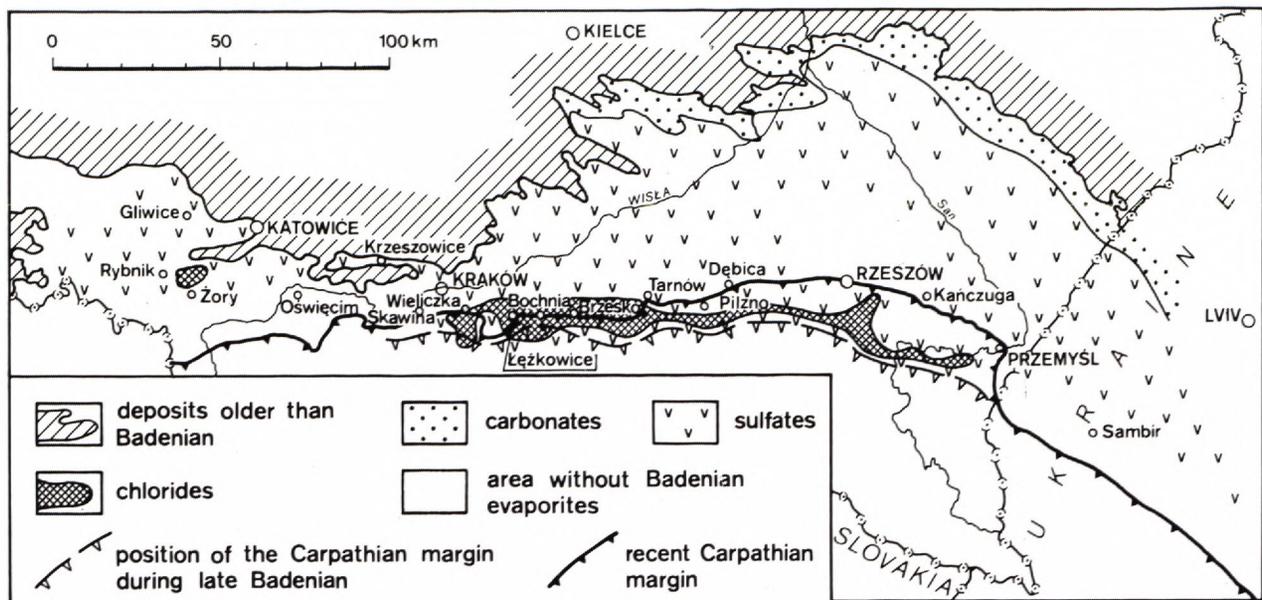


Fig. 1. Distribution of the Upper Badenian evaporites in the Carpathian Foredeep (after Garlicki, 1979).

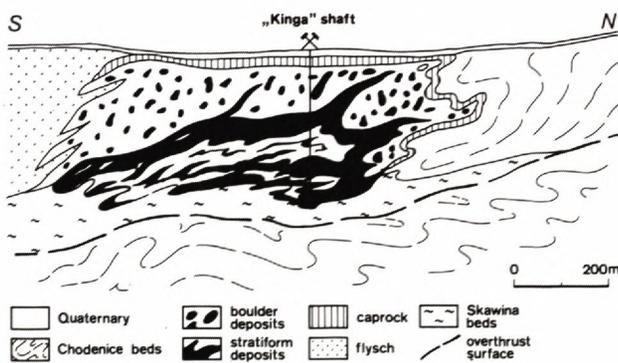


Fig. 2. Transverse cross-section through the Wieliczka salt deposit" (after Poborski & Skoczylas-Ciszewska, 1963, modified).

salt and coarse-grain salt that appear in the roof of the horizon (Wiewiórka, 1988). The salt is relatively clean and contains about 90-95% of NaCl (Pawlikowski, 1975). The oldest salt has been compared to the spiza salt (see below). Directly over the oldest salt, a layer of barren rocks occurs. It consists of sandstones, siltstones and anhydrite mudstones. In the literature it is called "undersalt sandstone" (Gawel, 1962), as it is supposed that sedimentary salts precipitated afterwards. In detail it is described by Bukowski (1997).

Above, a unit of bedded green salt occurs. The unit consists of 4-5 layers of rock salt which are separated by layers of mudstones with anhydrite. The average thickness of salt layers varies from 0.5 to 3 m. The maximum thickness of intercalated layers is 1.0 m. The salt is coarsely crystalline and clayey. The crystal sizes reach

several cm in length. The NaCl content is 80%. The shaft salt continues the sedimentary rhythm of green salt, and is separated from it by a thin layer of terrigenous rock that forms the homogeneous horizon with a thickness of 1.2-1.8 m throughout the entire deposit. The shaft salt is medium-grained, light-yellow with bitumen admixture, and usually is very clean.

The next complex of so-called "spiza salt" is the most widespread in the deposit. This salt is fine- and medium grained, the NaCl content is 90%. In addition, a very clean salt type (with the NaCl content of about 99%) occurs (so-called eagle or royal salt). The spiza salt is typically bedded and laminated, with clay layers delineating the beds and laminae. Inside the complex the changes in lithology and structure particularities of salts are noticed. The sizes of halite grains as well as the contents of sand, clay and charred plant residue vary. Several meters above the layer base, a unit of terrigenous rocks, called "central boundary", is developed, and it subdivides the complex into the lower and upper spiza salt. In the upper spiza salt the coarse crystalline type of salt (ocellar salt) is present. Near the top a gradual increase of sand content is noticed with a change of the rock character into sandstone with salt cement. The whole spiza salt complex is about 20-30 m thick.

In the 10-meter section of overlying mudstones and siltstones with anhydrite the content of sulfates decreases upwards to zero (Wiewiórka, 1988). These rocks terminate the salt sequence of the bedded part section.

The deposits of the boulder part have been identified as a facies variety of bedded salts (Poborski & Skoczylas-Ciszewska, 1963; Garlicki, 1979), precipitated in a more shallow evaporite basin situated closer to the Car-



Fig. 3. Salt Mine Wieliczka. Stratiform deposit - fold of spiza salt, in an unnamed chamber near Karolina gallery, 2nd level.

pathian border (Bukowski, 1994). These deposits were dislocated by folding and flow and individual boulders were mixed with barren rocks. On the whole, the salt of the boulder part may be subdivided into two main types (Szybist, 1975): green microlayered salt and coarse crystalline salt. The microlayered green salt is represented by fine-to-medium and coarse crystalline varieties. The rocks are composed mainly of crushed chevron crystals which are less than several cm long. The banding of salt is formed by mostly discontinuous layers of clay. This salt contains only about 5% of foreign admixtures. It is represented by isolated boulders of initial thickness up to 20 m (Wiewiórka, 1988).

The stained-glass window salt is coarse crystalline salt with individual crystal sizes of several cm. Separate boulders of stained-glass window salt consist of halite clasts of different sizes (max. about 10 cm) with chevron structures, anhydrite nodules, and unzoned halite grains. Between individual grains clay occurs forming the typical mosaic structure that gives the name to the rock.

In addition, there are two other salt varieties in subordinate amounts in the boulder deposit: banded salt and dolomitic salt (Prochazka & Wala, 1959). They form small boulders of average size of 2-3 m. The above mentioned salts are overlain by zuber or marl clays with many grains and crystals of halite, that are situated disorderly,

and also by dark-gray and black clays and marly mudstones. These zuber often contain cracks filled by fibrous halite and gypsum.

#### Analytical methods

The chemical composition of individual brine inclusions has been determined by means of ultramicrochemical analysis (Petrichenko, 1973). This method allows the determination of  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$  concentrations. Minimal size of inclusions is 40  $\mu m$ . We have determined the contents of  $K^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  in the inclusions from halite of the Wieliczka deposit. The content of other major ions:  $Na^+$  and  $Cl^-$ , and the general concentration of brines of this chemical type may be calculated by correlation with results of evaporation of modern seawater (Valiashko, 1962), as the brine inclusions are saturated in respect to NaCl. The error of determination of each ion content after 2-3 parallel analyses does not exceed 17%.

#### Fluid inclusions in halite

The Wieliczka deposit is unique from the point of view of the number and size of chevron crystals of halite. In many layers of rock salt they are well seen in large salt

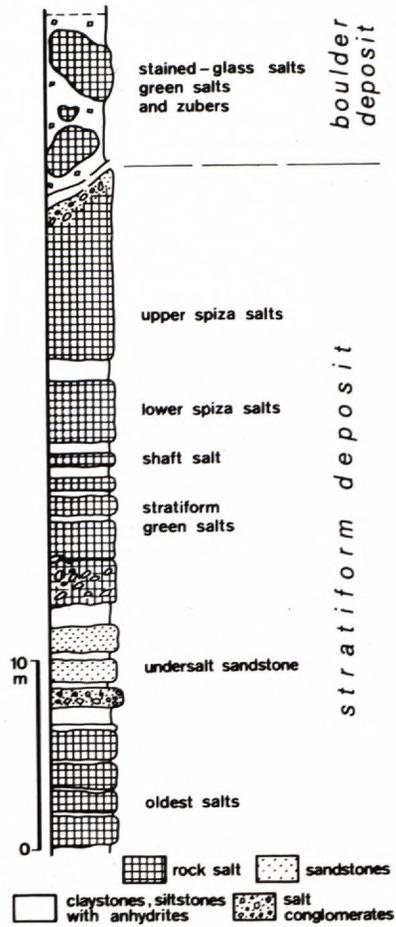


Fig. 4. Lithostratigraphic profile of the salt deposits at Wieliczka.

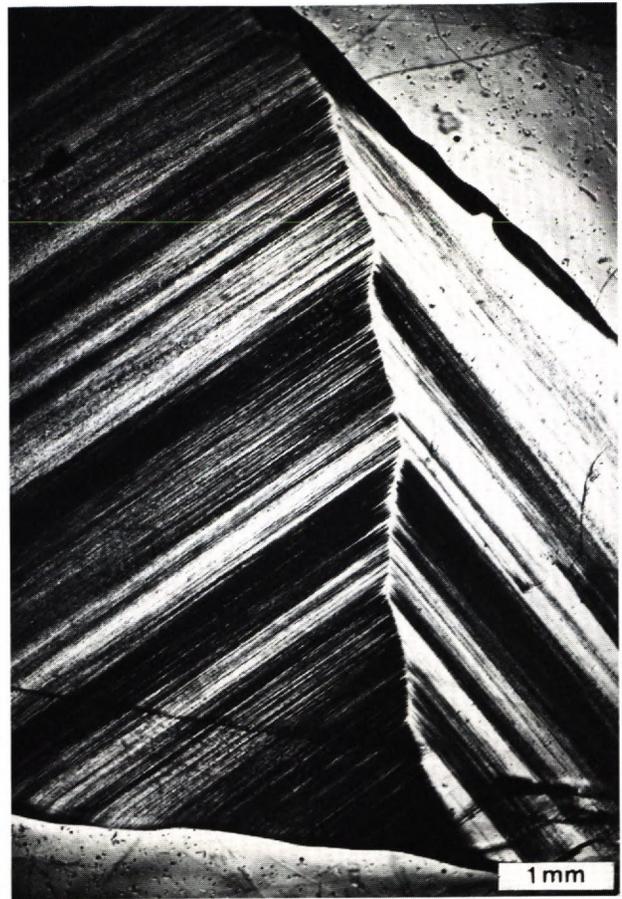


Fig. 5. Zonation (with elements of rhythms), formed by minute fluid inclusions.

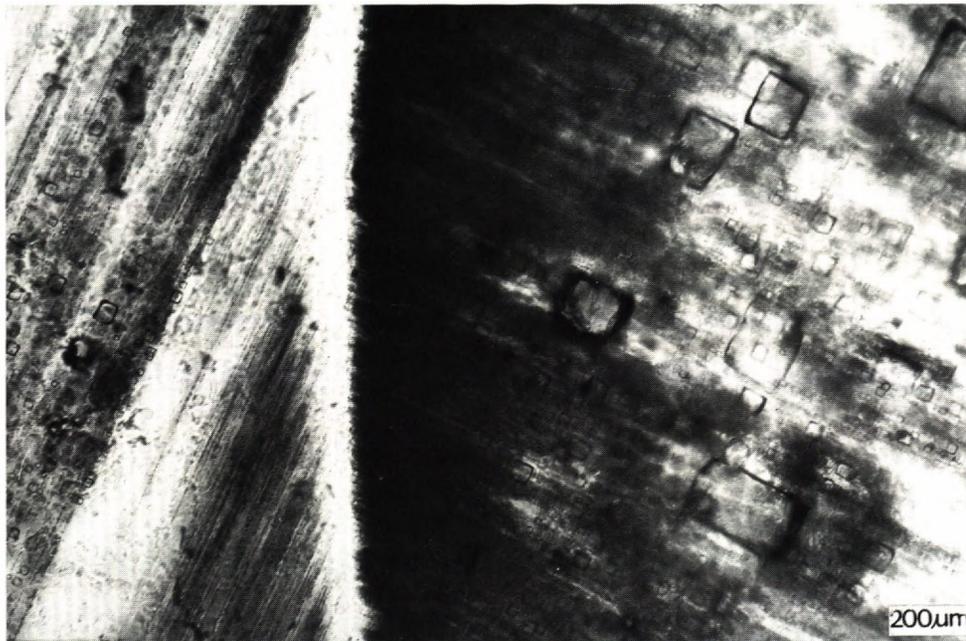


Fig. 6. Asymmetric construction of chevron halite. In right part of structure large fluid inclusions are present.

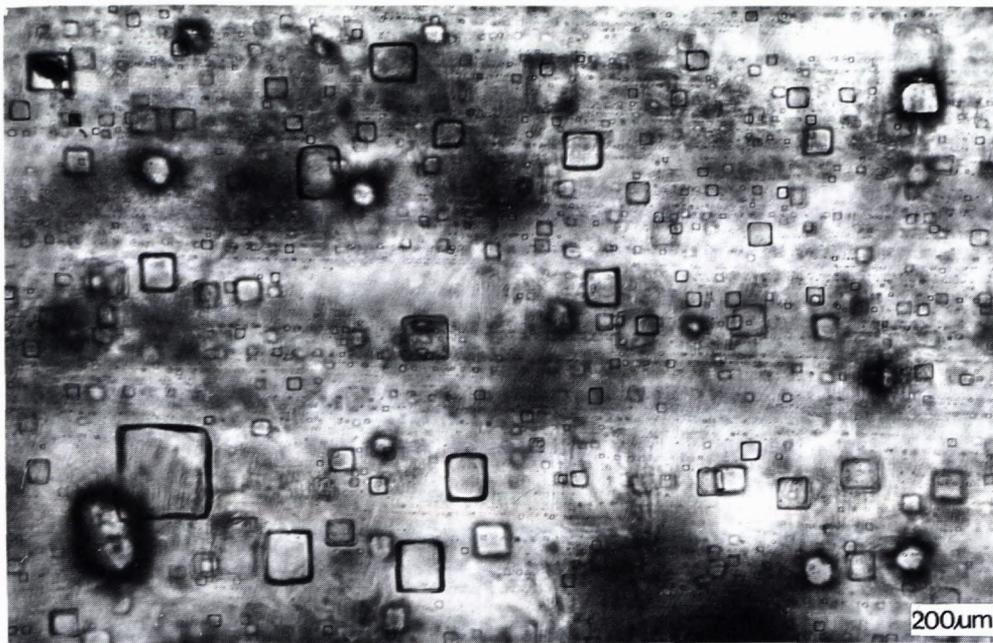


Fig. 7. Fragment of zonal halite with relatively large one-phase fluid inclusions

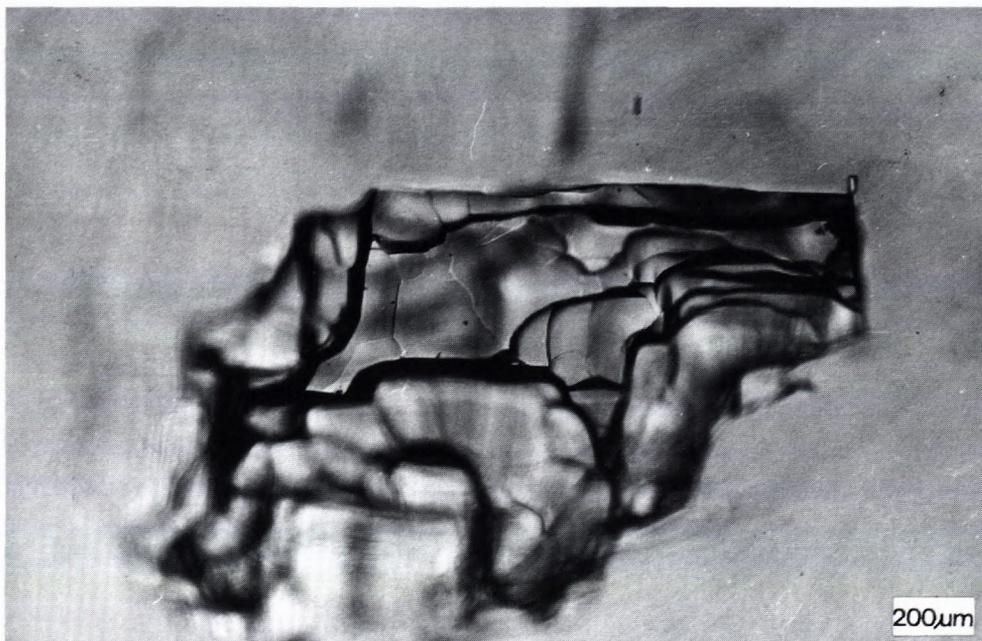


Fig. 8. The structure of the walls of a large fluid inclusion with irregular shape in transparent halite.

crystals, and in layers of green and stained-glass window rock salt their sizes sometimes reach 15 cm. Individual chevron crystals differ one from another by character of zonation and by inclusion sizes. There is a zonation with rhythmic elements, formed by minute inclusions (Fig. 5). Also crystals with asymmetric structure of chevron are present (Fig. 6) that is caused by different amount of inclusions, located on both sides of zonation axis. This asymmetric structure is a result of differentiated growth of two neighboring sides of halite crystal.

Inclusions in chevron halite are, as a rule, one-phase fluid and cubic or close to cubic in shape (Fig. 7). Their sizes range widely from fractions of to 600 μm. In some inclusions the terrigenous parts or elongated anhydrite crystals are noticed. In transparent halite that does not contain chevrons at all or only rare chevron relics, single fluid inclusions, that are arranged without any regularity, are present. Sometimes they reach giant sizes (up to 2-4 mm across), and have irregular shape and typical step structure of inner walls (Fig. 8). Their formation, appar-

ently, is related to crystallization and recrystallization of chevron crystals at postsedimentary stages of deposit development.

For chemical analyses the inclusions from the inner parts of chevron crystals of halite have been used.

### Results of analyses and conclusions

The results of analyses are shown in Table 1 and in Fig. 9. The location of points of brine compositions on the Jänecke diagram at 25°C is shown in Fig. 10.

Table 1. Content of ions in brine inclusions in the Wieliczka halite. In brackets the number of analyses is indicated.

Number of sample	Content of ions [g/l]		
	K <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
105	6.1 (3)	17.9 (2)	13.9 (3)
106	6.0 (3)	17.7 (3)	10.7 (2)
107	5.5 (2)	17.8 (3)	10.3 (2)
16	6.5 (3)	19.0 (2)	12.0 (2)
120	6.0 (3)	20.0 (2)	10.1 (2)
118	7.7 (2)	19.6 (2)	12.2 (2)
117	7.3 (4)	19.9 (2)	10.2 (3)
98	7.5 (7)	18.7 (2)	10.3 (3)
100	7.5 (6)	18.7 (2)	11.2 (3)
99	5.5 (3)	18.2 (2)	11.1 (3)
97	4.3 (2)	16.5 (2)	10.6 (2)
6	5.2 (3)	17.7 (2)	12.8 (2)
87	5.2 (2)	18.8 (2)	11.4 (2)
91	7.4 (4)	22.3 (2)	11.4 (2)
89	7.3 (2)	22.5 (3)	12.4 (3)
12	5.2 (7)	18.8 (2)	11.6 (3)
10	5.6 (4)	20.0 (3)	12.4 (3)
9	4.7 (3)	20.3 (2)	11.1 (3)
8	4.5 (3)	18.9 (2)	12.1 (3)
20	4.9(3)	17.0(3)	13.2(4)

Recent marine water concentrated to the beginning of:

- halite precipitation	3.3	15.5	1.0
- sylvite precipitation	33.8	75.7	79.1

The obtained data show that brines belonged to Na-K-Mg-Cl-SO<sub>4</sub> type. The ratios of major ions in the Badenian brine are close to those in modern sea water evaporated to the initial or middle stages of halite precipitation (see Table 1). The bromine content (67-20 ppm) in halite from Wieliczka mine (Garlicki & Wiewiórka, 1981) also indicates the marine source of brines and a relatively low grade of their evaporation. Significant fluctuations in composition and concentration of brines in the vertical profile of salt deposit are not observed. K content is slightly increased and SO<sub>4</sub> content is decreased in comparison to modern seawater evaporated to the corresponding stage. The brines of similar composition and concentration are typical, on the whole, for the Badenian salt-forming

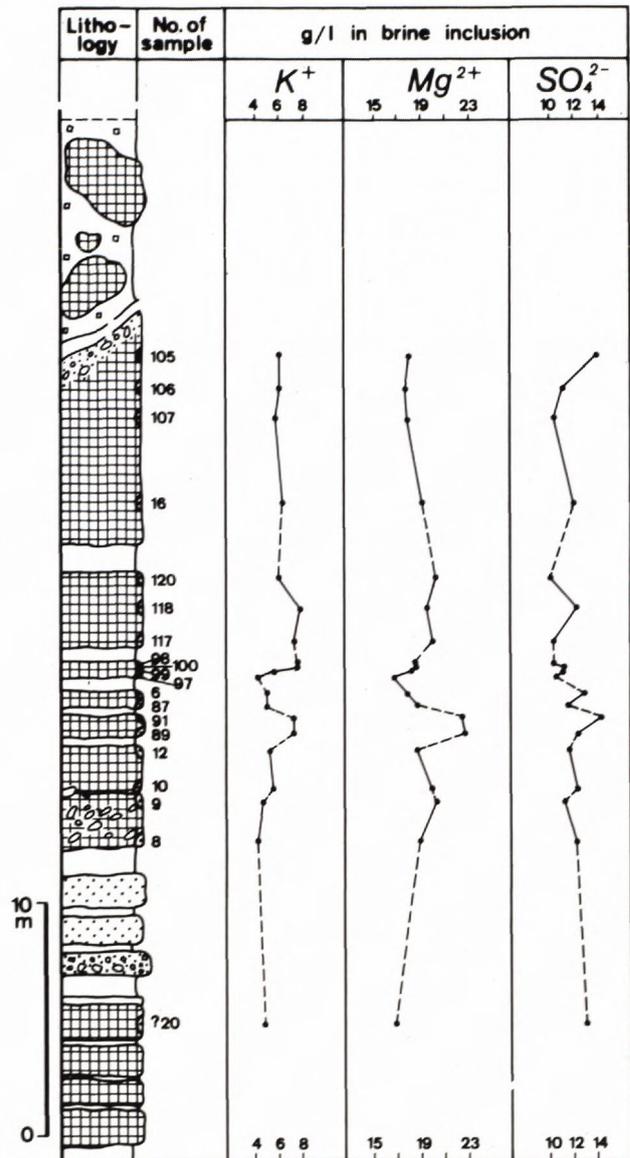


Fig. 9. The changes of K<sup>+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> content in brine inclusions in sedimentary halite. See Fig. 4 for explanation.

basins of the Carpathian region (Petrichenko, 1988; Kovalevich, 1990; Shaidetska, 1971; Poberegsky, 1991). The increased content of K in brines might be caused by a partial dissolution of earlier-precipitated potash salts of the lower salt-bearing formation of the Carpathian Foredeep. The reason of decreased content of SO<sub>4</sub>-ion, probably, was the inflow of large amounts of surface water from the continent.

The presence of many halite chevron crystals, including very large crystals with rhythmic zonation, testifies to halite crystallization on the basin bottom due to evaporation, and a relatively shallow basin depth. Taking into account the low grade of brine evaporation, the probability of potash resources in that region may be estimated as very low.

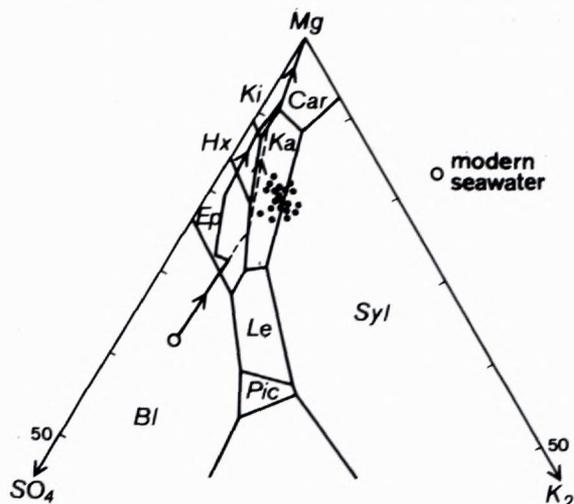


Fig. 10. Analyses of brine inclusions from Wieliczka halite plotted on the Jänecke projection of the quinary system  $\text{Na-K-Mg-SO}_4\text{-Cl-H}_2\text{O}$  saturated with respect to halite at  $25^\circ\text{C}$  (Eugster et al., 1980). The stability fields of Bl, bloedite; Car, carnallite; Ep, epsomite; Hx, hexahydrite; Ka, kainite; Ki, kieserite; Le, leonite; Pic, picromerite; Syl, sylvite, are indicated. Solid line - equilibrium path, dashed line - fractionation path.

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