Pecularities of gypsum sedimentation in the Middle Miocene Badenian evaporite basin of Carpathian Foredeep

OLEG I. PETRICHENKO[1], TADEUSZ M. PERYT[2], ANDREI V. POBEREGSKY[1]

[1]Institute of Geology and Geochemistry, National Academy of Sciences of Ukraine, Naukova 3a, 290053 Lviv, Ukraine
[2]Państwowy Instytut Geologiczny, ul. Rakowiecka 4, 00-975 Warszawa, Poland

Abstract. Based on the Badenian evaporite sequence as recorded in the borehole Hucuł 1 near Kosiv (Ukraine) we assume that gypsum deposits in the marginal parts of the basin would correspond to the upper part of the evaporite sequence in the basin center. The study of primary fluid inclusions in gypsum showed a low concentration of brine inclusions which was 27 g/l on average. The obtained data on chemical composition of brine inclusions indicate that the Badenian water during gypsum precipitation essentially differed from modern seawater and shows some similarity to some continental and continental-marine basins, such as the Aral Sea. Accordingly, the chemical composition of Badenian waters, especially in the north-western part of the basin, is a mixture of relict seawater (depleted in NaCl), underground water (enriched in calcium sulfate) and surface run-off.

Key words: Miocene, gypsum, geochemistry, fluid inclusions, Carpathian Foredeep.

Introduction

A very characteristic feature of the Carpathian Foredeep in the Ukraine and Poland is a wide distribution of gypsum deposits (Fig. 1) and related big economic deposits of sulfur in the middle Miocene Badenian (*e.g.* Aleksenko, 1967; Pawłowski *et al.*, 1979; Kubica, 1997). Gypsum deposits are commonly a few tens of meters thick (*e.g.* Panow & Płotnikow, 1996; Peryt, 1996; Kubica, 1997) The Badenian gypsum basin terminates a long period of evaporite sedimentation in the Central Paratethys which started in the Aquitanian (Petryczenko *et al.*, 1994). Due to a very low content of terrigenous impurities in some regions, the gypsum is the raw material for alabaster, building stones and production of facing plates. The fine preservation of original structures and textures makes possible reconstruction of sedimentary environments in the Badenian evaporite basin at the stage of calcium sulfate precipitation (*e.g.* Bąbel, 1987; Kubica, 1992; Kasprzyk, 1993a; Peryt & Jasionowski, 1994; Peryt *et al.*, 1994, 1997; Peryt, 1996), and establishes a geochemical model using information obtained during study of fluid inclusions in gypsum (*e.g.* Kultchetska, 1987; Poberegski, 1991; Petryczenko *et al.*, 1995; Petrichenko *et al.*, 1996; Peryt *et al.*, 1997).

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chemistry of Combustible Materials, National Academy of Sciences of Ukraine, Lviv and Państwowy Instytut Geologiczny, Warszawa.

Stages of Badenian evaporite accumulation

As in many evaporite basins, correlation of evaporites occurring in different parts of the Badenian basin, and hence reconstruction of basin history during deposition of evaporites, are subject to controversies. Based on the Badenian evaporite sequence as recorded in the borehole Hucuł 1 near Kosiv (Fig. 1) where sulfates occur in the lower part of evaporites, halite in the middle part and sulfates in the upper part (Wyszyńki, 1939), as well as on interpretation of other boreholes in the inner zone of the Carpathian Foredeep (*e.g.* Petrichenko *et al.*, 1974), the following interpretation is proposed.

The beginning of precipitation due to evaporation of seawater took place in a narrow zone adjacent to the rising Carpathian Mountains. The precipitation of terrigenous-sulfate and sulfate, mostly gypsum, deposits occurred on eroded Upper Cretaceous deposits, omitting the stage of sulfate-carbonate precipitation. Subsequently, this terrigenous-sulfate and sulfate precipitation was changed by sodium chloride precipitation. The study of brine inclusions in sedimentary halite indicates that the basin water did not differ significantly from evapo-
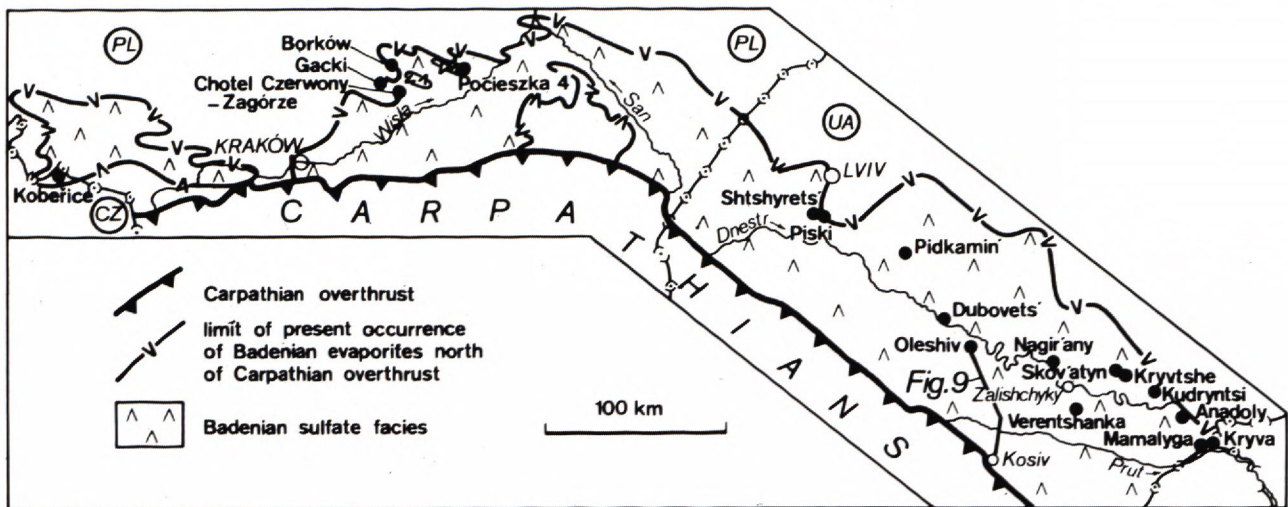
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Fig. 1. Occurrence of Badenian gypsum in the Carpathian Foredeep basin

Fig. 2. Characteristic profiles of Badenian gypsum

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rated marine water (Petrichenko et al., 1974; Kovalevich & Petrichenko, 1997). The halite precipitation in different parts of the basin alternated with precipitation of calcium sulfate and terrigenous material. The halite stage was followed by the calcium-sulfate stage and terrigenous sedimentation.

Accordingly, it is assumed that the basin had two periods of evaporite development, and between them there occurred a break in evaporite sedimentation which was characterized by erosion of earlier-deposited halite and sulfate deposits. Later, due to increase of water concentration, the conditions favouring calcium sulfate precipitation appeared again but this time in the peripheral part of the basin. Therefore, gypsum deposits in the marginal parts of the basin would correspond to the upper part of the evaporite sequence in the basin center.

Cyclic gypsum accumulation

Two main gypsum varieties occur in the Badenian sequence: bottom-growth crystalline gypsum and fine grained gypsum which precipitated at an air-brine interface and/or in the water mass (Fig. 2-5).

Bottom growth gypsum was growing in stable physico-chemical conditions at slow and even evaporation of surface water such that particular crystal individuals commonly are a few tens of centimeters in length (Fig. 3d), and even a few meters as in the case of giant gypsum intergrowths forming the base of the gypsum sequence (Fig. 3a).

Fine-grained gypsum (Fig. 4-c) originated in the upper part of water mass, and, possibly, on the water surface itself. Commonly these incipient crystals (less than 0.1 mm across) had a cylindrical shape as indicated by study of solid inclusions in bottom growth gypsum (Fig. 6c). The intensity of gypsum growth at the water surface or in the water mass varied widely in time and space. Due to extensive precipitation of fine-grained gypsum the crystallization of bottom growth gypsum slowed or even completely stopped following its burial.

The formation of a gypsum deposit that is composed of crystalline gypsum in the bottom part and of fine-grained gypsum in the top part, may be regarded as indicating individual cycles of sedimentation (Fig. 3c, 5a, b). The thickness of such sedimentary cycles in Piski (West Ukraine) varies from 1.5 to 14.5 cm and occasionally it is more than 20-30 cm. A similar range of thickness has been recorded in other gypsum sections.

The cyclic occurrence of gypsum sedimentation was genetically related to water mass stratification into two layers. The lower layer was characterized by more dense brines and more stable physico-chemical conditions where large crystals have been growing during long (tens and hundreds of years), and the upper layer was less dense and undersaturated in respect to calcium sulfate. When the pycnocline disappeared due to different reasons, the lower layer rose to the surface what promoted the intensive evaporation of calcium sulfate-saturated waters. In such conditions the common generation of centers of gypsum crystallization resulted in the origin of bottom-growth gypsum (Fig. 3a,b,d). This could be continued for a long time. Sometimes the lower layer was exposed for a short time, possibly due to wind effect; this promoted a simultaneous bottom-growth and surface gypsum precipitation.

As a rule, during the breaks in gypsum deposition calcium carbonate and aeolian siliciclastic material were accumulating (Fig. 4b,c). Terrigenous particles are composed of poorly-rounded quartz grains and pelitic clayey material. The breaks may be considered as preparatory stages when the gradual increase of water concentration took place for generation of centers of gypsum crystallization. Thus the complete sedimentary cycle is composed of three elements: the lower carbonate-terrigenous layer that is the basis for generation of coarse-crystalline bottom-growth gypsum which in turn is overlain by fine-grained gypsum (Fig. 4a-c).

The next indicator of sedimentary conditions in Badenian basin is the intensity of calcium sulfate accumulation as determined by zonation of crystalline gypsum and lamination of fine-grained gypsum.

Zonation of gypsum

The zonation of any mineral indicates the periodical alteration of physico-chemical parameters in environment of mineral crystallization. As the crystalline gypsum grew in the basin which was subject to seasonal climatic changes, the zonation of this mineral reflects the alteration of conditions during one year. Such a relation is confirmed by the study of present temporary lakes in arid zones (Fersman, 1953). In the Badenian crystalline gypsum we recorded two types of zonation. The first type is caused by changing regime of gypsum growth due to the alteration of physico-chemical conditions such as evaporation rate, temperature, and water concentration, directly in the environment of mineral crystallization. In such a case the gypsum zonation is connected with breaks in mineral growth and origin of zones with fluid inclusions (Fig. 6b) and inclusions of small grains of terrigenous material. The zones vary from 0.1 to 0.4 mm in width. This zonation type is very rare and is not characteristic of bottom-growth gypsum of the Fore-Carpathian region. In the southern part of the Ukrainian segment of the Carpathian Foredeep this zonation type is lacking.

The second zonation type of bottom-growth gypsum is related to seasonal dying of microorganisms in the gypsum and their periodical preservation by gypsum
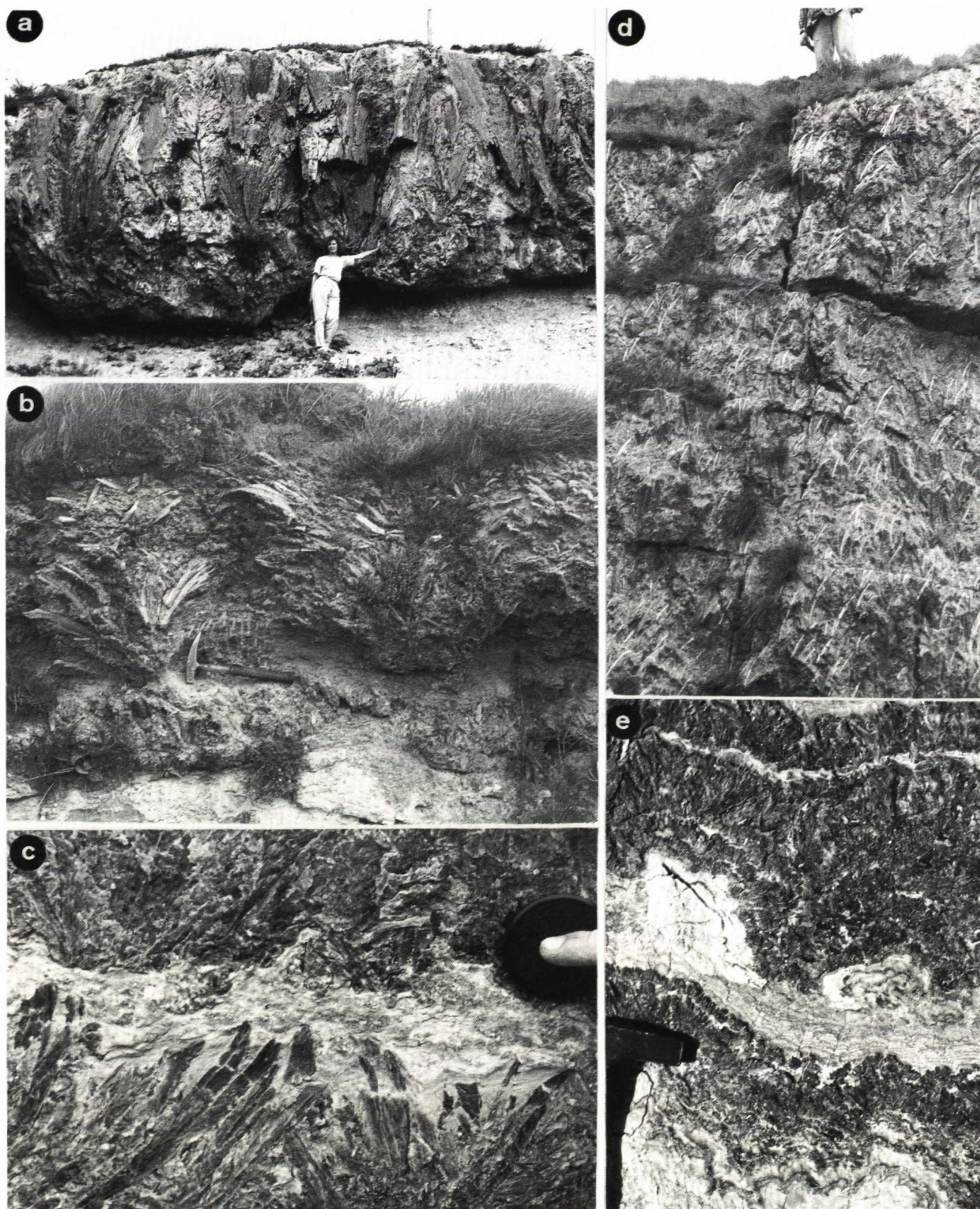
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Fig. 3. Aspects of Badenian gypsum.
a - Giant gypsum intergrowths in the lowermost part of the Gacki section;b - Nucleation cones of sabre gypsum in laminated gypsum. Pidkamin';c, e - Intercalations of stromatolitic and selenitic gypsum (c - Dubovets', e - Verentshanka); d - Sabre gypsum with uniformly oriented, strongly elongated selenite crystals in Pidkamin'.
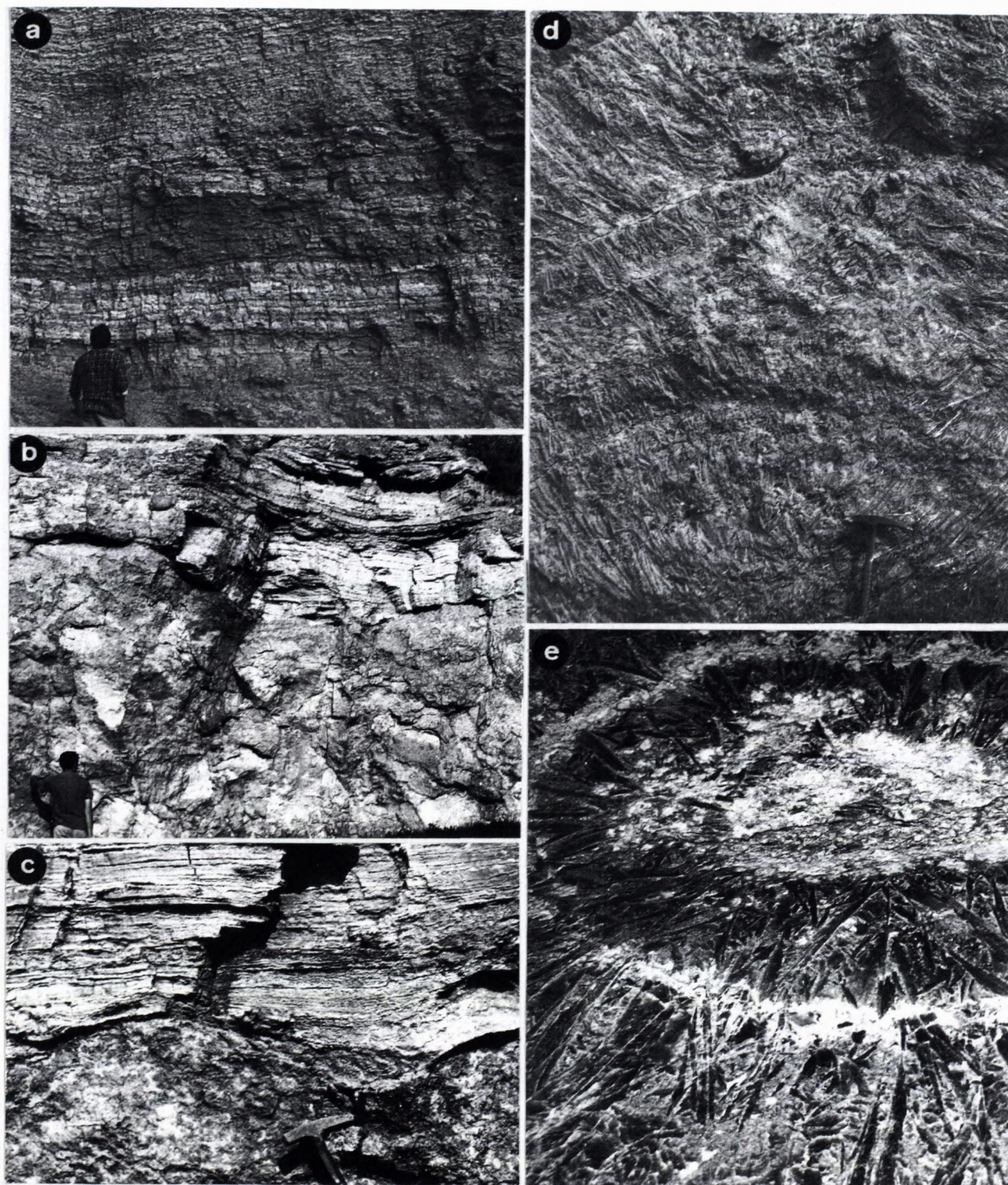
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Fig. 4. Aspects of Badenian gypsum.
a - Laminated gypsum from the upper part of the Borków section; b - Bedded clastic and laminated gypsum in the upper part of the
gypsum sequence in Anadoly overlying the recrystallized gypsum forming the lower part; c - Close-up of the boundary of two gypsum
units in Anadoly; d - Gypsum dome built of radially arranged, strongly elongated gypsum crystals which tend to have a vertical
orientation. Skov'atyn; e - Horizontal section of gypsum dome in Crystal Cave (Kryvtshe). The width of photo is ca. 2 m.

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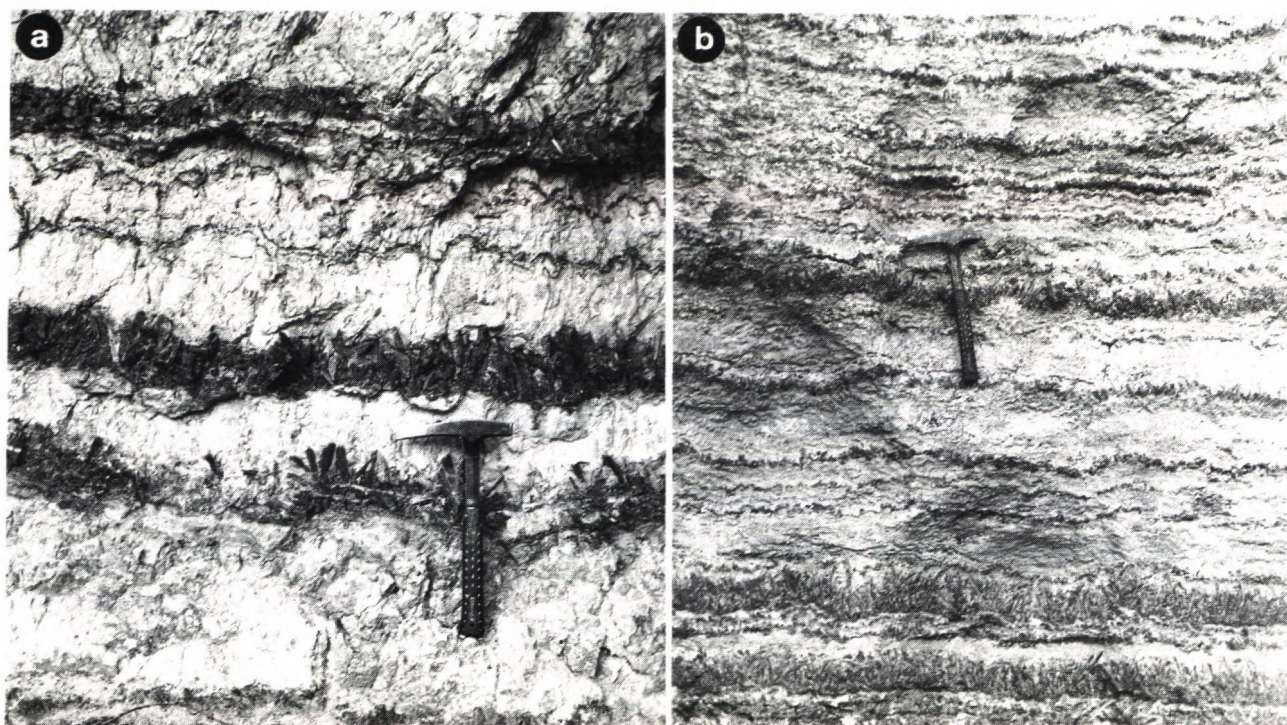
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Fig. 5. Aspects of Badenian gypsum.
a - Grass-like gypsum with interbeds of stromatolitic gypsum in Oleshiv; b - Interbedded selenitic and alabastrine gypsum in the lower part of the Chotel Czerwony-Zagórze section;

usually by growing face (111). The width of these zones ranges from 0.3 to 1.1 mm and in average is 0.78 mm. The zonality within one gypsum crystal is often sharply broken and separate zonal parts have different features. Irregularities of zones are obviously connected with unequal biological activity of basin water in different years. An individual zone is composed of two parts: transparent gypsum and gypsum with microorganic inclusions; their width ratio is 1:0.7. It is assumed that the transparent part was formed during summer when evaporation rate was the highest. The gypsum with inclusions formed in turn during autumn when microorganisms were dying out. By analogy to recent environments (Valiashko, 1962) it may be supposed that the growth rate of the bottom-growth gypsum was about 0.01 mm per day.

Unlike the bottom-growth gypsum, the zonation of gypsum formed on brine-air interface is not always clearly expressed and it characterizes only diurnal changes. Obviously, fine crystal nuclei of this gypsum have been kept by forces of surface tension during one to four days what is evidenced by definite zonations and the presence of minute (3-6 μm) gas inclusions on boundaries of zones. These inclusions are probably relics of ancient atmosphere. The width of zones changes from 0.03 to 0.05 mm so the growth rate of surface gypsum averaged 0.035 mm per day, i.e. three to four times higher than the growth rate of bottom-growth gypsum. Its

faster growth rate is also indicated by measurement data of laminated gypsum. In Piski, Shtshyrets', Darabany and other outcrops in West Ukraine the laminae are 1.8 to 2.5 mm (2.1 mm in average) thick. In Poland the scatter is more wide - from 0.26 to 9.0 mm (Kwiatkowski, 1972). Therefore, it may be accepted that the average rate of accumulation of fine-grained gypsum was 2-3 mm per year or 0.02-0.03 mm per day during summer-autumn season. Such a value corresponds to measurements of other ancient sulfate deposits (Duff et al., 1967).

Accumulation rate

Considering the mentioned data on accumulation rate of fine-grained gypsum and linear rate of growth of gypsum crystals we assume that the average rate of calcium sulfate accumulation in the Badenian basin was 1.5 to 2.0 mm per year. For comparative purposes we have studied the zonality of sedimentary gypsum in recent lakes in Crimea such as Sivash, Aktash and Saki. It was found that the zonation resulted from fluid and solid inclusions (terrigenous material) and the width of zones varies from 0.9 to 2.1 mm (1.4 mm on average), and only slighly differs from values recorded in the Badenian gypsum.

Considering the intensity of gypsum accumulation during one year (or season) it is possible to calculate the necessary sulfate-saturated water volume which evapo-
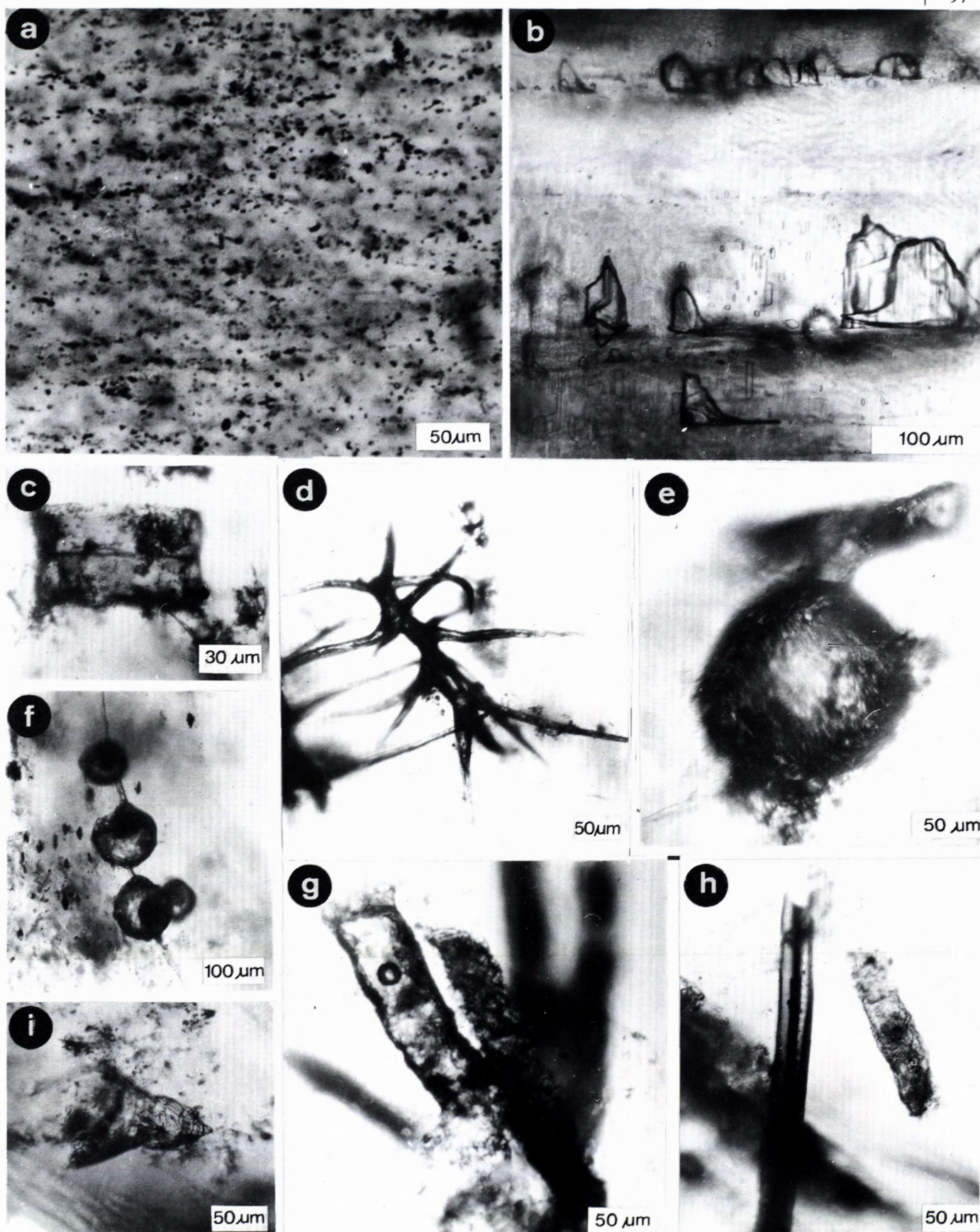
Fig. 6. Inclusions of microorganisms in the Badenian gypsum.

a - Mass occurrence of calcareous nannoplankton in sedimentary gypsum showing weak zonality. Kudryntsi; b - Fluid inclusion zones in upright-growth gypsum in Kudryntsi; c - Inclusions of gypsum crystals precipitated in water bed and incorporated into bottom-growth gypsum crystal. Pocieszka 4 borehole, depth 62.55 m; d - Charophyte structure. Pocieszka 4 borehole, depth 62.65 m; e - Gas inclusions in bottom-growth gypsum crystal. Shtshyrets'; f - Inclusions of coccoid cyanobacteria. Shtshyrets';g - Grouping of cells of filamentous alga. Borków;h, i - Inclusions of problematic microfossils. Borków.

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rated in the Badenian gypsum. The solubility of gypsum in low concentrated seawater at 20-25°C temperature is 0.35% or approximately 3.5 g/l (Posnjak, 1940), so to precipitate gypsum lamina 1.5-2.0 mm thick it is necessary to evaporate the water layer of 70-100 cm thick. This value may be compared to evaporation of water of total concentration of 10% in Sivash Lake during the evaporation season (April-October) which is 65.5 cm (Ponizovski, 1965), and in some other lakes of arid zone is 150 to 220 cm per year. The maximum evaporation of ocean water is 134 cm per year (Horne, 1969).

The total duration of Late Badenian was about 1.0 Ma (Oszczypko, 1996). However, it is very difficult to determine the time of existence of sedimentary basin in which the gypsum has accumulated. If we assume that the lamina 1.5-2.0 mm thick was precipitated during one year, then the accumulation time of gypsum sequence 50 m thick was 25,000-35,000 years. This is 2-3% of total time of basin existence so the chemical accumulation was only an episode in the basin history.

The depth of deposition

The shallow conditions in the marginal part are indicated by the existence of stromatolitic gypsum (Fig. 3e, 5a; Kwiatkowski, 1972; Kropacheva, 1981; Kasprzyk, 1993b; Peryt, 1996), however, it is reasonable to assume that the main volume of gypsum deposits has been formed at greater depths (e.g. Peryt et al., 1997). This is also supported by the extensive occurrence of individual gypsum beds over large areas (Peryt et al., 1994).

The study of inclusions in bottom growth gypsum gave more detailed information. In one sample which was taken 2-3 m above the bottom of the gypsum sequence in Shtshyrets' in West Ukraine (i.e. in a bed with sabre gypsum overlying the laminated gypsum - Fig. 2), two gas inclusions have been found which are interpreted by us as trapped by growing gypsum crystal at the bottom of the basin (Fig. 6e). After the opening of these inclusions by dissolution of gypsum in 20% water solution of ammonium citrate we determined that the volume of these spherical gas bubbles increased approximately three times. This indicates the former pressure of 2-3 atmospheres what corresponds to 20-30 m thick, low mineralized water layer overlying the gypsum crystal.

A possibility exists that this particular bed known also from other localities in Ukraine (Fig. 3d) and Poland is the result of longer time of holomictic conditions in the Badenian basin. In the Dead Sea, when the winter freshwater influx exceeds the amount that will be evaporated during the succeeding year, the lake remains strongly stratified (meromictic conditions) and when winter inflows are low, the entire upper water layer is concentrated by evaporation during the summer and the density

contrast disappears and the entire brine column is uniform in winter (holomictic conditions) (Anati & Stiller, 1991). It is thus possible to explain the ancient evaporites characterized by the presence of both laminated evaporites and bottom-growth evaporites as due to the change between holomictic and meromictic conditions (Kendall & Harwood, 1996): large influxes during winter induce meromictic conditions and deposition of laminae while small influxes cause holomictic conditions and formation of bottom crusts. It is remarkable that the discussed particular bed does not occur in Kobeřice (Czechia) where the winter influxes were in general very significant (cf. Peryt et al., 1997).

The second, indirect indicator of basin depth is the absence of zonation in bottom-growth gypsum, caused by changes of physical-chemical conditions of in situ growth of the mineral.

Water concentration and temperature

The information about total concentration of salt in the Badenian basin brines was obtained through study of individual primary inclusions in bottom-growth crystalline gypsum from many sections of the Carpathian Foredeep. Because it is impossible to determine the chemical composition of brine inclusions which are smaller than 70-90 mm across by means of the applied method (Petrichenko method of glass capillaries - see Petrichenko, 1973), the information about total brine concentration was obtained by determination of temperatures of ice thawing after its previous freezing. This method of cryometric investigation of inclusions in minerals is fairly precise and very sensitive (Kulchetska, 1977). The systematic and numerous determinations (about 900 analyses in total) of brine concentration in inclusions in gypsum of the Carpathian Foredeep was done by Kulchetska (1987, 1988). The data derived from exposures: Shtshyrets', Oleshiv, Kudryntsi, Zalishchyky which are many kilometers apart (see Fig. 1) show that the total concentration of solutions precipitating bottom-growth gypsum was ranging from 16 to 65 g/l and in average was close to 45 g/l. Our individual measurements showed a low concentration of brine inclusions which was 27 g/l in average (Table 1).

Table 1. Results of cryometric analyses of fluid inclusions in bottom-growth gypsum of Carpathian Foredeep

locality	number of measurements	melting temperature	equiv. NaCl content g/l
Kudryntsi (UA)	3	-0.7	18
Borków (PL)	7	-0.8	19
Borków (PL)	4	-1.0	27
Kobeřice (CZ)	5	-1.5	33
Piski (UA)	7	-1.2	20
Verentshanka UA)	3	-2.5	45

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Those investigations of individual inclusions in gypsum indicate an essentially decreased water salinity when compared to marine-derived, calcium sulfate-saturated water. It should be stressed that gypsum precipitation from sea water at 20-25°C begins after the decrease of initial volume of seawater by 80% and the increase of total concentration of solutes to 130-140 g/l. Thus the total mineralization of Badenian water on stage of gypsum precipitation was several times lower than is characteristic for modern, calcium sulfate-saturated seawater.

Cryometric investigations seem to indicate that the water mineralization varied strongly throughout the entire basin. It is usually accepted that the brine concentration is greater on the basin bottom than in its surface parts, i.e. the brine body is density-stratified. The occurrence of pelagic and planktonic fauna in some sections (e.g. Krach, 1956) and Peryt et al., 1997 in the Upper Silesia) strongly suggests such a possibility.

For bottom-growth gypsum single-phase fluid inclusions are characteristic what indicates relatively low temperatures (below 35°C) of crystallization environment.

Chemical composition of water

As was earlier discussed, the total mineralization of brines in fluid inclusions in Badenian gypsum was considerably lower than could be expected. Therefore, to check such a conclusion, the method of water and alcohol leachates from separate crystals of bottom-growth gypsum containing similar inclusions as well as results of analyses of brine solutions in individual inclusions have been used.

The study of leachates makes possible to determine the chemical association in relict brines as well as the approximate ratios of particular components, as the method is qualitative. Table 2 shows selected results of analyses which indicate that the Badenian water had the set of chemical components that is typical for modern seawater. However, their proportions in water leachates are different: the Mg/K ratio is decreased due to the decreased concentration of Mg, and the content of NaCl is considerably smaller (in seawater NaCl/(K+Mg) is 16.3 - Horne, 1969). The presence of calcium carbonate and calcium sulfate in the leachates is related to the dissolution of gypsum and calcite during the preparation of water leachates.

A low mineralization of brines in fluid inclusions in gypsum, the unstability during the opening of inclusion and a very limited number of inclusions that are suitable for fluid-inclusion study cause that chemical analyses of individual brine inclusions in gypsum are methodologically difficult. Therefore, the opening of inclusions was performed by spliting the gypsum plates along the cleavage planes in moist atmosphere. Brine inclusions - which

Table 2. Chemical composition of water leachates from sedimentary Badenian gypsum of Carpathian Foredeep

locality	Na	Cl	K	Mg	NaCl	NaCl/(K+Mg)	Cl/Mg
Kryva (Moldova)	0.07	0.12	0.05	0.01	0.17	2.8	1.7
Verentshanka (UA)	0.07	0.10	0.04	0.06	0.17	1.7	1.4
Piski & Shtshyrets' (UA)	0.08	0.16	0.07	0.02	0.20	2.2	2.0
Borków (PL)	0.03	0.04	-	-	0.07	-	1.3

formed the microdrops (up to 10-20 μm in diameter) on spliting surface of gypsum plate were picked up by capillaries and analyzed. The results are semiquantitative but they give useful data on ratios of various elements and their contents in brine inclusions. As the chemical analyses were done for brine inclusions of varied total concentration (from 5 to 60 g/l). Table 3 shows results in % of the sum of dissolved salts. It permits to compare the composition of individual brine inclusions as well as to compare them to the composition of marine or continental waters.

The information that has been obtained in such a way corresponds, in general, to data from water leachates. As in water leachates, it was recorded the deficit of NaCl in respect to potassium and magnesium salts (if the chemical composition of seawater is taken for standard), the presence of natrium sulfate and potassium sulfate in solutions, and the high content of calcium sulfate when compared to other chemical components. Such a composition places the studied solutions within thenardite field on physico-chemical diagram (Fig. 7).

The investigation of solid phase under the microscope during the evaporation of water (both of leachates and brine inclusions) confirms the results of chemical analyses. Except of gypsum, first minerals which precipitate are halite and mirabillite, and they are followed by hexahydrite, occasional astrakhanite and other minerals which are difficult to diagnose (perhaps polyhalite and glaserite). Halite, in general, is present in subordinate quantity in relation to the total volume of precipitated minerals.

The above-presented data and considerations make it possible to construct the most probable quantitative model of chemical composition of water in the Badenian gypsum basin. During the precipitation of the bottom-growth gypsum in Verentchanka, the water of total mineralization of water of 53-54 g/l contained (in g/l): 36.4 of NaCl, 8.1 of K_2SO_4, 5.9 of $MgSO_4$, and 3.1 of $CaSO_4$. The content of $CaSO_4$, NaCl, Na_2SO_4, $MgSO_4$, and K_2SO_4 in the north-western part of the basin (Borków - during deposition od sabre-like gypsum and

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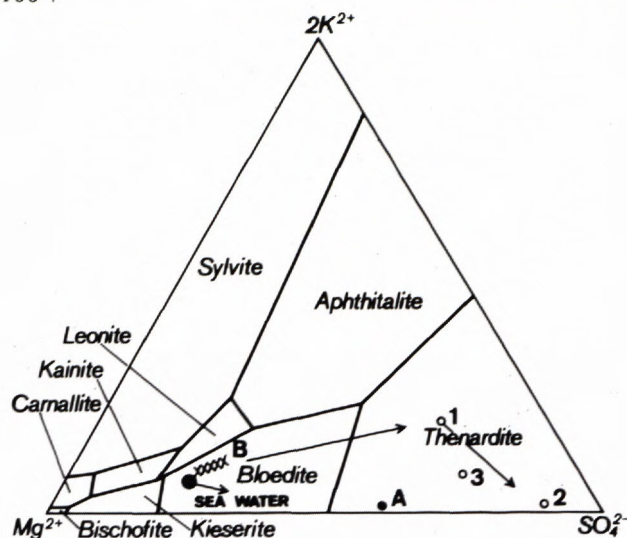
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Fig. 7. Points showing composition of brine inclusions in the Badenian sedimentary gypsum of Carpathian Foredeep on the diagram after Stewart (1963) for 25°C.
1 - Verentshanka, 2 - Borków, 3 - Kobeřice, A - Aral Sea water, B - Badenian basin during halite sedimentation (after Petrichenko et al., 1974), SW - recent marine water. Arrow indicates general trend of evolution of basin water from the stage of halite sedimentation (point B) to the stage of gypsum precipitation (points 1, 2, and 3).

Kobeřice - during deposition of giant gypsum intergrowths) was (in g/l): 2.7, 2.7, 1.3, 1.1, 0.2, respectively.

Although the presence of calcium hydrocarbonate was not directly recorded in the brine inclusions in gypsum, the presence of calcite in gypsum from traces to 0.6 % (Zolotukhin, 1954) allows us to assume the calcium -hydrocarbonate saturation of water in the Badenian basin at the stage of gypsum precipitation. Considering the data on solubility of this component in seawater (Zolotukhin, 1954) it may be assumed that its concentration could reach 0.038 g/l.

A decreased ratio of $NaCl/(K+Mg)$ in brine inclusions in relation to seawater may be explained by an active halite sedimentation at the first stage of existence of evaporite basin when such deposits of rock salt accumulated: Wieliczka, Bochnia, Zabolotiv, Kosiv and many others. The chemical composition of this water, as shown by Petrichenko et al. (1974), did not differ from modern seawater concentrated to the stage of halite precipitation (see Fig. 7).

The obtained data on chemical composition of brine inclusions indicate that the Badenian water during gypsum precipitation essentially differed from modern seawater and show some similarity to some continental and continental-marine basins (Table 3), such as the Aral Sea. The water of the Aral Sea, genetically linked to the marine basins of Eastern Paratethys (Rubanov, 1977; Blagovidov, 1978), is enriched in calcium sulfate (up to 1.5-1.6 g/l).

It was also found that towards the north-western part of the Carpathian Foredeep basin, along with the decrease of total mineralization of water, the content of sulfate was increasing, what was undoubtedly connected with the influence of continental surface waters. An important role in the chemical composition of the Badenian water was played by the underground waters enriched in calcium sulfate. In the places of their inflow into the basin dome-like structures (such as described by Turczynow and Andrijczuk, 1995 - Fig. 4d, e) could developed as recorded in some places.

Accordingly, the chemical composition of Badenian waters, especially in the north-western part of the basin, is a mixture of relict seawater (depleted in NaCl), underground water (enriched in calcium sulfate) and surface run-off.

It should be stressed, however, that the interpretations presented above refer to the lower part of the gypsum sequence, as they are based on study of samples which were taken from that interval. There is no doubt that during the entire time of gypsum deposition the chemical composition of water did not remain stable as indicated by the presence of molds of halite crystals indicating increased salinity (Bąbel, 1991; Peryt et al., 1997) and the laminae or beds of terrigenous clays in the entire area of the Carpathian Foredeep which indicate considerable refreshening of basin waters.

Life in gypsum basin

The decreased water mineralization, shallow depth, important influence of surface run-off, stagnant conditions, relatively increased temperatures - all these factors were ideal for an intensive development of life. We have already mentioned the common occurrence of microorganic inclusions in sedimentary gypsum. Estimated calculations show that in some gypsum crystals, or their parts, the volume of inclusions reaches 7-9 % of total crystal. The determination of Corg. in zoned gypsum showed that the content is 0.202 to 0.331 % (Table 4), and in gypsum-terrigenous material filling the intercrystalline space the content of Corg (up to 0.92 %) is several times greater. Such a high quantity of organic material in gypsum crystals and between them is a direct evidence of proliferous development of algae and other organisms in upper layer of the Badenian water column. In nearshore, more shallow parts of the basin, cyanobacterial mats have been flourishing as indicated by common occurrence of gypsum stromatolites (e.g. Peryt et al., 1994; Peryt, 1996).

Inclusions of microorganisms in bottom-growth gypsum in the entire north-western part of the Carpathian Foredeep are characterized by constant ratios between individual representatives of cyanobacteria (Petryczenko

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Table 3. Chemical composition of solutions in fluid inclusions in gypsum of the Carpathian Foredeep. For comparison, data for ocean (Horne, 1969) and Aral Sea (Zdanovski, 1972) are shown.

	Kobeřice	Borków	Verentshanka	Ocean	Aral Sea
Na^+	21.3	15.7	25.8	30.6	22.0
K^+	1.8	0.9	6.5	16.1	0.9
Mg^{2+}	3.7	1.8	2.2	3.7	5.5
Ca^{2+}	6.5	13.6	2.7	1.2	4.5
Cl^-	25.0	15.2	39.8	55.6	35.4
SO_4^{2-}	41.7	52.8	23.0	7.8	31.9
NaCl	41.2	25.1	65.6	78.3	54.1
Na_2SO_4	15.7	18.0	-	-	-
KCl	-	-	-	1.7	1.8
K_2SO_4	4.0	2.0	14.4	-	-
$MgSO_4$	18.3	8.9	10.9	6.4	26.0
$MgCl_2$	-	-	-	9.4	0.7
$CaSO_4$	20.2	46.2	9.2	3.6	15.4
NaCl/(K+Mg)	7.5	9.3	7.5	16.3	8.7
Cl/Na	1.2	1.0	1.6	1.8	1.6
Water concentration (g/l)	up to 10	up to 7	up to 50	35	10-11

et al., 1995). The most frequent (over 90%) are filamentous (Fig. 6g, 8b) and coccoidal forms (Fig. 6f, 8d). In addition, individual specimens of algae (Fig. 6d, 8a) and other organisms (Fig. 6h,i, 8c) occur.

South of Shtshyrets'-Piski the quantity of gypsum occurrences with filamentous inclusions is quickly dropping and the main role is played by the coccoid forms, and still southward, in Kryva (Moldova), only inclusions of nannoplankton occur in sedimentary gypsum (Fig. 6a). Different filamentous algae have been recorded: the most frequent are segmented algae. In gypsum usually individual cells (70-200 μm in diameter) have been concerved, and only rarely groups of cells that are jointed together, were recorded (Fig. 6g). Particular inclusions in many cases are filled by low-mineralized water solutions (a few grams per liter) with organic remains of brown color and small scales (up to 1.0 mm) of black color. The material of these inclusions shows no luminescence. Chloroform leachate from gypsum with such inclusions possesses wax-like consistency of dark-brown color, and under the luminescence microscope shows blue color. Infra-red spectroscopy analysis indicated the presence of aromatic compounds, oliphatic ephires, ketons and carbonate acids in these leachates.

Inclusions of coccoid structure commonly occur within the mass of filamentous forms. Such ideal spherical forms (10-60 μm in diameter) are grey in reflected light. They are usually composed of three parts: the outer rim (1 μm thick), fluid (possibly water solution) and shapeless wax-like body of brown color and 4-18 μm across (Fig. 8d). In luminescent light these algae show darkened yellowish color. The outer rim is porous, elastic and does not disssolve in organic dissolvents such as benzene spirit, chloroform, and spirit.

Very rare are algal inclusions of charophyte structure. Such branchy forms, up to 600 μm long, are composed of one organic tissue with thin channels filled by fluids (Fig. 8a). This organic tissue is relatively strong (resistant for tearing up), elastic and does not dissolve in organic dissolvents.

In the Badenian gypsum basin also other organisms were living as also fragments of insects, fish teeth and other fragments have been recorded (Fig. 6h,i, 8c). In addition, planktonic foraminifers and calcareous nannoplankton occur in clayey intercalations in gypsum sequences of different sections (e.g. Peryt et al., 1994, 1997). South of Verentchanka, in sedimentary gypsum relics of nannoplankton (less than 2 μm across) have been found. These relics are usually dispersed in gypsum crystals but occasionally they are arranged in zones what reflects the seasonal dying of these organisms. The width of such zones is 180 to 750 μm.

Table 4. Content of Corg. (%) in sedimentary upright-growth crystalline gypsum in the Ukrainian part of the Carpathian Foredeep

Verentshanka	0.202
	0.272
Shtshyrets'	0.309
Piski	0.258
Nagir'any	0.301
Kudryntsi	0.331
	0.298
Mamalyga	0.314

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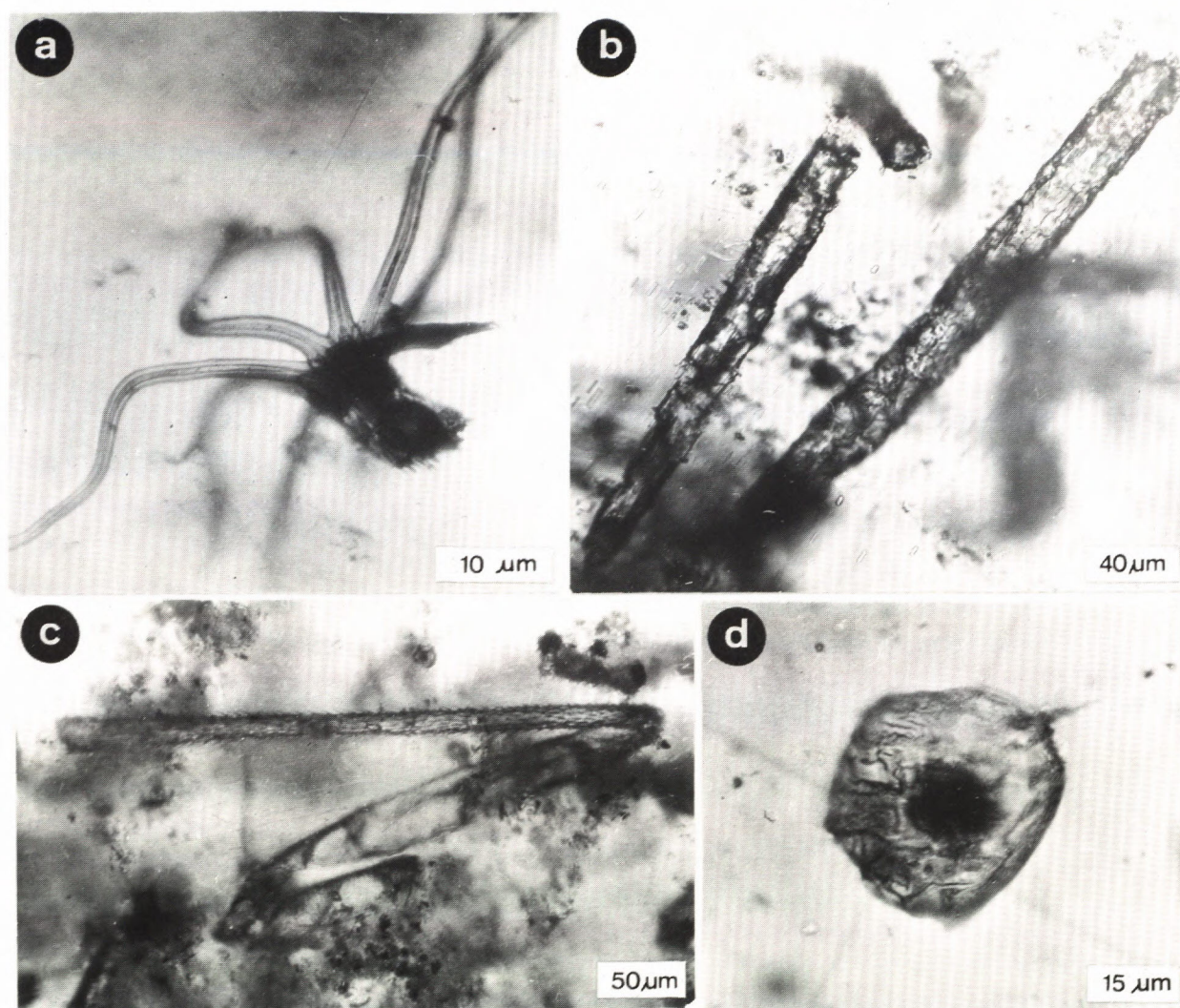
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Fig. 8. Inclusions of microorganisms in the Badenian gypsum.
a - Fragment of charophyte inclusion. Narrow channel is filled by fluid. Pocieszka 4 borehole, depth 62.65 m; b - Inclusion of a cell of filamentous alga filled by water solution with organic remains. Shtshyrets';c - Inclusion of problematic microfossil. Borków;d - Structure of spherical (coccoid) alga: 1 - outer rim, 2 - fluid (water solution), 3 - wax-like nucleus. Kudryntsi.

The flourishing life is expressed by the presence of phosphorus and nitrogen in gypsum (Table 5). In some cases (Kudryntsi, Shtshyrets') collofan was found in form of stringers (0.1-0.8 mm across). This is brown semi-transparent matter of wax-like polish, structureless, showing poor pleochrosity and wavy polarization in dark-gray colors; Np = 1.6002.

There is no doubt that life processes in the Badenian water had an important influence of geochemical regime. In particular, these processes were controlling Eh-pH parameters, composition of gases dissolved in water, possibility of migration of some chemical elements (such as sulfur, phosphorus, nitrogen)

and degree of saturation of waters with organic matter. As an example the north-western increase of bioactivity in the Badenian gypsum basin shows a correlation with the intensity of sulfur mineralization. This might indicate that a specific biochemical regime in the basin was controlling factor which served as a catalyzator during later processes of sulfur formation (cf. Aleksenko, 1967; Ivanov, 1964).

The organic material dissolved in water was influencing the ontogeny of gypsum crystals, as was supported by experiments in laboratory conditions (Sonnenfeld, 1984). It seems that the specific form and size of some gypsum crystals (such as giant gypsum in-

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Table 5. Content (in %) of some minor chemical components in sedimentary gypsum (tr - traces)

	P_2O_5	NH_4	Fe_2O_3	FeO	$CaCO_3$
Borków (PL)	0.0025	tr.	0.002	<0.005	1.07
Shtshyrets' (UA)	0.0025	tr.	0.004	<0.005	1.22
Piski (UA)	0.0010	-	0.010	-	1.54
Kudryntsi (UA)	0.0013	<0.005	0.004	<0.005	0.20
	0.0026	<0.005	0.003	<0.005	0.10

tergrowths and sabre gypsum crystals) might be controlled to some extent by organic compounds.

Finally, the problem of hydrocarbon presence in gypsum should be discussed. There is no doubt that hydrocarbons occur as inclusions in gypsum (Kulchetska, 1987, 1988) although their origin remains an open problem. It was proposed (Kulchetska, 1987, 1988) that hydrocarbons contaminated the entire water but our observations of inclusions do not support such a concept. We think that the origin of wax-like and fluid hydrocarbons originated during transformation of preserved microorganisms (Petrichenko et al., 1996).

Eh-pH conditions

The information about alkalinity of water and oxidizing-reducing potential of the environment of bottom-growth gypsum is only indirect as it was not possible to obtain these parameters even qualitatively by a direct study of fluid inclusions. However, a good preservation of microorganisms that were conserved in sedimentary gypsum during its crystallization indicates the lack of dissolved oxygen in solutions of bottom water. Accordingly, considering the growth rate of gypsum, dead organisms did not suffer essential decay during 2-3 months, and such an inerty is possible only in strongly reducing, stable anaerobic conditions. The active reproduction of microorganisms has led to a considerable saturation of water by dissolved material what in turn was leading to the lowering of water alkalinity. In such a way during periods of microbial flourishing, especially in the north-western part of the basin, the bottom of the basin was located within reducing, neutral or weakly oxidizing conditions (Fig. 9). The Eh-pH conditions of the upper water layer were controlled by the chemical composition of inflowing waters and the degree of solubility of atmospheric oxygen.

In the south-eastern part of the basin in Ukraine (Kudrytsi-Verentshanka region), gypsum is commonly
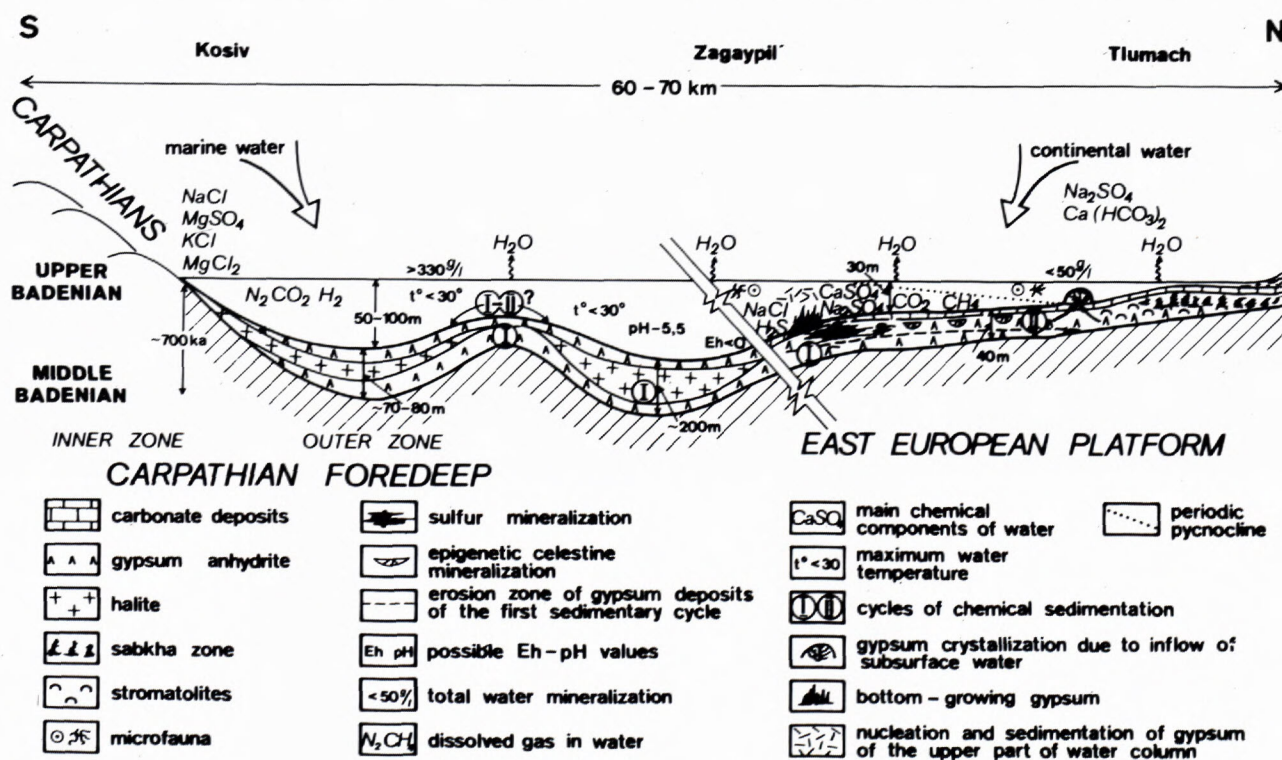

Fig. 9. Chemical model of the Badenian evaporite basin in the south-eastern part of the Carpathian Foredeep in Ukraine (the line of cross-section is shown in Fig. 1).

light-brown in color due to admixtures of iron oxides. This fact allows to propose that there existed not only reducing but also oxidizing conditions. The occurrence of inclusions of carbonate nannoplankton in this gypsum indicates that pH of mineralizing solutions was neutral or weakly alkaline.

Physico-chemical parameters of conditions of chemical sedimentation in the south-eastern part of the Carpathian Foredeep basin in West Ukraine are summarized in Figure 9.

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