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# SLOVAK GEOLOGICAL MAGAZINE

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- Sonnenfeld, P.*: The Environment of Miocene Salt Basins in Cis- and Transcarpathia \_\_\_\_\_ 83
- Petrichenko, O. I., Peryt, T. M., Poberegsky, A. V.*: Peculiarities of gypsum sedimentation in the Middle Miocene Badenian evaporite basin of Carpathian Foredeep \_\_\_\_\_ 91
- Peryt, T. M., Karoli, S., Peryt, D., Petrichenko, O. I., Gedl, P., Narkiewicz, W., Ďurkovičová, J., Dobieszyńska, Z.*: Westernmost occurrence of the Middle Miocene Badenian gypsum in central Paratethys (Kobeřice, Moravia, Czech Republic) \_\_\_\_\_ 105
- Kubica B.*: Relation of sulfur-forming processes to lithofacies and structural features of Badenian chemical sediments in the Carpathian Foredeep (Poland) \_\_\_\_\_ 121
- Parafiniuk, J., Hatas, S.*: Sulfur- and oxygen-isotope composition as the genetic indicator for celestite from the Miocene evaporites of the Carpathian Foredeep \_\_\_\_\_ 131
- Ślącza, A., Kolasa, K.*: Resedimented salt in the Northern Carpathians Foredeep (Wieliczka, Poland) \_\_\_\_\_ 135
- Bukowski, K.*: Sedimentation of clastic strata associated with Miocene salts in Wieliczka (Southern Poland) \_\_\_\_\_ 157
- Galamay, A. R., Bukowski, K., Przybyło, J.*: Chemical composition and origin of brines in the Badenian evaporite basin of the Carpathian Foredeep: fluid inclusion data from Wieliczka (Poland) \_\_\_\_\_ 165



Geological Survey of Slovak Republic, Bratislava  
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2/97

# 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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Andrusov D., Bystrický J. & Fusán O., 1973: Outline of the Structure of the West Carpathians. Guide-book for geol. exc. X. Congr. CBGA, Geol. Úst. D. Štúra, Bratislava, 5 - 44.

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# SLOVAK GEOLOGICAL MAGAZINE

VOLUME 3 NO 1

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Evaporite Formations of the Carpathians Mts.

Part I. - Badenian

The Publisher notifies the readers of an error that occurred on the title page of this issue of the Slovak Geological Magazine. The misprinted **VOLUME 3 No 1** should read **VOLUME 3 No 2**. The Publisher appologizes for this inconsistency.



Geological Survey of Slovak Republic, Bratislava  
Dionýz Štúr Publishers



2/97



## Contents

<i>Sonnenfeld, P.</i> : The Environment of Miocene Salt Basins in Cis- and Transcarpathia _____	83
<i>Petrichenko, O. I., Peryt, T. M., Poberegsky, A. V.</i> : Peculiarities of gypsum sedimentation in the Middle Miocene Badenian evaporite basin of Carpathian Foredeep _____	91
<i>Peryt, T. M., Karoli, S., Peryt, D., Petrichenko, O. I., Gedl, P., Narkiewicz, W., Ďurkovičová, J., Dobieszyńska, Z.</i> : Westernmost occurrence of the Middle Miocene Badenian gypsum in central Paratethys (Kobeřice, Moravia, Czech Republic) _____	105
<i>Kubica B.</i> : Relation of sulfur-forming processes to lithofacies and structural features of Badenian chemical sediments in the Carpathian Foredeep (Poland) _____	121
<i>Parafiniuk, J., Hatas, S.</i> : Sulfur- and oxygen-isotope composition as the genetic indicator for celestite from the Miocene evaporites of the Carpathian Foredeep _____	131
<i>Ślączka, A., Kolasa, K.</i> : Resedimented salt in the Northern Carpathians Foredeep (Wieliczka, Poland) _____	135
<i>Bukowski, K.</i> : Sedimentation of clastic strata associated with Miocene salts in Wieliczka (Southern Poland) _____	157
<i>Galamay, A. R., Bukowski, K., Przybyło, J.</i> : Chemical composition and origin of brines in the Badenian evaporite basin of the Carpathian Foredeep: fluid inclusion data from Wieliczka (Poland) _____	165

*The evaporite formations of Carpathian Mts. are described by Ukrainian, Polish, Czech and Slovak authors in two issues of Slovak Geological Magazine in a form of summary contributions. Although, most attention was paid to Neogene evaporites, several papers deal with the evaporite sequences in the stratigraphically older horizons. The concept of two subsequent volumes of Slovak Geological Magazine Vol. 3 - 2/97, 3/97, issued by the Dionýz Štúr Publishers, was to present in the first mainly the papers on Badenian evaporites and in the second the papers on evaporite formations in other stratigraphical horizons.*

*The edition and publication of two monothematic issues of the Slovak Geological Magazine is a result of activities of the Sedimentological Commission of the CBGA (Carpatho-Balkan Geological Association) and especially of the joint action of geological staff of the Polish Geological Survey (Panstwowy Instytut Geologiczny, Warszawa) and of the Geological Survey of Slovak Republic (Geologická služba Slovenskej republiky, Bratislava).*

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*Tadeusz Marek Peryt (Warszawa),  
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## The Environment of Miocene Salt Basins in Cis- and Transcarpathia

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**Abstract.** Miocene salt basins in Cis- and Transcarpathia formed in a semiarid climate that extended farther north than today. All these basins were lined by shallow shelves that became covered with gypsum, while more rapidly deepening parts became the sites of chloride precipitation. Virtually all precipitates are of marine origin, as they display the typical marine sequence of minerals; no continental evaporite minerals are present, nor is the full sequence curtailed as in leached and recycled marine evaporites. As rivers are rare in a semiarid climate, flash floods are the major suppliers of siliciclastic sediments. While the coarse fraction settles near the shores as gypsiferous sandstones, the fines float at the interface between inflow and resident brine. When they finally settle as a blanket, they retain permeability until compacted. If sea level is oscillating before or after an ice age, eroding gypsum of shelves can enter and get into contact with potash horizons, converting them from chlorides to sulfates. Economically, salt basins are not only major suppliers of halite and of potash fertilizer, but in many cases the surrounding porous strata, e.g., reef complexes, also contain hydrocarbons or lead-zinc deposits.

**Key words:** Miocene, evaporites, mineralogy Carpathian region

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### Occurrence

Miocene evaporites are mainly preserved in four circum-Carpathian areas. Cis-Carpathian locations encompass (1) a salt basin in eastern Slovakia abutting against the mountain range to the north, (2) a salt basin in Transylvania enclosed by the Carpathian arc and the Muntii Apuseni Mountains, and (3) small salt basins bounded by spurs at the end of the Carpathian arc. The Transcarpathian salt basin was covered by one continuous water surface and covered a large part of the northern foothills area in southern Poland and the adjacent Ukraine (Fig. 1).

All the basins faced south towards their entrance channels. Basins facing south or east require a lower entrance sill to entrap and concentrate resident brines than basins facing west or north. This is due to the vertical component of the Coriolis effect.

### Extent of peri-Carpathian salt basins

Miocene salt basins extended much farther north than salt basins do today along western margins of continents. The wider belt of a semiarid climate was caused by an increased diameter of the subtropical anticyclones, which produce a string of high-pressure cells along the Horse Latitudes.

Salt basins require a climatic regime, in which

$$E/t > (P + G + R)/t \quad (1)$$

i.e., in a unit of time (t) the water loss through evaporation (E) is greater than the combined atmospheric precipitation (P), groundwater (G) and river (R) discharge. A Mediterranean climate, marked by winter rains and a long dry season, was defined by W. Koeppen (1931) to represent a ratio of

$$1 < P(T + k) < 2 \quad (2)$$

whereby P and T are atmospheric precipitation and temperature, and k is a constant.

As the jet stream slows down due to a reduced solar energy intake, it assumes a meandering pattern with wider amplitude. This is apt to get the high-pressure cells stuck in one place for some time and the adiabatic heating in them is reduced.

A reduced intake of solar energy translates into a cold spell with reduced winter rains in a shortened wet season, while the dry season is lengthened. The amount of annual water loss is thus increased despite the cooler climate.

The Miocene salt basins vary slightly in their age, which indicates that cold spells were repeatedly interrupted by slightly warmer periods, when some of the depressions would either freshen or dry out. The climatic oscillations also affected the sea level, which became



Fig. 1. The present distribution of Miocene Ciscarpathian and Transcarpathian salt basins.

slightly variable, be it through melting of the margins of incipient polar ice caps and glaciers, or a change in the thermal expansion of the water masses.

#### Onset of precipitation

Aragonite is the most common marine carbonate, while primary calcite occurs in lacustrine environments. Above a Mg/Ca ratio of 11.75 aragonite is the only stable phase (Berner, 1975). It reaches a maximum at a molar Mg/Ca ratio of 5.0; in seawater this ratio stands at 5.05. It is the only phase precipitated, once the Mg-concentration exceeds 243 ppm, even though it is thermodynamically unstable at surface temperatures and pressures (Sonnenfeld, 1984). Aragonite [ $\text{CaCO}_3$ ] begins to precipitate in seawater at 1.8-fold concentration (McCaffrey *et al.*, 1987). However, it is always produced by bacterial activity and does not occur in a sterile environment (Billy *et al.*, 1976).

No bicarbonate can remain in solution at a 3-4-fold concentration of a brine derived from seawater (Wattenberg, 1936). At gypsum saturation, reached at about 3.8-fold concentration (McCaffrey *et al.*, 1987), the partial pressure of carbon dioxide has dropped below  $10^{-3.7}$  (Stumm & Morgan, 1970) or about  $2 \times 10^{-4}$ .

Gypsum is not a straight precipitate of the inflowing sulfate and calcium ions. Anaerobic sulfur bacteria destroy over 90% of all incoming sulfate ions to get at the oxygen (Butler *et al.*, 1973). Thiobacteria and cyanophyta that live along the interface of the resident brine and the inflow produce new oxygen by photosynthesis. They need warm, sunlit shelves to prosper. Their oxygen reconverts the hydrogen sulfate generated by anaerobic sulfur bacteria back into sulfate ions.

A surplus of hydrogen ions and an excess of cations resulting from hydrogen sulfide removal raise the pH and increases the stability of  $\text{CaCO}_3$ . Bicarbonate ions,

unstable in hygroscopic brines of high pH, turn into CO<sub>2</sub>. Concentrating marine brines can entrap only minimal quantities of CO<sub>2</sub>, but fluid inclusions in many halites, sylvites and carnallites contain some. No bicarbonate ions remain in solution at gypsum saturation and CO<sub>2</sub>-solubility drops below 200 ppm (Sonnenfeld, 1984). Carbonate minerals cease to precipitate and the brine is virtually anoxic, containing less than 4 ppm of oxygen (Kinsman *et al.*, 1974).

One or several pink horizons (called "bacterial plates") develop within the mixing zone between surface waters and bottom brines. They are mainly composed of oxygen producing cyanophyta and thiobacteria, which reoxidize hydrogen sulfide into sulfate ions. Reconstituted sulfate ions convert aragonite into gypsum; gypsified algal stromatolites are common in modern shallow lagoons. Blue-green algae and bacterial photosynthesizers continue to flourish in gypsum layers, because gypsum is transparent to ultraviolet radiation. Gypsum precipitation depends on algal oxygen supplies and is restricted to water depths within the photic zone, to shallow shelves and shoals.

As the inflow concentrates, carbonate sedimentation retreats to the entrance or to supratidal parts of the shore as beach rock. Gypsum precipitates in subtropical lagoons at a brine density of 1.115 g/cm<sup>3</sup>, or 4.5-fold concentration, at a rate of about 0.5-1.0 mm/yr. Hite and Buckner (1981) estimated an average of 0.8 mm/yr. Initially, gypsum spreads throughout the lagoon. As long as the subsidence does not drop the bay floor below the photic zone, the brine exchange equilibrates in the gypsum field and the system continues to accumulate gypsum. Gypsum precipitates on shallow shelves and shoals, but precipitation ceases where the net subsidence rate drops the bay floor below the photic zone. Gypsum scavenging can then take over unless halite precipitation coats the bottom.

The original gypsum contains a fraction of celestite [SrSO<sub>4</sub>], built into the crystal lattice or forming small druses. Its solubility is over twenty times smaller than that of gypsum, but it has largely been leached during the conversion of gypsum to anhydrite. At most ambient temperatures prevailing in the subtropical belt, namely, at any water temperature above 18°C (Braitsch, 1964), a brine saturated for halite is hygroscopic enough to convert gypsum to anhydrite. Gypsum is then a very unstable mineral. Most of the trace elements trapped in the crystal lattice of gypsum are also removed during the dehydration of the gypsum. That is particularly true of traces of base metals.

Limestones, such as reefs, marginal to a salt basin can become dolomitized by the interaction of meteoric with evaporitic waters (Magaritz & Peryt, 1994). Indeed, most of the limestones situated paleohydrologically down

slope from an evaporite basin, are dolomitized, but also those are dolomitized in which a porous limestone bed in a salt basin allows meteoric waters to encroach.

Saturation for individual solutes is achieved when the ratio between the cross sectional area of the entrance strait and the brine surface area exceeds a given amount: for gypsum this is about 10<sup>6</sup>, rises for halite to 10<sup>8</sup> and for carnallite to 10<sup>9</sup> (Lucia, 1972). The inflow/outflow ratio likewise determines the degree of saturation: for gypsum it is greater than 4.69, for halite 8.69, for sylvite 13.21, for carnallite 13.81 and for tachyhydrite 16.13 (Sonnenfeld, 1984). It follows that gypsum flats, as indicators of an evaporitic environment, are much more common than salt basins.

A simple calculation of prevailing evaporation rates of modern marine embayments and declining rates of concentrating brines shows that the water surface has to be a multiple of the area in which the chlorides precipitate. Commonly, the ratio between gypsum precipitating shelf and halite precipitating depressions is in the range of 2.5-4.0 (Sonnenfeld, 1984). In contrast to gypsum, rock salt deposition requires a prograding transgressive phase (Friedman, 1980; Jauzein & Hubert, 1984), attaining a maximum during potash precipitation (Matthews, 1975)

#### The thickness of the salt basins

Thick evaporite sequences are thus the product of syn-sedimentary subsidence; alternating evaporite minerals of different solubility are due to oscillating subsidence rates (Jauzein & Hubert, 1984). Where the sea floor remained reasonably flat without grabens and other depressions, such as e.g. throughout the Pannonian plain, the Tyrrhenian, Aegean and Adriatic Seas including the post-Miocene Po Valley depression, the brine produced only gypsum and all other solutes flowed out as undercurrent throughout the entrance straight. Busson (1984) referred to a basin arrested in such a position as an "aborted evaporite basin". He cited the Upper Cretaceous gypsum flats of the Maghreb in Northwest Africa as an example, coeval with an anoxic event in the ancestral tropical Atlantic Ocean. Most of these gypsum flats show textures indicative of a shallow-water environment. Invariably they also show a positive  $\delta^{34}\text{S}$ .

The rate of salt precipitation is at least two orders of magnitude greater than the rate of synsedimentary subsidence. It thus could fill rapidly all synsedimentary depressions. During storms, flash floods, or even winter rains, much of the salt redissolves, only to be added to the next precipitation cycle. All major salt basins contain several such cycles. The amount of salt that is preserved is thus strictly a function of the rate of synsedimentary subsidence and the continuity of marine water supplies. It is not a function of the relative aridity.

### Brine depth

Each salt basin has started as a shallow pan, in which gypsum eventually reached saturation. The depth of salt basins, formerly equated with salt thicknesses disregarding any synsedimentary subsidence. Davies and Ludlam (1973) defined an evaporite basin merely as "a basin with water depth great enough relative to water transparency, wave fetch, and other hydrographic parameters, to permit development of a stable, chemically controlled, density stratification, where photosynthesis below the chemocline was slight or non-existent."

Hovorka (1987) presented evidence of water depths in the 10-metre range, or only 5-10 m (Adams, 1969), shallowing to 2-10 m in many parts, since influx repeatedly could dissolve evaporite rock (Adams, 1970). Amieux (1980) estimated the water depths of Lower Oligocene evaporites in the Alsace to have been in the centimeter to meter range on the basis of gypsarenite levels, desiccation cracks, and erosion of white gypsiferous dolomite. On the basis of the proportionality of precipitate to mother liquor, Strakhov (1962) assigned a brine depth of 2-6 m to both the potash deposits west of the Urals and the ones in the Alsace.

The subsiding salt basins on either flank of the concurrently rising Carpathian Mountains apparently form a couplet of compensating vertical movements along normal faults. They are obviously instigated by events in the upper mantle, such as a lateral displacement of mass, yielding a mass deficiency under the rising mountains and an excess dragging down the subsiding basins. However, our knowledge of the causes of vertical movements in the earth crust is far inferior to that about the horizontal displacement of plates.

### The source of the precipitates

Virtually all the precipitated salts are of marine origin because of the full upward sequence of anhydrite/gypsum, halite, K-Mg-salts, halite and gypsum. They do not represent leached and recycled evaporites. Neither are they evaporites of continental origin, as they would then display a different mineralogical sequence.

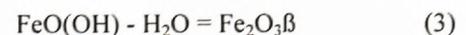
A survey of available quantities of halites and K-Mg-salts precludes a continental source, even by redissolving more ancient (Permian?) deposits. Much of the basement is formed by rocks metamorphosed during mid- and late Paleozoic orogenic events and thus has been eliminated long ago as a source of leached evaporites.

Each peri-Carpathian salt basin is framed by anhydrites that originally represented gypsum shelves. Concentrating brines could slide from these into synsedimentary subsidence centres. Halite and other components of the solute were either deposited in these subsidence centres or expelled through the bottom outflow.

The brine concentrates further in depressions within the basin and quickly reaches halite saturation. The bulk of the solute is represented by sodium chloride and thus its precipitation depletes the sodium and leaves only a very concentrated mother liquor mainly containing KMg-chlorides. The total absence of magnesium sulfate salts, so prevalent in seawater, even though they are less soluble than sylvite and carnallite, indicates the early development of a massive sulfur deficiency in the brine (Borchert & Muir, 1964) due to sulfate reduction by anaerobic bacteria. Once saturation is again reached, potassium chloride minerals start precipitating, which are originally of two types:

(1) the slowly nucleating sylvite [KCl] accumulates under the protection of the inflow that separates it from the atmosphere. Here, beneath the cover of the inflow, the N-hydrides (e.g., urea, ammonium chloride) derived from the decomposition of proteins increase the pH, decrease the solubility of potassium chloride and raise that of magnesium chloride (Seidel, 1917; Emons, 1967) until it becomes infinitely soluble. At the same time, bivalent iron compounds, derived from the decomposition of chlorophyll and hemoglobin are also protected. The primary sylvite is thus white in colour.

(2) the resident brine comes in contact with the atmosphere beyond the inflow wedge. Here the N-hydrides are destroyed and the rapidly nucleating carnallite [KCl.MgCl<sub>2</sub>.6H<sub>2</sub>O] precipitates. Primary carnallite is much more common than primary sylvite, because the area covered by the inflow is much smaller than the exposed water surface. The abundant organic nitrogen in fluid inclusions of carnallite confirm the original presence of N-hydrides and gives the rock its nickname "popcorn salt." The dissolved bivalent iron compounds settle out at the same time as goethite [FeO(OH)]. In the intensely hygroscopic brine this goethite quickly converts to hematite as



The carnallite becomes thus shot through with hematite needles and platelets. Consequently, primary carnallite is red.

Downward circulating waters can leach MgCl<sub>2</sub> out of red carnallites leaving a red sylvite behind at some reduction in volume. They can eventually recrystallize the sylvite and expel all hematite to the crystal boundaries, leaving the sylvite crystals themselves clear. Since an addition of MgCl<sub>2</sub> to sylvite requires a volume increase, it is much rarer and occurs only as a carnallite coating. The ultimate in leaching is reached when all K-Mg-chlorides are removed, leaving a red halite. However, a red halite also occurs in thin halite veins in shales, where the iron has been leached out of the vein walls.

Most marine evaporite basins that reached halite saturation also produced intercalated potash horizons, even

though the precipitation of K-phases requires a more than 90-fold concentration of the brine (McCaffrey et al., 1987). They are usually found in two positions within the basin:

(1) K-Mg-chlorides reduce their solubility upon cooling and thus precipitate on the basin floor, wherever there is a cool groundwater discharge. They then form an intimate mixture with the halite slush present. Such a rock is called sylvinite or carnallite, respectively

(2) K-Mg-chloride brines have a tendency to rise upon cooling and to float against the shelf margin. Because of the rotation of the earth, they abut preferentially against gypsum shelves on the western or north-western side of depressions. They then form pure layers that are gradually thickening westward towards the shelf edge and are abruptly terminated by the reach of ancient rain wash.

As the halite is compacted, the permeability of a basin floor is bound to decrease over time, causing a decrease in leakage through the basin floor and, thereafter, the appearance of the more soluble salts near the top of a chloride sequence (Casas and Lowenstein, 1989; Sanford and Wood, 1991).

It should be mentioned here that the control of K-Mg-chloride facies by decomposition products of proteins or of chlorophyll is an organic steering process of precipitation, in line with the organic control of gypsum precipitation.

Basins with steep sides, delineated by normal faults with substantial throw, do not produce gypsum shelves. They show a gypsum deficiency, e.g., the Lower Cretaceous Sergipe Basin of Brazil, Khorat Basin of Thailand, Cuanza Basin of Gabon or Sannakon Basin of Laos. The calcium stays in solution and the hydrogen sulfide derived from inflowing sulfate ions escapes. The sequence then goes beyond carnallite to tachyhydrite [ $\text{CaCl}_2 \cdot 2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$ ], which can be seen as a Ca-carnallite (Wardlaw, 1972). Tachyhydrite does not contain any organic decomposition products, but may contain some sergipite [ $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ] (Sonnenfeld and Kühn, 1993). Basins with such steep sides and no shelves do not occur in the Carpathian realm.

The ratio of the individual evaporite facies confirms a continuous inflow/outflow regime, inasmuch as there is a distinct shortage of precipitates of higher, compared to those of lower solubility. The existence of a continuous inflow is indicated by an absence of a frequent drying out of the basin, of an outflow by the absence of an isochemical distribution of precipitates. That does not preclude frequent redissolution events by flash floods or by storms mixing surface waters into the brine along deep drafts of seiches.

### Bromine in evaporite deposits

Bromine is incorporated into the halite and sylvite lattices, substituting for chlorine. In carnallites it substitutes preferentially in  $\text{MgCl}_2$  and this depletes surrounding halite. The amount of substitution increases with brine concentration. Where bromine has been leached out of a crystal lattice, the metallic sodium is left behind as platelets and produces a blue colour in halite, metallic potassium a violet colour in sylvite (Sonnenfeld, 1995), and in both cases an increased porosity.

### Siliciclastic sediments

Siliciclastics are fining towards the shores of evaporite basins; chemical weathering yields a lateritic soil. Alternate freeze-thawing in a rich dew and exfoliation or spalling comminute surrounding soil. Limonitic coatings become red hematitic coatings in the dry air, hence the ubiquitous occurrence of "red beds" composed of clays and silts around marine evaporite basins.

Semiarid climates are marked by a dearth of rivers and creeks. The main supplier of clastic sediments are flash floods. These bring material from farther inland and deposit coarse sediments onto gypsum shelves, producing gypsiferous sandstones or arenaceous gypsum. The contribution of silt and clay from nearshore areas is unusually large. These fines are swept out along the interface between surface inflow and resident waters (Sonnenfeld & Hudec, 1985). They settle slowly as a blanket soaked in local brine onto the preexisting halite surface, which may be corroded by partial redissolution. As such the fines can carry with them totally unabraded estuarine fossils that give the false impression that they may have lived far out into the salt basin. The clay layers are mainly composed of members of the Mg-chlorite family and thus represent a sink for magnesium. In Paleozoic evaporites these clays are often converted to illite.

Beyond the reach of the clay laminae there occurs a thin gypsum layer that is witness to the temporary freshening of the brine down to the sediment surface. Farther out into the basin, only a corrosion surface may mark the flash flood.

A resumption of the brine concentration then covers the clay layers with new halite before the interstitial brines could be expelled. That leaves a pipeline of a porous and permeable sediment layer sandwiched between impervious halite, until compaction collapses the porosity and laterally expels the brine.

In the Carpathian realm the rise of the Carpathian Mountains during the salt deposition led to chaotic breccias at the basin margins and to frequent spreads of clay horizons. However, the orogenic movements did not split

existing basins. Instead, they merely accentuated the sills between basins that were originally interconnected by narrow channels. For instance, it is today almost impossible to judge whether the Ciscarpathian salt basin in northeastern Slovakia was ever connected through a narrow passage to the Transcarpathian basin in southeastern Poland, or whether the individual small salt basins along the Muntii Apuseni were once part of a larger depression.

### Epigenetic alterations

Salt basins that were unable to compact before they were affected by major sea level oscillations, remained open to an input of meteoric waters long after they were covered by other sediments. This happened worldwide to all Neogene salt basins, before that to Permian ones, and before that to Infracambrian ones. There must be a connection to the pre- and post-glacial nervousity of sea level. In other ages, only salt basins were affected that were tectonically disturbed and opened up to influx of meteoric waters, e.g., the salt basins in the Zagros Mountains of Iran and the Salt Range of Pakistan. Coeval undisturbed salt basins on the Angara Shield remained undisturbed.

In the Carpathian realm it is not so much the tectonic effect of the rising Carpathian arc (although this may have contributed), as the nervousity of the sea level due to the early manifestations of the Plio-Pleistocene ice age. This contrasts with the Permian sea level oscillations that affected salt basins primarily in the aftermath of an ice age.

As the sea level drops, the gypsum shelves become exposed to rain and runoff. Any gypsum converted to halite by hygroscopic halite-saturated brines is reconverted back to gypsum by the runoff. Although gypsum solubility is small in pure rain water ( $1.017 \text{ m}^3/\text{m}^3$  of rainwater at  $20^\circ\text{C}$  or  $1.0086 \text{ m}^3/\text{m}^3$  at  $30^\circ\text{C}$ ), its solubility increases more than fourfold as soon as some halite dissolves with it. Such a brine can then diffuse into the still permeable clay layers and reach K-Mg-salts that are thickest at the outer limit of rainwash.

The reaction of sylvite and carnallite with incoming brines saturated with calcium and sulfate ions, but also containing rising amounts of sodium and chloride ions, leads to a series of secondary K-Mg-sulfate minerals and some calcium chloride. The first to be leached is  $\text{MgCl}_2$ , which, as magnesium sulfate, replaces gypsum laminae. This produces a reciprocal relationship between thicknesses of gypsum and kieserite [ $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ]. The chloride ions thereby combine with the calcium to form the highly soluble  $\text{CaCl}_2$ . A secondary dehydration converts the gypsum back to anhydrite.

It is noteworthy that kieserite cannot be produced in the laboratory below  $110^\circ\text{C}$  (Braitsch, 1964), a tempera-

ture unlikely to have been attained either on the brine floor or in shallow, uncompacted layers immediately below it. The geothermal gradient would have produced a rock temperature of this magnitude only at a depth of 2,000-2,500 m. There is no evidence that the salt basins were ever buried that deep.

Once also the potassium chloride fraction of carnallite dissolves, the gypsum laminae marginal to the shelves are replaced by polyhalite [ $\text{K}_2\text{SO}_4 \cdot 2(\text{MgSO}_4 \cdot \text{H}_2\text{O})$ ] or in rare cases syngenite [ $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4$ ] after sylvite [KCl].

Further conversion of the potash horizons leads to a kainite hat [ $(\text{KCl} \cdot \text{MgSO}_4)_4 \cdot 11 \text{H}_2\text{O}$ ] by cooler brines descending from above and to langbeinite [ $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$ ] by warmer brines ascending from below. At a temperature of  $83^\circ\text{C}$  kainite is unstable and with halite generates kieserite, sylvite and langbeinite, as well as  $\text{MgCl}_2$  (aq) (Herbert, 1995). A whole series of KMg-sulfates can be produced by a further input of  $\text{Ca-SO}_4$ -brines laced with Na-Cl-brines. Eventually all potassium and magnesium is removed and replaced by sodium.

Retroconversion of sulfatic minerals can also occur. In that case, carnallite is white as well as sylvite, and thus almost indistinguishable from primary deposits.

Since the conversion of KMg-chlorides to KMg-sulfates could have occurred only as long as access to the KMg-layers was provided by an incompletely compacted clay layer, the conversion must have occurred very early. It is, therefore, a moot point to argue whether the KMg-sulfates are secondary or primary. Many conversions of carbonate minerals occur along the Persian Gulf within one cycle of seasons and primary versus secondary minerals often cannot distinguished.

### Economic considerations

The conversion of KMg-chlorides to KMg-sulfates reduced the total volume of potash deposits present and often produced convolute bedding planes. It usually increased the tenor of potash layers and thus rendered them more profitable to mine for fertilizer.

It is interesting to note also, that on their former margins most evaporite basins contain significant hydrocarbon deposits. Evaporite basins generate about three orders of magnitude more organic matter than do the open ocean. Due to the metabolic activity of microorganisms, especially prokaryotes (Rothschild *et al.*, 1994), organic matter is converted into hydrocarbons even in the halite precipitating part of the basin. The hydrocarbon deposits are frequently crude oils near the halite margin, because sodium chloride catalyzes the liquification of organic matter. This is the case both at the southern margin of the Carpathian arc as on its northern rim. Gypsum, on the other hand, fosters the gasification of organic matter.

Heavy metal concentrations and biogenic enrichment in microbial environments, such as algal mats (Taher *et al.*, 1994), are common in salt basins. Since primary gypsum is shot through with algal layers on account of the transparency of gypsum to ultraviolet rays, are lodged in crystal lattice errors in gypsum.

## Conclusion

Miocene salt basins in Cis- and Transcarpathia formed in a semiarid climate that extended farther north than today. These basins were lined by shallow shelves that eventually were covered with gypsum, while more rapidly deepening parts were the site of chloride precipitation. Virtually all precipitates are of marine origin, for they display the typical marine sequence of minerals; no continental evaporite minerals are present, nor is the full sequence curtailed, as is the case in leached and recycled marine evaporites. As KCl- and MgCl<sub>2</sub>-brines become less dense upon cooling, they rise and form wedges against the shelf, due to the Coriolis effect, preferentially on the northwest side of the basin. Inasmuch rivers are rare in a semiarid climate, flash floods are the major suppliers of siliciclastic sediments. While the coarse fraction produces gypsiferous sandstones near the shores, the fines float out at the interface between inflow and resident brine. When the fines finally settle, they retain permeability until compacted. An oscillating sea level before or after an ice age bares the shelves. Eroding gypsum of shelves can enter and get into contact with potash horizons, converting them from chlorides to sulfates. Economically, salt basins are not only major suppliers of halite and of potash fertilizer, but often also contain in surrounding porous strata, e.g., reef complexes, either hydrocarbons or lead-zinc deposits.

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

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**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.

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### 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; Poberecki, 1991; Petryczenko *et al.*, 1995; Petrichenko *et al.*, 1996; Peryt *et al.*, 1997).

The present paper summarizes the results of joint research program of the Institute of Geology and Geo-

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 (Wyszyński, 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-

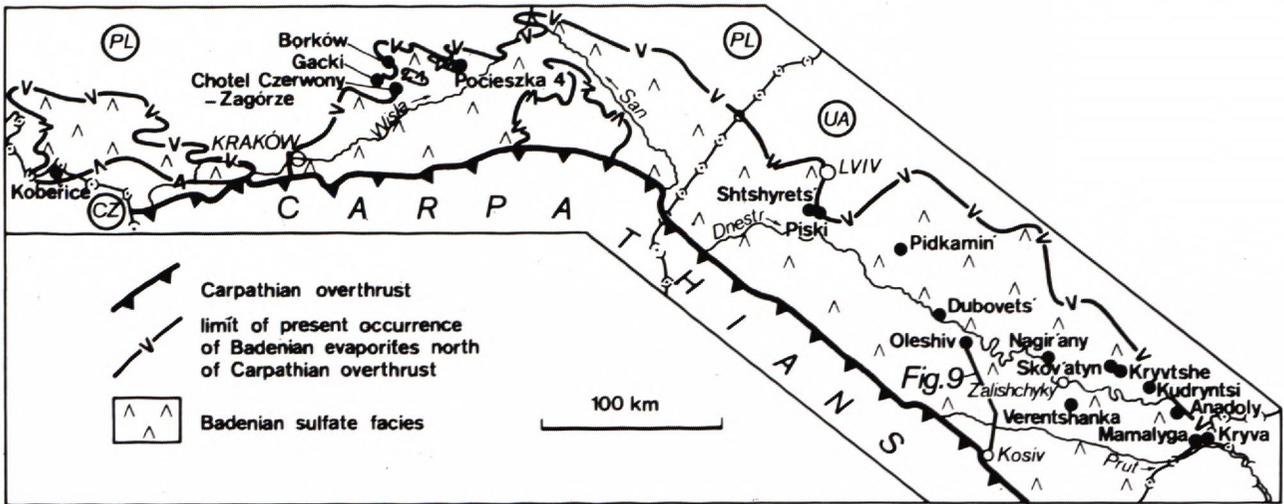


Fig. 1. Occurrence of Badenian gypsum in the Carpathian Foredeep basin

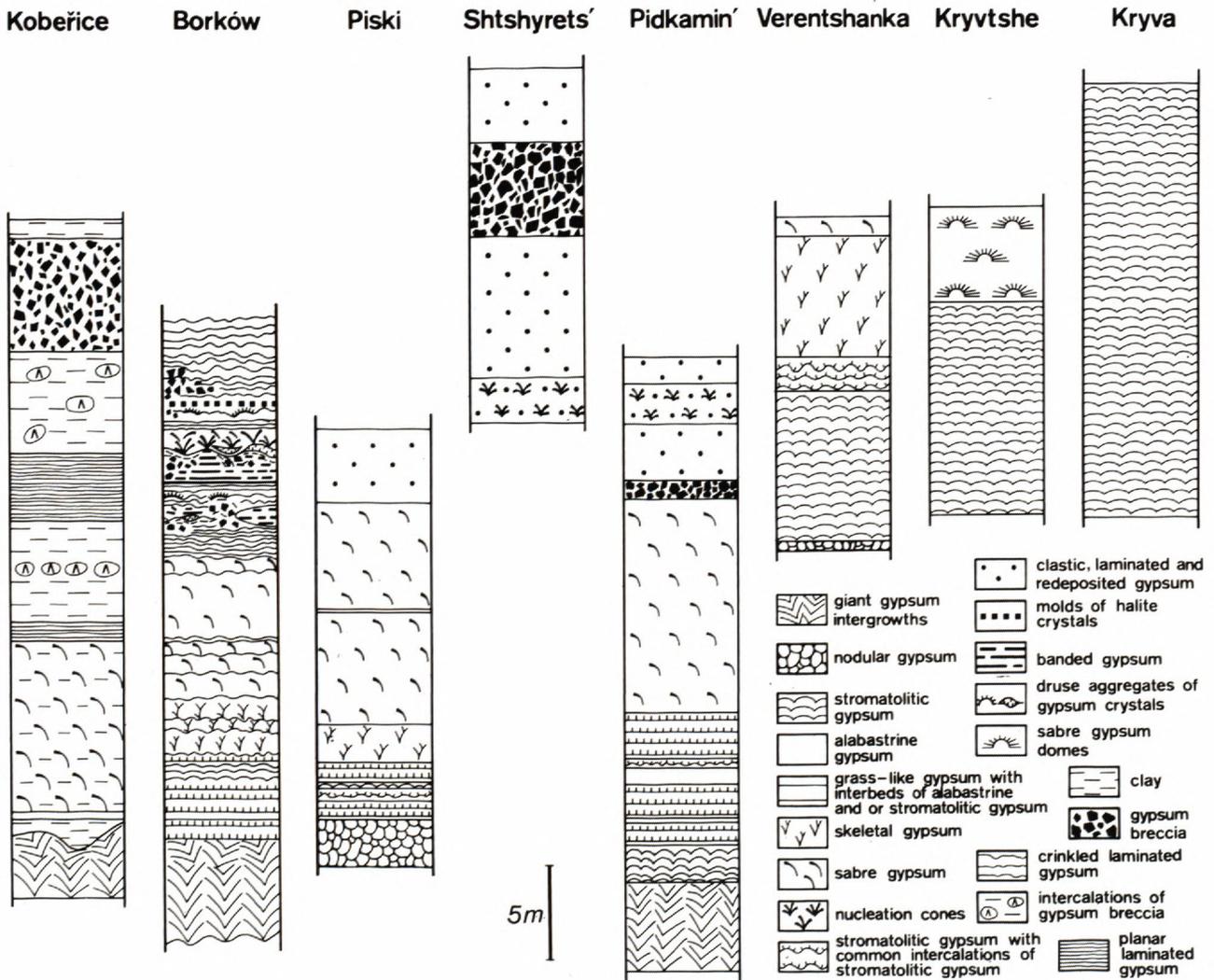


Fig. 2. Characteristic profiles of Badenian gypsum

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

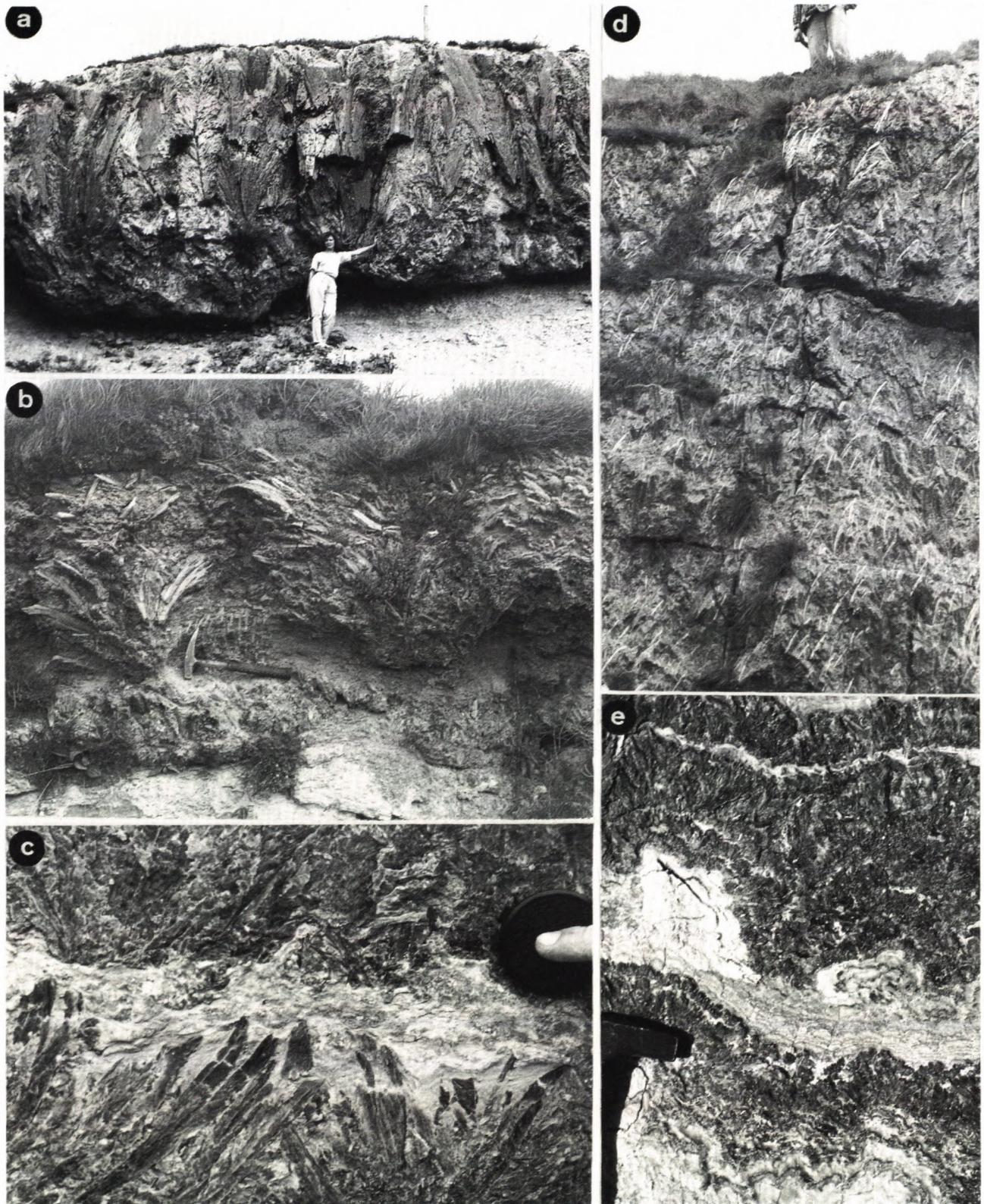


Fig. 3. Aspects of Badenian gypsum.

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'.

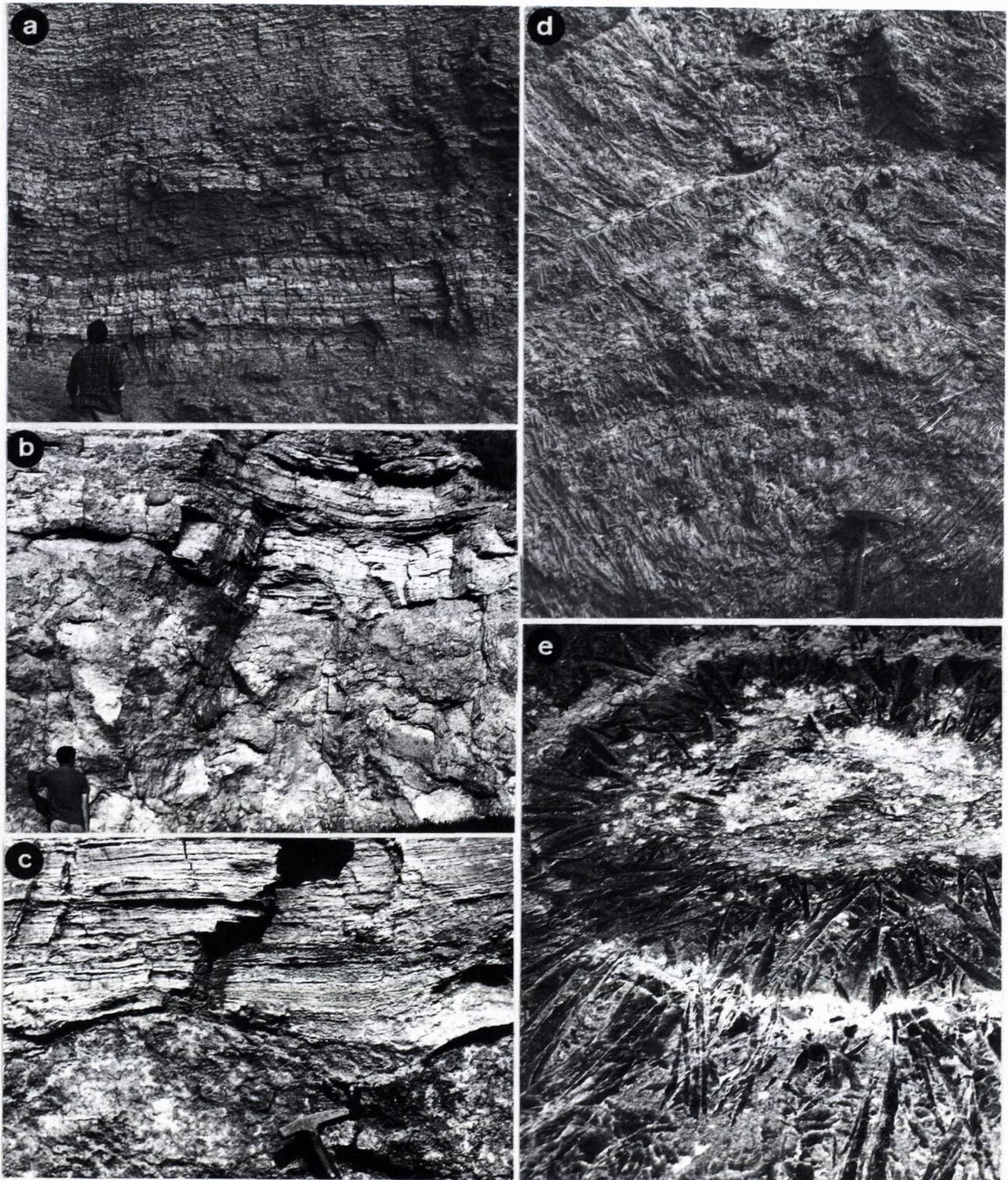


Fig. 4. Aspects of Badenian gypsum.

*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.

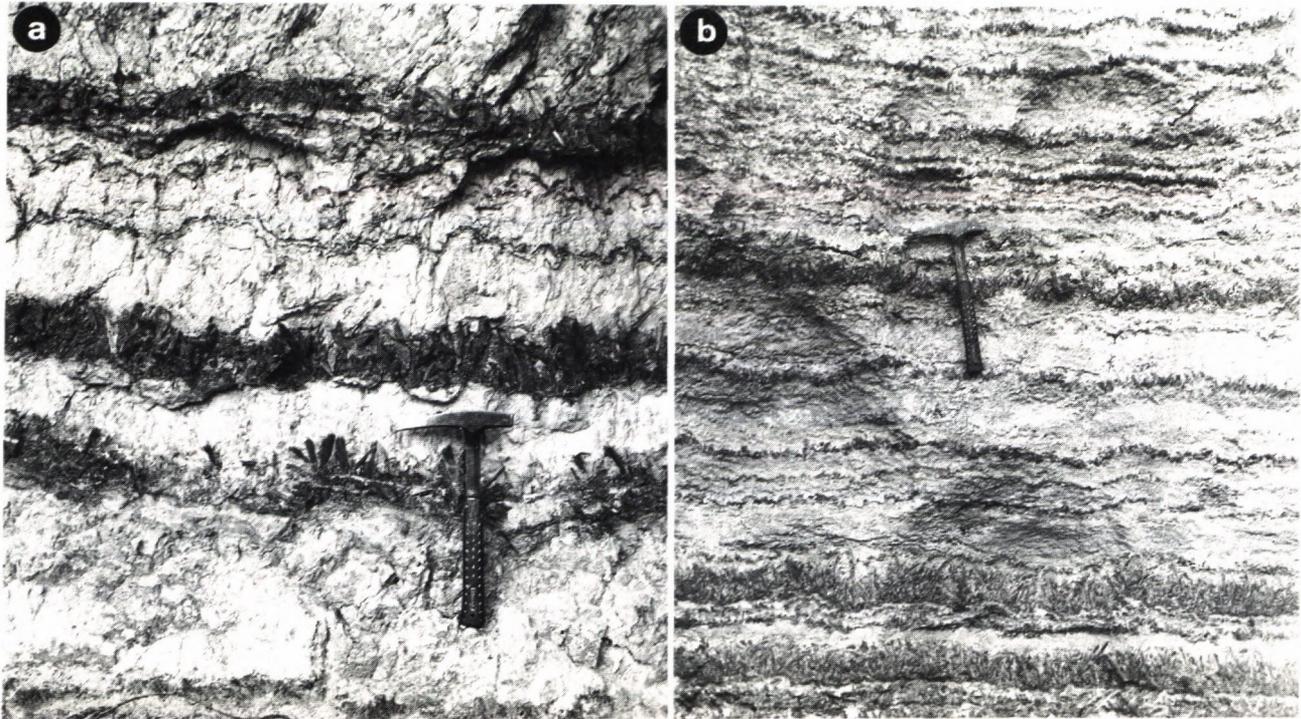


Fig. 5. Aspects of Badenian gypsum.

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  $\mu\text{m}$ ) 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 slightly 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-

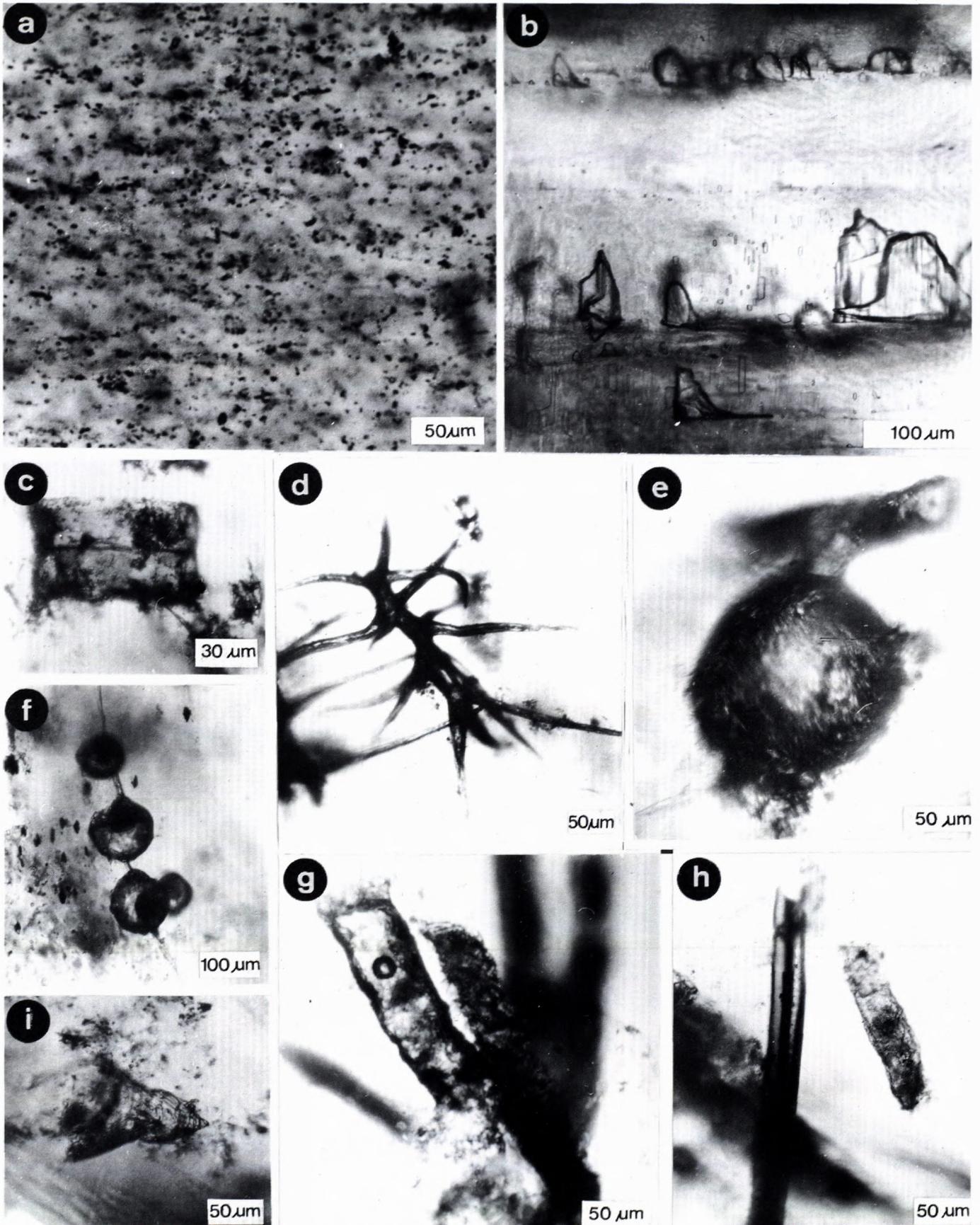


Fig. 6. Inclusions of microorganisms in the Badenian gypsum.

a - Mass occurrence of calcareous nannoplankton in sedimentary gypsum showing weak zonation. 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 algae. Borków; h, i - Inclusions of problematic microfossils. Borków.

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 fresh-water 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 Koberice (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, Zalizhchyky 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
Koberice (CZ)	5	-1.5	33
Piski (UA)	7	-1.2	20
Verentshanka UA)	3	-2.5	45

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 splitting 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 splitting 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 sodium 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 the thernardite 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 mirabilite, 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 Verentshanka, the water of total mineralization of water of 53-54 g/l contained (in g/l): 36.4 of NaCl, 8.1 of K<sub>2</sub>SO<sub>4</sub>, 5.9 of MgSO<sub>4</sub>, and 3.1 of CaSO<sub>4</sub>. The content of CaSO<sub>4</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> in the north-western part of the basin (Borków - during deposition of sabre-like gypsum and

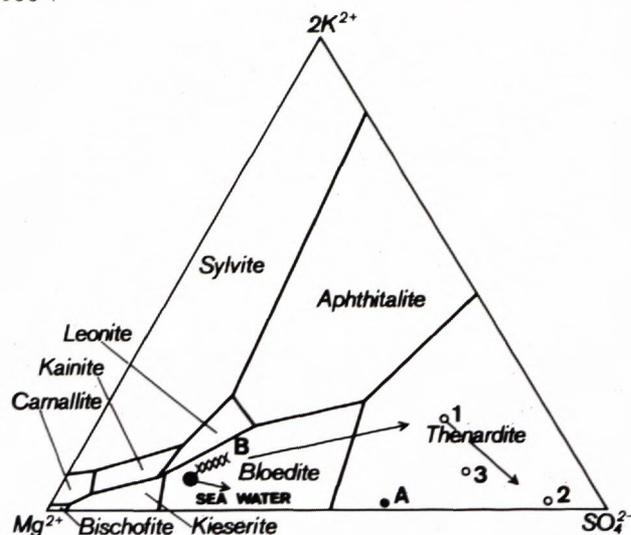


Fig. 7. Points showing composition of brine inclusions in the Badenian sedimentary gypsum of Carpathian Foredeep on the diagram after Stewart (1963) for 25°C.

1 - Verentshanka, 2 - Borków, 3 - Koberice, 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).

Koberice - 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 (Babel, 1991; Peryt *et al.*, 1997) and the laminae or beds of terrigenous clays in the entire area of the Carpathian Foredeep which indicate considerable refreshing 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

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 <sup>+</sup>	21.3	15.7	25.8	30.6	22.0
K <sup>+</sup>	1.8	0.9	6.5	16.1	0.9
Mg <sup>2+</sup>	3.7	1.8	2.2	3.7	5.5
Ca <sup>2+</sup>	6.5	13.6	2.7	1.2	4.5
Cl <sup>-</sup>	25.0	15.2	39.8	55.6	35.4
SO <sub>4</sub> <sup>2-</sup>	41.7	52.8	23.0	7.8	31.9
NaCl	41.2	25.1	65.6	78.3	54.1
Na <sub>2</sub> SO <sub>4</sub>	15.7	18.0	-	-	-
KCl	-	-	-	1.7	1.8
K <sub>2</sub> SO <sub>4</sub>	4.0	2.0	14.4	-	-
MgSO <sub>4</sub>	18.3	8.9	10.9	6.4	26.0
MgCl <sub>2</sub>	-	-	-	9.4	0.7
CaSO <sub>4</sub>	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 nanoplankton 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 conserved, 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, elas-

tic and does not dissolve in organic solvents 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 solvents.

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 nanoplankton occur in clayey intercalations in gypsum sequences of different sections (*e.g.* Peryt *et al.*, 1994, 1997). South of Verentshanka, in sedimentary gypsum relics of nanoplankton (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

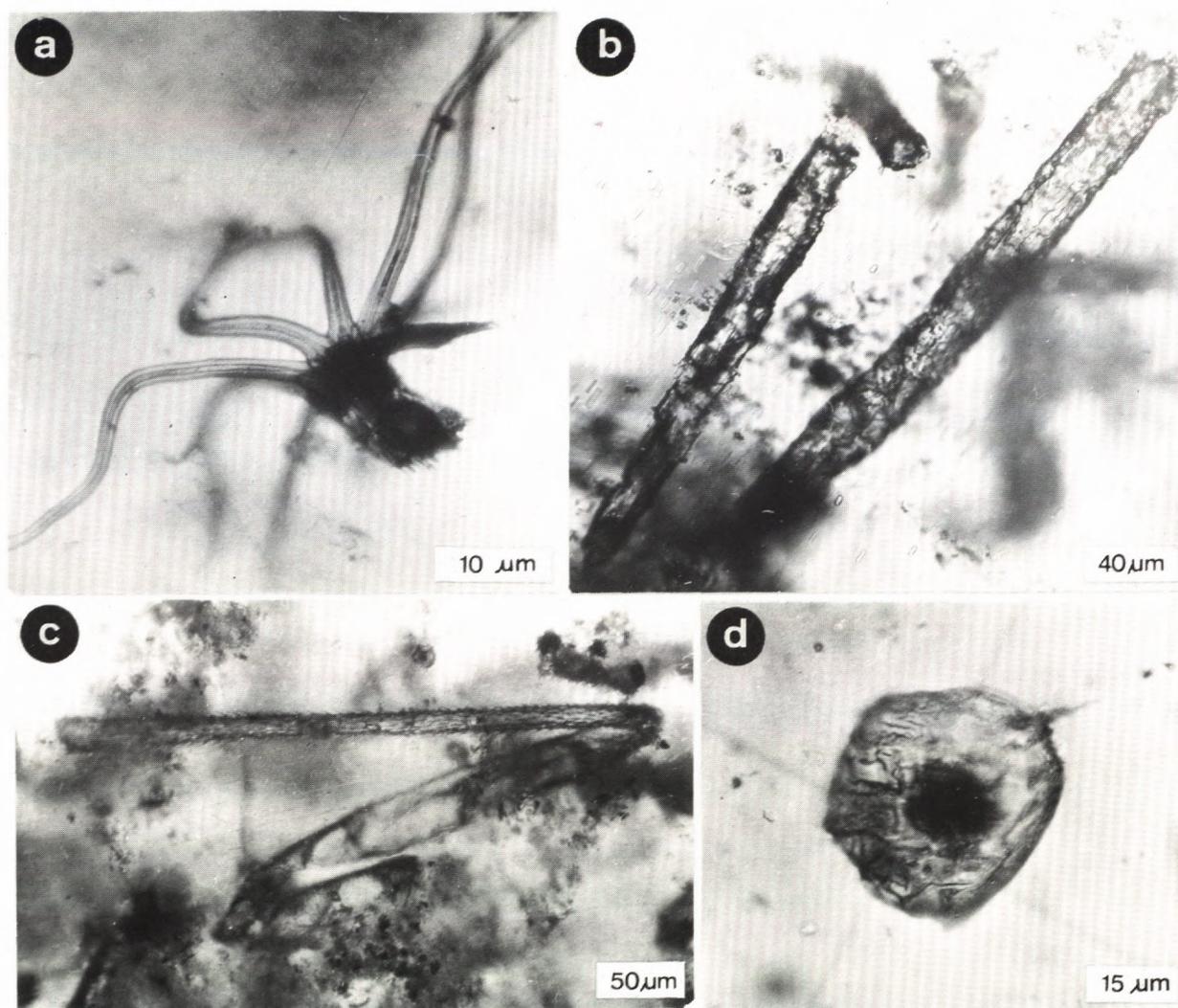


Fig. 8. Inclusions of microorganisms in the Badenian gypsum.

*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 pleochroism and wavy polarization in dark-gray colors;  $N_p = 1.6002$ .

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-

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

	P <sub>2</sub> O <sub>5</sub>	NH <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaCO <sub>3</sub>
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 inertia 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 (Kudryntsi-Verentshanka region), gypsum is commonly

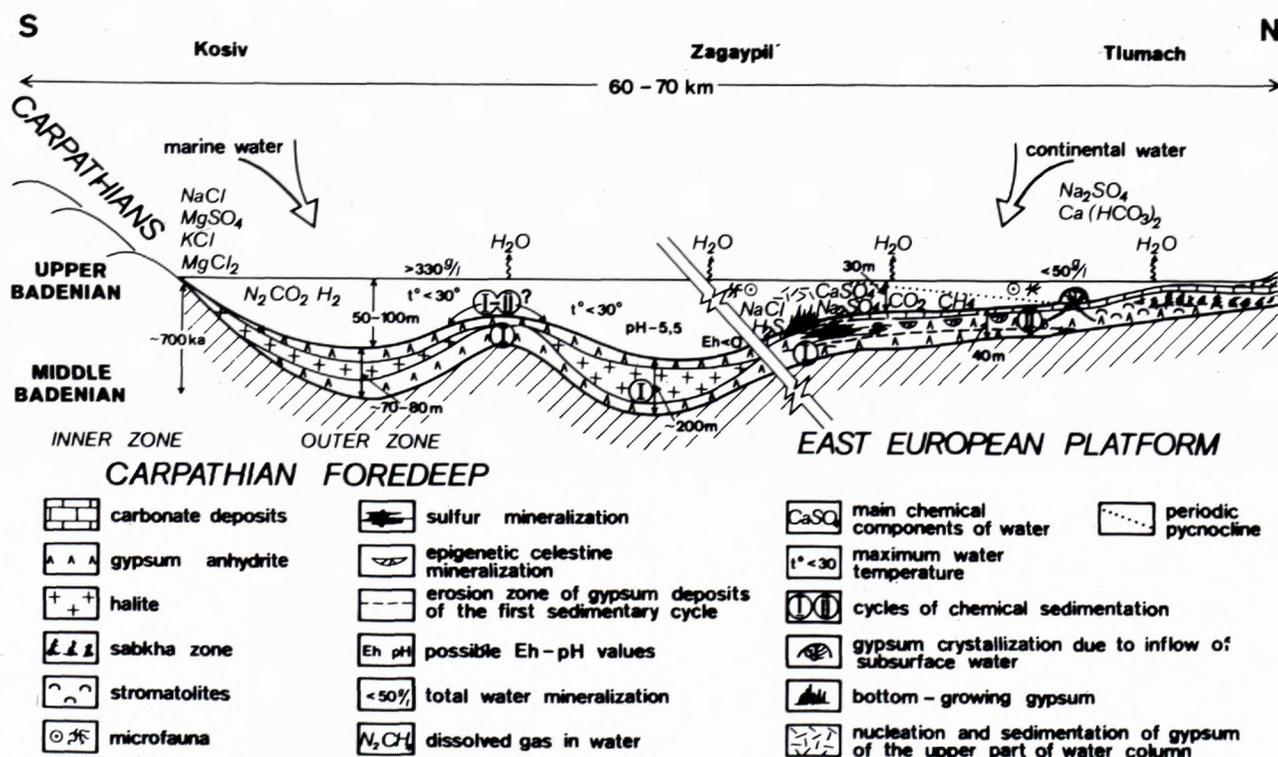


Fig. 9. Chemical model of the Badenian evaporite basin in the south-eastern part of the Carpathian Foredeep in Ukraine (the line of cross-section is shown in Fig. 1).

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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## Westernmost occurrence of the Middle Miocene Badenian gypsum in central Paratethys (Kobeřice, Moravia, Czech Republic)

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**Abstract.** The gypsum sequence outcropping in an active gypsum quarry in Kobeřice shows many similarities to other sections known from the northern marginal part of the Badenian basin. However, the peculiarities of Kobeřice gypsum section indicate its more basinward location when compared to other gypsum exposures known from Poland and West Ukraine. The lower part consists of crystalline gypsum (giant gypsum intergrowths, sabre gypsum) accompanied by gypsiferous claystones and microcrystalline gypsum, and the upper part consists of interbedded laminated gypsum, gypsiferous claystones and breccias. These breccias are interpreted as debrites. The laminated gypsum units can be interpreted as fall-out from a low-density turbid layer. The major part of the gypsum sequence of Kobeřice originated thus in deeper, density-stratified waters. The only exceptions to rather deeper water conditions prevailing during gypsum (and related claystone) deposition are exposure episodes following deposition of giant gypsum intergrowths and during the alabastrization phases. Particular gypsum units are common throughout the quarry, although some distinct lateral changes are observed. Amount of clay material in the facies of giant gypsum intergrowths increases toward the east and this increase is accompanied by change of massive facies to skeletal facies of giant gypsum intergrowths. Also the thickness of laminated gypsum units as well as the number and thickness of breccias in the upper part of gypsum sequence increase toward the east, whereas the frequency of amalgamates of supercones decrease toward the east. These changes observed in the quarry reflect the presence of a paleoslope.

**Key words:** Badenian, gypsum, facies, sedimentology, micropaleontology, geochemistry, Paratethys

### Introduction

In the middle Miocene Badenian evaporite basin of the Carpathian foreland basin, broad zones of sulfate deposits occur in the marginal parts, and narrow zones of chloride sediments are restricted to the basin center. The origin of these evaporites is related to the salinity crisis at the end of middle Badenian that was caused by the regression of the Paratethys Sea toward the Mediterranean Tethys and the Indopacific and the regression of the sea (Seneš, 1989).

The time and facies relations of evaporites occurring in marginal and central parts of the Carpathian foreland basin are still unclear and different correlations have been proposed for particular parts of the basin. However, it is possible to correlate particular marker beds in both domains over a distance of hundreds of kilometers (e.g. Garlicki, 1994; Peryt *et al.*, 1994) suggesting common

controls of evaporite deposition regardless of the geological setting.

Outcrops of Middle Miocene Badenian gypsum are known from a considerable number of localities. The best studied examples are those from the northern marginal part of the basin in southern Poland (Kwiatkowski, 1972; Babel, 1987, 1991; Kubica, 1992; Kasprzyk, 1993; Peryt & Jasionowski, 1994) and West Ukraine (Peryt, 1996). In this paper we would like to characterize the gypsum outcropping in an active gypsum quarry in Kobeřice that is the westernmost occurrence of the Badenian gypsum in the Central Paratethys Basin. The Kobeřice outcrop is also important because it illustrates significant lateral changes in gypsum facies.

The field studies in Kobeřice were done during 1991-1996. Because the exploitation front in the quarry

migrates with time, it was possible to establish geometrical relations among the particular gypsum units. The paper summarizes the research done so far that was supported mainly by the National Fund of Environment Protection and Water Management (Projects 2.29.5029.00.0 and 2.14.0100.00.0). The initial results have been presented during the international symposium "Neogene evaporites of Central Paratethys: facies, mineral resources, ecology", Lviv 1994 (Karoli et al., 1994).

**Geological setting**

The Koberice quarry lies in front of the flysch nappes of the Western Carpathians, in the Opava Basin that is filled by Badenian deposits which transgressed over the Culm deposits or older rocks (Fig. 1). Lower Badenian rocks that underlie the gypsiferous section occur west of Opava. Their maximum thickness reach 300 m; in Koberice the Lower Badenian deposits are 50 m thick

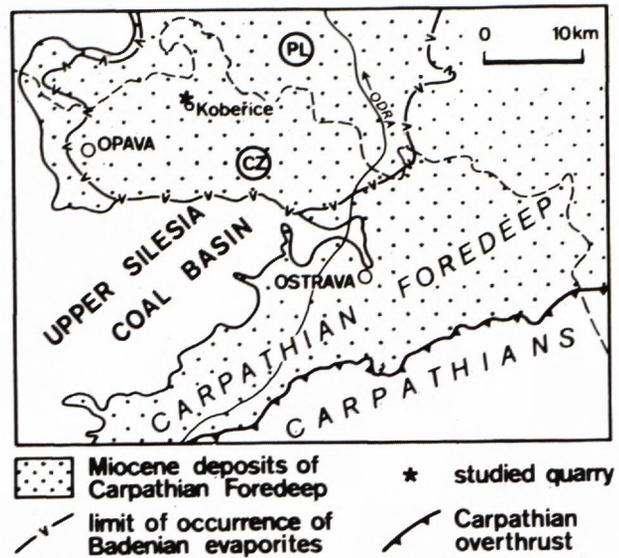


Fig. 1. Location of the Koberice quarry.

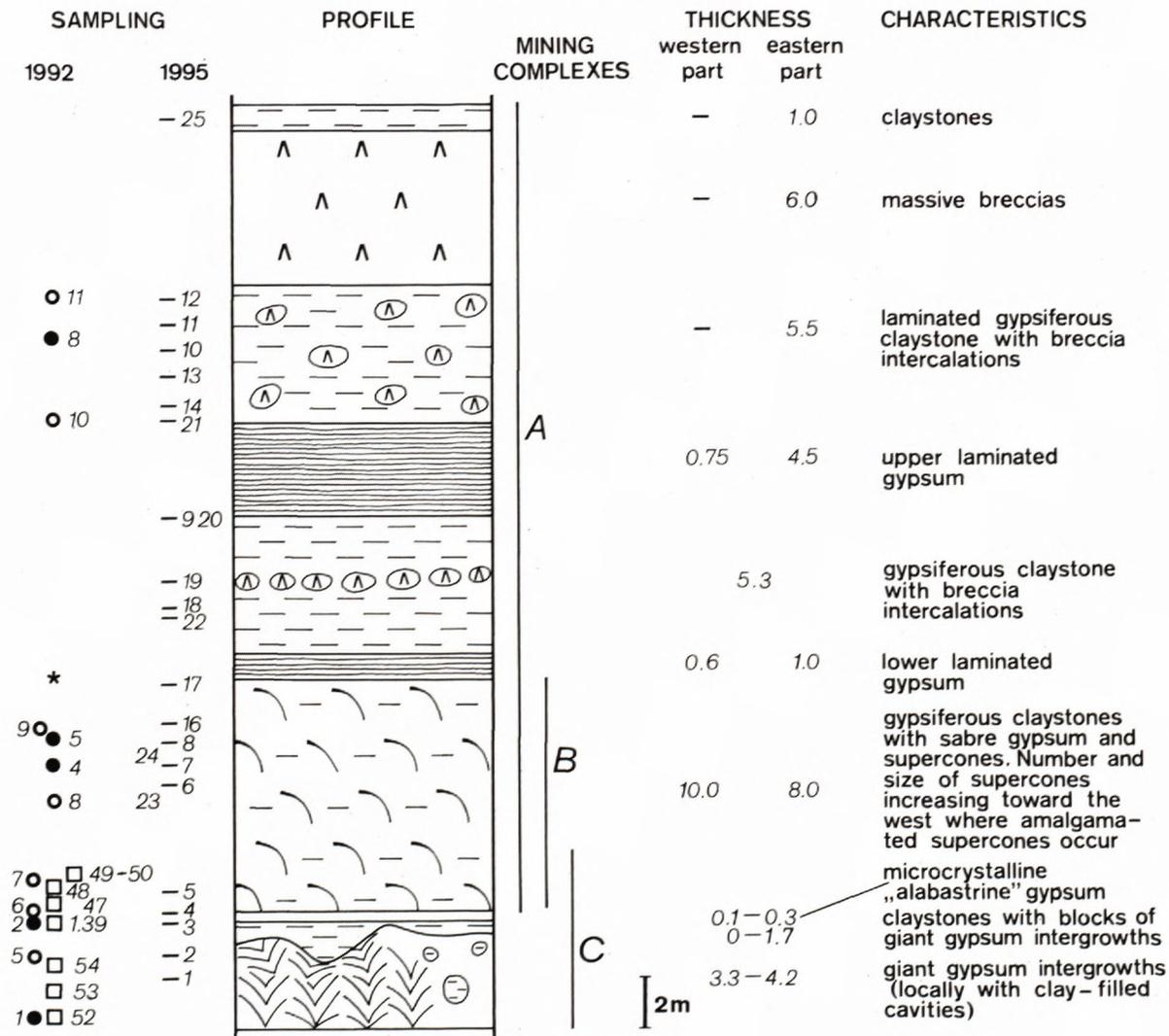


Fig. 2. The gypsum section exposed in the Koberice quarry showing the sampling points in 1992 and 1995. In 1992 sampling, filled circles show samples for isotopes, empty circles are for micropaleontological studies, squares are for fluid inclusion study, and the star is the sample used for organic geochemical study.

(Matl et al., 1979). The Lower Badenian sequence begins with basal conglomerates although these are lacking in places; variegated clays and sands occur locally (Roth et al., 1962). At Kobeřice, the sequence contains volcanites and beds of breccia and conglomerates with volcanic material. These beds are overlain by red or grey clays that contain thin beds of volcanoclastics, occasionally with effusives or nepheline basanite. A rich microfauna with *Orbulina suturalis*, the Moravian index species (Matl et al., 1979), characterizes these deposits.

The Middle Badenian deposits are 50-300 m thick; thinner parts are related to paleo-highs in the Culm deposits. In Kobeřice the thickness of the Middle Badenian is 50-70 m. The basal part contains clays with *Bulimina striata*, *Uvigerina asperula*, *Globigerina decoraperta* and others, and the upper part contains a gypsum complex with clay intercalations. Below the gypsum complex, glauconite grains as well as coal fragments occur on paleo-highs.

Three general varieties of gypsum development are distinguished by mining engineers (Fig. 2). In the basal part (complex C in the mining terminology) that is 1 - 9 m thick, coarsely crystalline gypsum occurs, overlain by thin microcrystalline gypsum and claystone laminated with gypsum. The middle part (complex B) is 1 - 10 m thick and is called blocky because it is composed of blocks of crystalline gypsum that are enclosed in grey clays. The upper part (complex A) is 20 m - 40 m thick and consists of microcrystalline gypsum and clays with locally occurring gypsum-filled druses.

Above the gypsum complex are Upper Badenian sandy clays, 250 m in maximum thickness that contain an impoverished *Bulimina* microfauna (Matl et al., 1979). At Kobeřice, the Upper Badenian is only 20 m thick; limestone intercalations 0.5 m thick are present. Above the Badenian sequence are youngest Neogene sediments: Pliocene breccias 30 m thick.

The Kobeřice quarry is 600 m long. The greatest thickness of gypsum complex was recorded in the eastern part of the quarry. Particular gypsum units are common for the entire quarry (Fig. 2) but some distinct lateral trends of thickness and facies are visible as discussed below.

### Description of the section

The gypsum is conventionally subdivided into two parts. The lower part (12.5-14.5 m thick) consists of crystalline gypsum (giant gypsum intergrowths, sabre gypsum) accompanied by claystones and microcrystalline gypsum, and the upper part (up to 23.5 m thick) is built of interbedded laminated gypsum, gypsiferous claystones and breccias.

The mineralogical composition of claystones associated with gypsum in Kobeřice as indicated by X-ray diffraction studies is discussed in the next chapter.

**Unit of giant gypsum intergrowths.** A 4-m-thick unit of giant gypsum intergrowths occurs at the base of the sequence (Fig. 3a). The measured thickness of the unit is 3.3 to 4.2 m, and the variation results mostly from a very irregular relief of the upper surface of the unit.

The unit is built of big (up to 2.5 m high in the western part of the quarry) blocky crystalline intergrowths (Fig. 3b). Such large, vertically arranged gypsum crystals that form giant intergrowths have been earlier recorded in southern Poland (Babel, 1987, 1996) and West Ukraine (Peryt, 1996). The gypsum crystals are rich in clay material which results in their dark coloration. The amount of clay material increases towards the eastern part of the quarry. Babel (1987) discussed the arrangement of clay impurities in the gypsum crystals of central Poland and showed that the clay material was trapped along the boundaries between lenticular subcrystals (Babel, 1987, p. 11). Along with the increase of clay material in the unit, the facies changes from massive to skeletal. In the Nida Valley where such lateral changes have earlier been recorded by Babel (1996), massive facies of giant gypsum intergrowths is related to bottom elevations while skeletal facies characterizes bottom depressions (Babel, 1996, Fig. 7).

Large cavities (up to 1 m across) filled with claystones within the skeletal facies of giant gypsum intergrowths have been recorded in the unit of giant gypsum intergrowths in the eastern part of the quarry. Their distribution in the vertical profile is random. The large cavities are sedimentary features as indicated by growth directions of giant gypsum crystals toward these cavities that were filled initially by brine and clay. Within the unit of giant gypsum intergrowths in the eastern part of the quarry, common manifestations of alabastrization (crusts a few cm thick, clear nodules) can be seen; the distribution of these features is random.

The upper surface of the unit of giant gypsum intergrowths is furrowed (Fig. 3a), and the irregularities reach 1 m. These furrows are filled by clays and clasts of giant gypsum intergrowths, in places as much as 50 cm across. A similar, although not so intensively corroded, contact of giant gypsum intergrowths with overlying clays (not more than a few tens of centimeters thick) was recorded in southern Poland (Babel, 1987).

**Unit of clays overlying the unit of giant gypsum intergrowths.** The unit is a few tens of centimeters thick (Fig. 3a), rarely only 10 cm thick, and in a few places it is lacking. In such places, grass-like gypsum occurs (Fig. 3c). In these clays, planktonic foraminifers abound. Considering the existence of irregularities of the top of the overlying unit, the actual thickness of clays may be as much as 170 cm.

**Unit of microcrystalline ("alabastrine") gypsum.** The clays are overlain by a 10-32-cm-thick layer of alabastrine gypsum in the western part of the quarry (Fig. 3d).

A similarly developed unit has been recorded in other peripheral parts of the Badenian gypsum basin (Kasprzyk, 1993; Peryt *et al.*, 1994; Peryt, 1996). Toward the eastern part of the quarry, the number of alabastrine layers increases; the thickest of these is the uppermost one. Rarely, alabastrine gypsum overlies directly the giant gypsum intergrowths unit (Fig. 3c). The upper surface of the alabastrine gypsum unit is commonly rippled (with irregularities up to 1 cm) although in places it is very even. White alabastrine gypsum is considered as having been formed diagenetically by dehydration of gypsum to anhydrite and rehydration of anhydrite back to gypsum, as in the Messinian of Tuscany, Italy (Lugli & Testa, 1996).

Unit of gypsiferous laminated clays with sabre gypsum. The unit of microcrystalline ("alabastrine") gypsum is overlain by a unit of gypsiferous clays with sabre gypsum crystals as well as supercones built of sabre gypsum crystals and their amalgamates forming large gypsum bodies within the gypsiferous claystones (Fig. 4, 5). The sabre gypsum crystals in Kobefice (Fig. 4d) have many similarities to characteristically curved, strongly elongated crystals known from the middle part of Badenian gypsum sequence of southern Poland (sabre-like gypsum - Kwiatkowski, 1972) and Ukraine (sabre gypsum - Peryt, 1996).

The thickness of the unit is 10 m in the western part, where the gypsum content is the greatest, and decreases to the east to 8 m. The lower part of the unit is built of interlaminated gypsum and claystones (Fig. 4a, b). Higher up in the sequence clays occur with isolated bent sabre gypsum crystals (Fig. 4d) or with gypsum bodies (nucleation cones and their amalgamates - Fig. 4b, e, Fig. 5c). Sabre gypsum crystals have a very constant dip (10-20°) and strike (170°) throughout the quarry. Within the claystone framework, the distribution of supercones is bizarre. It is clearly seen that toward the east the number of gypsum bodies and their size decreases and the thickness of claystone between the alabastrine gypsum unit and the first gypsum body increases. In the central part of the quarry this distance is 140 cm.

Irregular lenticles of laminated claystone are observed within some larger gypsum bodies in the western part of the quarry (Fig. 4c). Contact of bodies built of sabre gypsum crystals with gypsiferous claystones is usually abrupt (Fig. 4d). Such contacts occur both at the base of the gypsum bodies and at their flanks.

The development of clusters or stellate groupings of gypsum is common where crystal nucleation took place on a soft substrate (Schreiber, 1988). The crystals sank into the underlying substrate under their own weight as they grew; the base of one such grouping is shown in Figure 5b. The sinking was partly responsible for greater

dips of sabre gypsum crystals. On the other hand, crystallization of such groupings could have led to disturbances above the grouping, such as thinning on laminae in the overlying claystones closer to the top of the grouping, as well as contortions of clay laminae on upper flanks of the grouping (Fig. 5a). These disturbances in laminae arrangement over the groupings resulted from compaction. In such cases, the selenite crystals are commonly upright, and their depositional origin is supported by the inclusions of microorganisms in gypsum crystals (cf. Fig. 11b, g).

The nucleation cones clearly depress the underlying laminated claystones (Fig. 5b, c). Such features are known from the Messinian gypsum of Sicily (Lo Cicero & Catalano, 1976) and Sorbas Basin (Dronkert, 1976, 1985). The supercones are thought to have formed by overgrowth of smaller precursors and by crystallization within a soft mud/clay.

These gypsum bodies built of sabre gypsum crystals are interpreted to have formed owing to brine circulation through a still partly soft and water-saturated sediment; accordingly, these bodies are early diagenetic formations (but depositional as they originated within the depositional environment - Spencer & Lowenstein, 1990). The sabre gypsum crystals are mostly sedimentary forms as indicated by inclusions of microorganisms (see below).

Upper part of the gypsum sequence. The upper part of the gypsum sequence consists of interbedded laminated gypsum, gypsiferous claystones and gypsum breccias (Fig. 6). At the base of this part, a unit of laminated gypsum occurs. It is 100 cm thick in the eastern part of the quarry, and toward the western part its thickness decreases to 60 cm. The unit is built of very finely laminated gypsum that is locally accompanied by internal folding which is attributed to lateral displacement (slumping) (Fig. 6b).

The unit of laminated gypsum in the quarry is overlain by a complex of 5.3-m-thick gypsiferous claystone that contains massive breccia intercalation in its middle part (Fig. 6a). The thickness of this intercalation varies: in some places it is lacking and in others it is a few meters thick. The breccias are characterized by blocks of the laminated gypsum as well as coal fragments. The base of these bodies is locally erosional (channels?) but more commonly it is sharp, and non erosional.

The upper laminated gypsum unit that overlies the unit of claystones and breccias is 75 cm thick in the western part of the quarry, and eastward the thickness increases and reaches 4.5 m in the easternmost part of the quarry. In this upper unit of laminated gypsum, pseudomorphs after halite crystals abound. The unit contains layers and flasers of more massive gypsum as well as breccias, very similar to those occurring in the laminated gypsum of the upper part

of the gypsum sequence (unit "n") in Borków, southern Poland (Peryt & Jasionowski, 1994).

The upper laminated gypsum unit gradually passes into laminated gypsiferous claystones (5.5 m thick; Fig. 6c) containing common breccia intercalations (Fig. 6d); this part of the section occurs only in the eastern part of the quarry. Above the laminated gypsiferous claystones, in the easternmost part of the quarry, 6 m of massive

breccias occurs where thick irregular beds can be distinguished in places. The breccias are overlain by 1-m-thick claystones that contain massive breccias, covered by Quaternary gravels. In these claystones, planktonic foraminifers have been recorded.

It seems that a considerable part of the upper part of gypsum sequence is made of coarse-grained gypsrudites or breccias that are interpreted as debrites



Fig. 3. The lower part of gypsum sequence in Kobeřice.

a - The lower part of gypsum complex: unit of giant gypsum intergrowths (a) showing a very irregular upper surface (arrowed) overlain by claystones (b) with large clasts of giant gypsum intergrowths (arrows) and then by a layer of white microcrystalline ("alabastrine") gypsum (c) followed by claystones interlaminated with gypsum (d). East-central part of the quarry; b - Giant gypsum intergrowths. Western part of the quarry; c - Two beds of white microcrystalline gypsum separated by grass-like gypsum. East-central part of the quarry; d - White microcrystalline gypsum overlain by claystones interlaminated with gypsum. West-central part of the quarry.

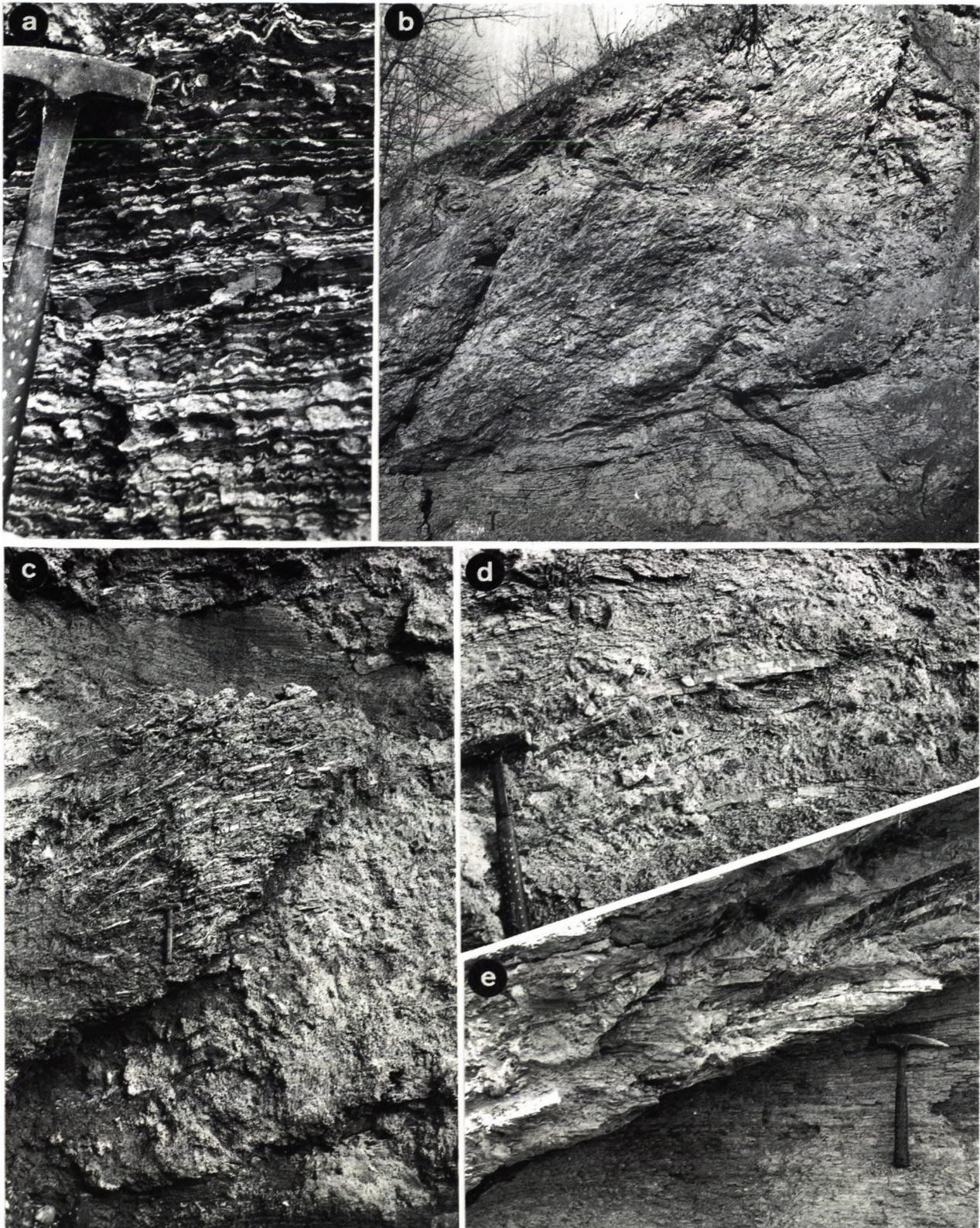
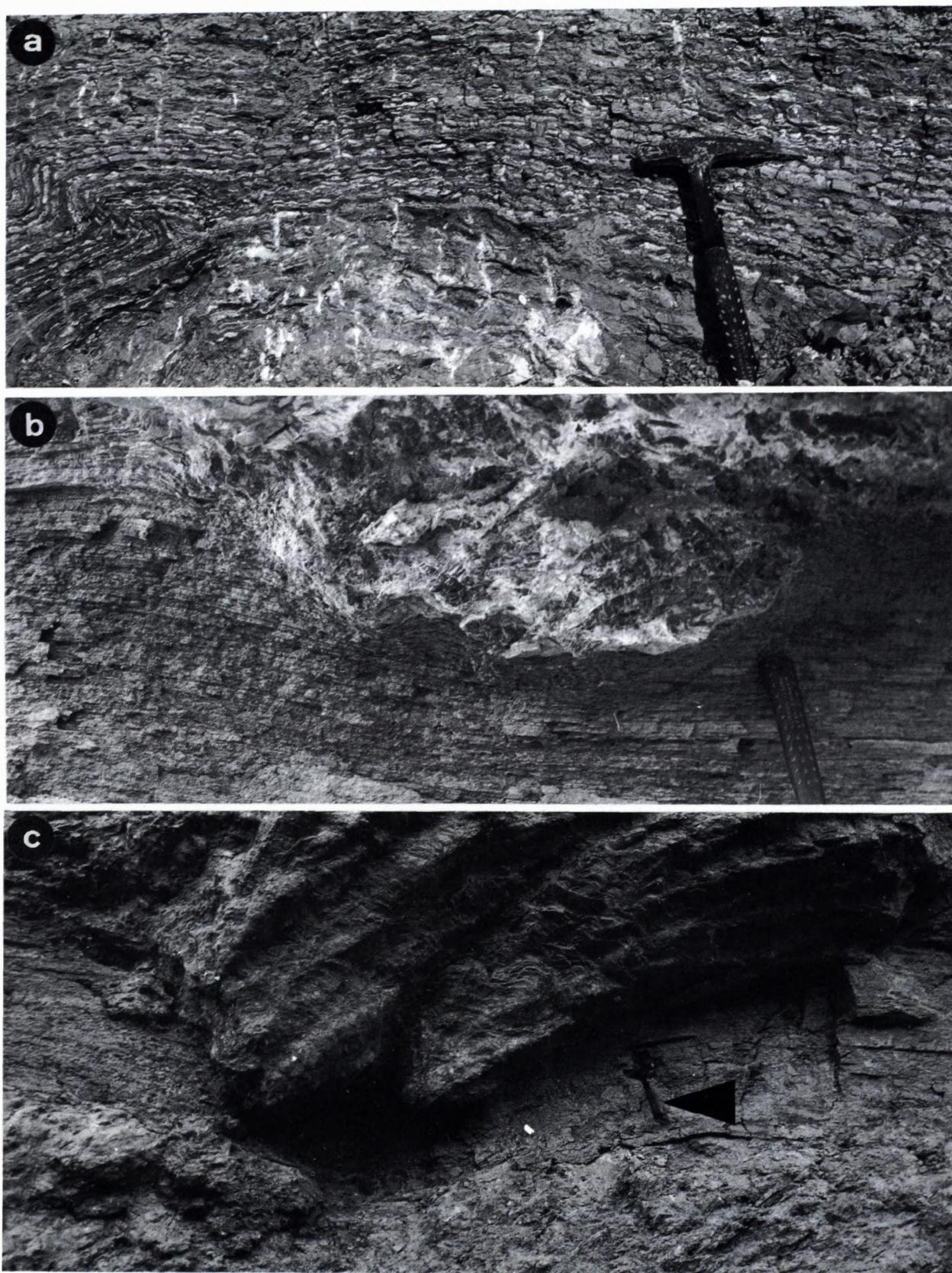


Fig. 4. Unit of gypsum laminated clays with sabre gypsum (a, c-e - west-central part of the quarry, b - western part of the quarry). a - Aspect of claystones with gypsum laminae that are continual or composed of nodules; b - Claystones with gypsum laminae (in the lower part) overlain by amalgamated bodies composed of sabre gypsum crystals; c - Photo showing relations of claystones and amalgamated bodies built of sabre gypsum crystals; d - Sabre gypsum crystals occurring in claystones; e - Contact of a body built of sabre gypsum crystals with claystones.



*Fig. 5. Deformations related to supercones (west-central part of the quarry).  
a - Top of a grouping of gypsum affecting the cover; b - Base of another grouping that sank into the substrate during growth, forming a typical depression cone; c - Contact of supercone with underlying claystones; hammer (arrowed) as a scale.*

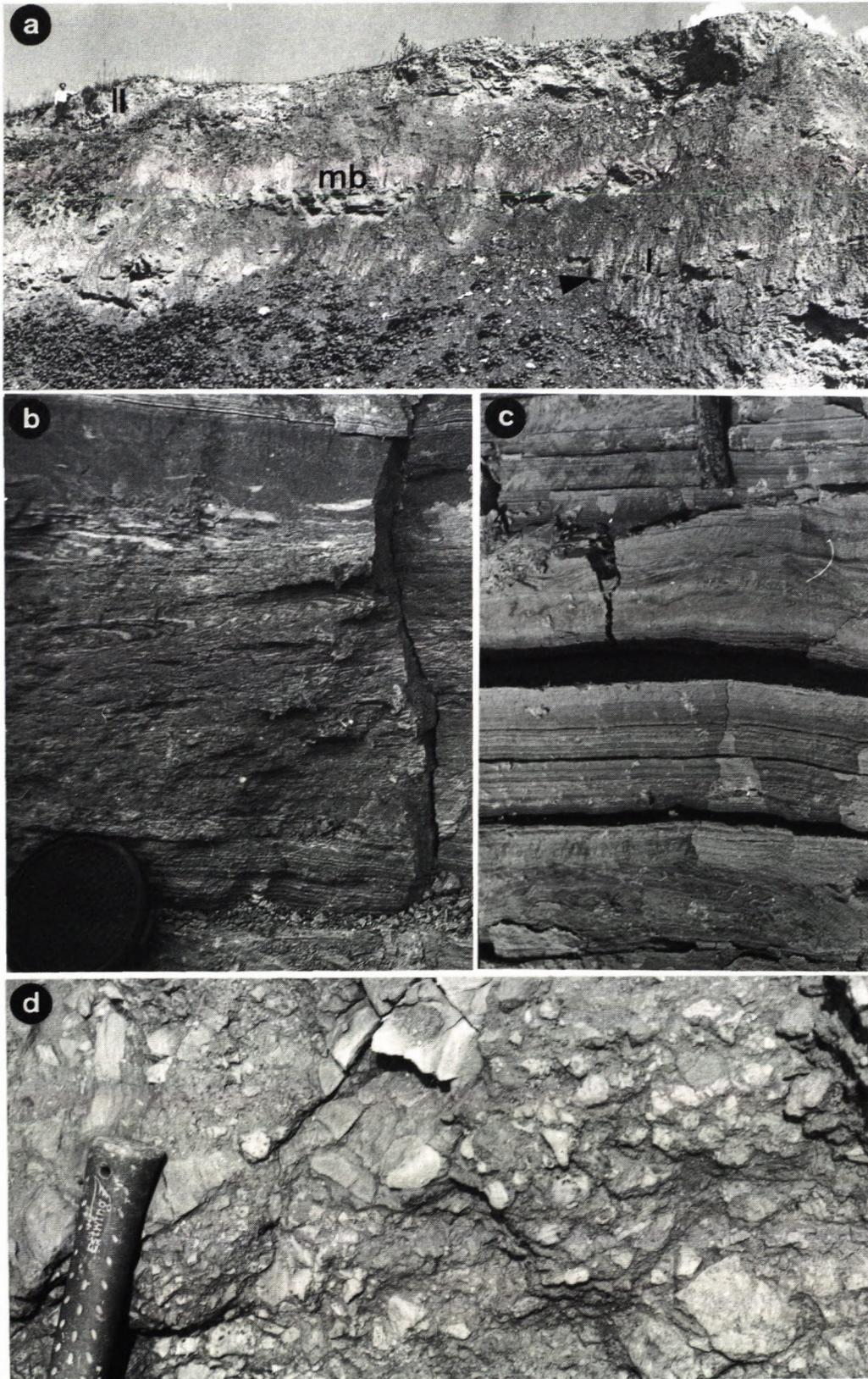


Fig. 6. Upper part of the gypsum sequence (a - west-central part of the quarry, b - east-central part, c, d - eastern part of the quarry).

a - Field photo showing the first (I) and second (II) units of laminated gypsum. The unit in the middle (mb) has an irregular form and is related to slumping. Arrow shows the place sampled for organical geochemical study; b - Laminated gypsum overlain by distorted and massive gypsum; c - Deformations within the gypsiferous claystones (3 m above the upper laminated gypsum unit); d - Gypsum breccia above the second unit of laminated gypsum.

(cf. Peryt & Jasionowski, 1994). The laminated gypsum units can be interpreted as fall-out from a low-density turbid layer. These deposits are related to a large body of brine present during deposition (cf. Kendall, 1992, p. 396).

### Analyses of mineralogical composition

Analyses of mineralogical composition were made using the X-ray diffraction method. The Philips Compact X-ray Diffractometer System PW1840 with Cu-tube and solid state detector provided with an automatic computerized powder identification system APD 1877 was used. The system allows a direct printout of the values of spacings in crystal planes and the counts (in pulses) of corresponding peaks, or a measurement of net intensity of selected peaks. Diffractometer measurements were made on raw samples in the  $3^{\circ}$ - $60^{\circ}$   $2\theta$  range of angles on pressed specimens, and on clayey fraction ( $<0.002$  mm) samples in the  $3^{\circ}$ - $20^{\circ}$   $2\theta$  range on oriented and heated specimens.

These studies showed that the main constituents are gypsum (occurring also in the clay fraction), quartz (10-25%, usually 15-20%), calcite (up to 5%). Iron compounds (1-2%) occur in only two samples (95-3 and 95-4; pyrite and goetite, respectively). The content of clay minerals is 2-10% (usually 5 to 8%) except in two samples where clay minerals are lacking. The following clay minerals have been identified: kaolinite, illite, chlorite, and in samples 95-19, 95-21 and 95-22 illite-montmorillonite mixed-layered minerals. The content of clay minerals varies. It is especially low (2%) in the unit of gypsiferous claystones with sabre gypsum and supercones where in particular samples illite or kaolinite dominate, and in samples 95-13 and 95-14 where they are practically lacking. The sample 95-25 from the top of the gypsum sequence is very similar in terms of phase composition to sample 95-12.

### Micropaleontological studies

Micropaleontological studies included examination of foraminifers, calcareous nannoplankton and palynofacies.

Seven samples have been examined aiming to establish the presence of foraminifers and calcareous nannoplankton; their location is shown in Figure 2. In addition, twenty four samples (the same set that was studied for mineralogy and palynofacies) have been used to study the foraminifers.

Preparation of slides with calcareous nannoplankton for study under the optical microscope was by the method described by Gorostidi and Lamolda (1995). Two samples appeared to be barren (see Fig. 7). In the remaining samples the calcareous nannoplankton are very scarce and very poorly preserved, with a few dominant cosmopolitan

species (*Coccolithus pelagicus*, *Reticulofenestra pseudo-umbilica*, *R. minuta*, *R. minutula* and *Helicosphaera carteri*) (Fig. 7). Occasional occurrence of *Sphenolithus abies* and *Helicosphaera walbersdorfensis* was recorded. It should be stressed that no *Discoaster* was found in the section and in many samples redeposited Cretaceous forms occur. Such an assemblage makes it difficult to date precisely the Kobeřice section although the lack of *Sphenolithus heteromorphus* (known from NN4 and NN5 zones - Martini, 1971; Lehotayová & Molčikova, 1978; Backman, 1984; Theodoridis, 1984; Perch-Nielsen, 1985) and the occurrence of *Helicosphaera walbersdorfensis* (known in the Central Paratethys from NN6 and NN7 zones - Müller, 1974; Rögl & Müller, 1976; Lehotayová & Molčikova, 1978) suggests that the studied interval belongs to a part of the NN6/7 zone.

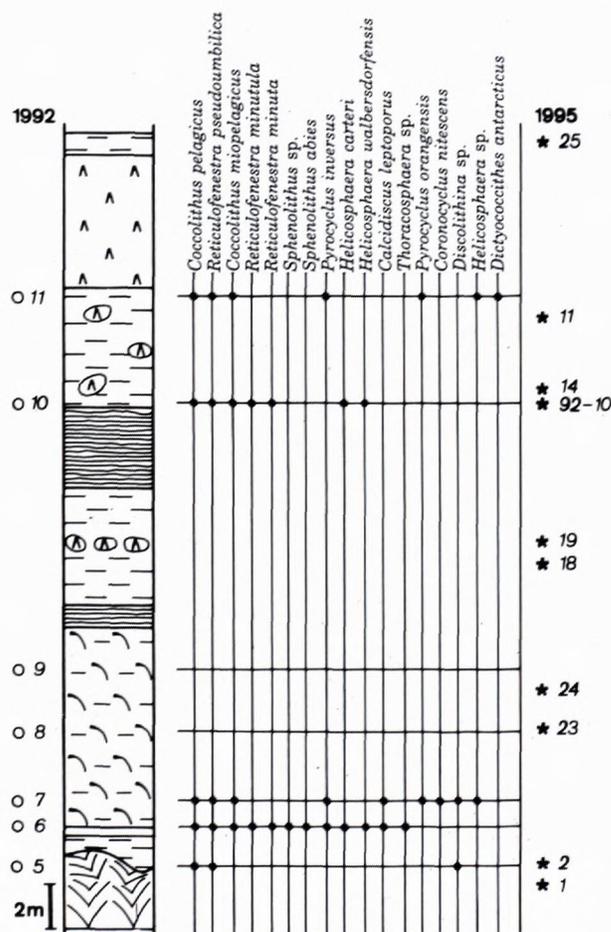


Fig. 7. Occurrence of coccoliths in the Kobeřice section.

In many samples planktonic foraminifers have been recorded; the location of those samples is asterisked in Figure 7. The following species have been found: *Globigerinoides trilobus* (Reuss), *Globigerina praebulloides* Blow (Fig. 8i-k), *G. bulloides* Blow, *G. falconensis* Blow

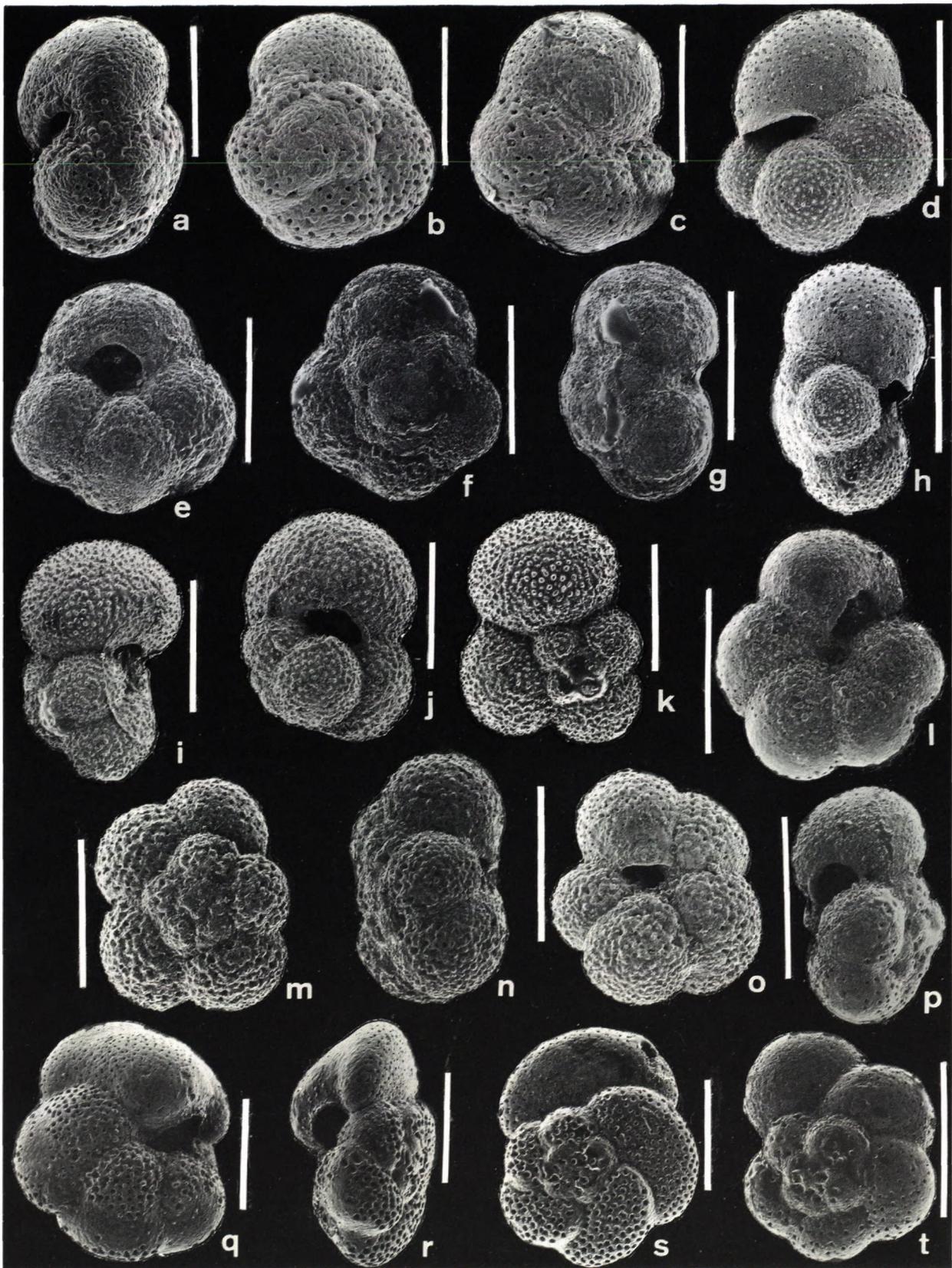


Fig. 8. Planktonic foraminifera in the Kobeřice gypsum sequence (scale bar = 100  $\mu\text{m}$ ).

a-c - *Paragloborotalia continuosa* (Blow); d,h - *Globigerina falconensis* Blow; e-g - *Globoturborotalita druryi* (Akers); i-k - *Globigerina praebulloides* Blow; l,p,t - *Paragloborotalia mayeri* (Cushman & Ellis); m-o - *Globigerina concinna* Reuss.; q-s - *Globorotalia bykova* (Aisenstat).

(Fig. 8d,h), *G. concinna* Reuss (Fig. 8m-o), *Globoborotalita druryi* (Akers) (Fig. 8e-g), *Paragloboborotalita tarchanensis* Subbotina & Chutzieva, *P. sp. cf. acostaensis* (Blow), *P. continuosa* (Blow) (Fig. 8a-c), *P. siakensis* (Le Roy), *P. mayeri* (Cushman & Ellisor) (Fig. 8l,p,t), and *Globoborotalia bykova* (Aisenstat) (Fig. 8q-s). Considering the ranges of those species except of *Globoborotalia bykova* (Aisenstat) in the Mediterranean Miocene (Iaccarino, 1985) it may be concluded that this assemblage represents Serravalian. *Globoborotalia bykova* (Aisenstat) has its last appearance in Central Paratethys in Wielician (Rögl, 1985).

It should be mentioned that in samples 95-1 and 95-2 coming from the unit of gypsiferous claystones overlying the unit of giant gypsum intergrowths, early Miocene planktonic foraminifers (such as *Globigerina dubia* Egger and *Globigerina bollii lentiana* Rögl) and calcareous nannoplankton (e.g. *Helicosphaera ampliapertura* Bramlette & Wilcoxon) have been recorded. The redeposition of microfauna and microflora postdated the subaerial exposure following deposition of the unit of giant gypsum intergrowths.

Twenty four samples of claystones have been studied palynologically (Fig. 9). About 30 g of a sample have been processed in 40% HCl, then sieved through 15 µm sieve, again processed in 38% HF and sieved, and next separated in heavy fluids (of density 2 g/cm<sup>3</sup>). It was found that all studied samples contain rich organic material that was subdivided into four groups according to the state of preservation and the origin: black non-translucent woody particles, brown structureless organic matter, fragments of plant tissues, sporomorphs and algae (Fig. 9).

The Kobeřice sequence is characterized by relatively constant distribution of palynofacies. Commonly the content of particular components is as follows: black woody particles, 18-25%; brown organic matter, 8-12%; plant tissues, 4-8%; sporomorphs (represented mainly by bisaccate pollen grains), 50-70%; and algae, 0-5%. No dinocysts have been recorded. In one sample (no. 95-3) the content of plant tissues reaches ca. 30%, and the content of black woody particles in samples nos. 95-18, 95-19, 95-13 and 95-14 reaches ca. 40% palynofacies. Accordingly, terrestrial elements strongly dominate, constituting almost 100% of the palynofacies. This indicates a close proximity of the land, although the predominance of sporomorphs may suggest a slightly more distant further located source area for organic material found in the Kobeřice section. A wider distribution of sporomorphs is suggested because of greater buoyancy potential of these bisaccate pollen grains. A relatively good state of preservation of palynomorphs indicates a decreased deposit oxidation and/or fast delivery of organic matter. The lack of dinocysts, commonly occurring in marine

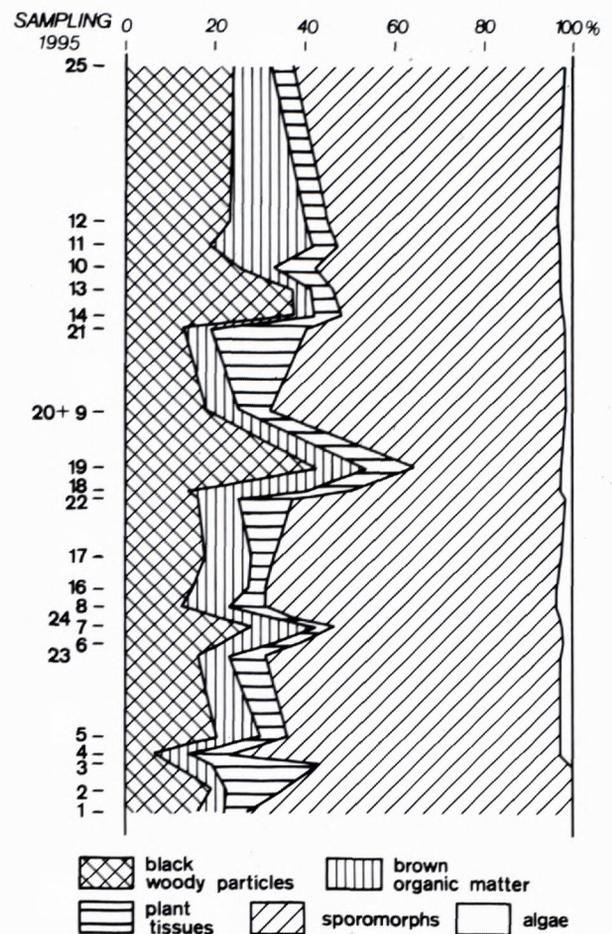


Fig. 9. Palynofacies in the Kobeřice section.

Miocene deposits, suggests the stress conditions (e.g. high salinity level) prevailing during deposition of the Kobeřice gypsum sequence.

#### Geochemical studies

Geochemical studies included the determination of boron content in claystones associated with gypsum (Fig. 10), study of fluid inclusions in crystalline gypsum units (Fig. 11), isotopic (oxygen and sulfur) analyses of gypsum samples (Table 1) as well as one analysis of organic matter (Fig. 12).

Determination of boron in claystones in the same set of samples that was subject to palynofacies and X-ray diffraction studies were done at the Central Chemical Laboratory of the Polish Geological Institute; locations of those samples (95-1 to 95-25) are shown in Fig. 2. The boron content was measured using Philips PV8060 Spectrometer; the error of determination is 3-5%. The values measured are from 24 to 111 ppm (average is 64 ppm), and such low values are considered to be charac-

teristic for clay deposits of freshwater origin (see Pasieczna, 1983, Table 4).

Nine samples of selenite gypsum have been studied for fluid inclusions; five samples came from the giant gypsum intergrowths (Nos. 1, 39, 52-54/1992) and four from the sabre gypsum crystals in a supercone from the lowest part of the unit (Nos. 47-50/1992). The studies have been performed in the Institute of Geology and Geochemistry of Combustible Minerals, National Academy of Sciences of Ukraine (Lviv) following the thermobarogeochemical procedure used there (Petrichenko, 1973, 1977). Inclusions are typically fluid. Most inclusions are dehermetized. Considering the freezing temperature (that is about 0°C) of fluid inclusions, the concentration of basin brines did not exceed 5-10 g/l. This conclusion is also supported by the lack of precipitate on the surface of plates following the evaporation of fluid inclusions. The analyses of water leachates and analysis of one fluid inclusion shows the following ratios of major components: Chlorine, 1.0; sulfate ion, 0.65; magnesium, 0.06; potassium, 0.05; calcium, 0.03. Sodium was not determined but its presence is clearly indicated by presence of mirabilite and halite in the solid phase of water leachates. Accordingly, it is assumed that basin waters were saturated in respect to calcium sulfate (what is evident considering that gypsum has precipitated) and also contained, along with sodium chloride, a high amount of sodium sulfate and small amount of potassium and magnesium salts. As a whole, such a composition would imply that the waters have been continental-marine and saturated in respect to calcium sulfate. The temperature of bottom water is hard to determine precisely but considering the presence of one-phase fluid inclusions it may be supposed that it was below 39-40°C.

Mineral inclusions (Fig. 11h) and inclusions of microorganisms are common. The latter have been recorded in giant gypsum intergrowths (Fig. 11a, c, f, h) as well as in sabre gypsum. Most common are inclusions of algae. The inclusions of microorganisms contain organic solutions (Fig. 11f) in addition to water solutions. The inclusions recorded in the gypsum of Koberice are very similar to the earlier-described inclusions of microorganisms from the Badenian gypsum of southern Poland and West Ukraine (Petryczenko *et al.*, 1995).

Oxygen and sulfur isotopic studies of five samples were done at Geologický ústav Dionýza Štúra (Bratislava); the locations of these samples are shown in Figure 2.  $\delta^{34}\text{S}$  values as well as  $\delta^{18}\text{O}$  values in the gypsum of Koberice (Table 1) are very similar to values earlier recorded from the Badenian gypsum of Borków quarry, southern Poland (Hałas *et al.*, 1996) and are characteristic of Tertiary sulfates of marine origin (cf. Claypool *et al.*, 1980).

One sample from the lower laminated gypsum unit, where bituminous material abounds, has been analysed

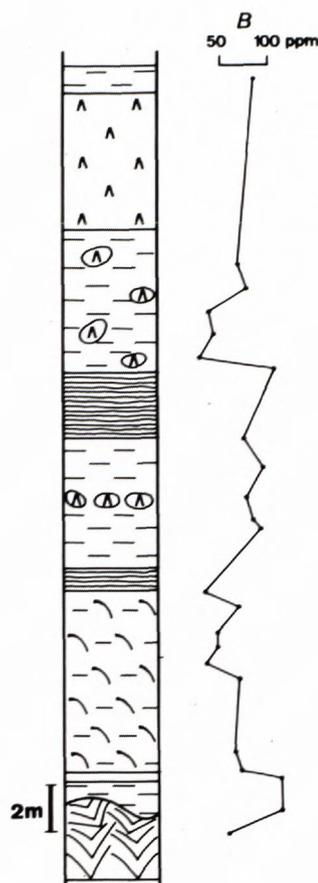


Fig. 10. Content of boron in the rocks of Koberice section.

at the Central Chemical Laboratory of the Polish Geological Institute, Warsaw. This bituminous material commonly is associated with sulfur efflorescences; the place from which the sample was taken is shown in Fig. 6a. The laminated gypsum sample contains 0.01% of bitumen, and the content of hydrocarbon in bitumens is 41%. The ratio of saturated to aromatic hydrocarbons is 41% which indicates the autochthonous nature of the hydrocarbons. The composition of n-alkanes is shown in Fig. 12. Such a pattern is related to primary mixture but with dominance of sapropel material.  $\text{CPI}_{\Sigma}$  is 1.26 which indicates a low metamorphism of organic matter.

Table 1. Results of stable isotopic study of samples from the gypsum sequence in Koberice.

Sample No.	$\delta^{18}\text{O}$ SMOW	$\delta^{34}\text{S}$ CDT
92-1	+13.47	23.00
92-2	+13.19	22.49
92-4	+11.99	no data
92-5	+13.00	22.19
92-8	no data	23.32

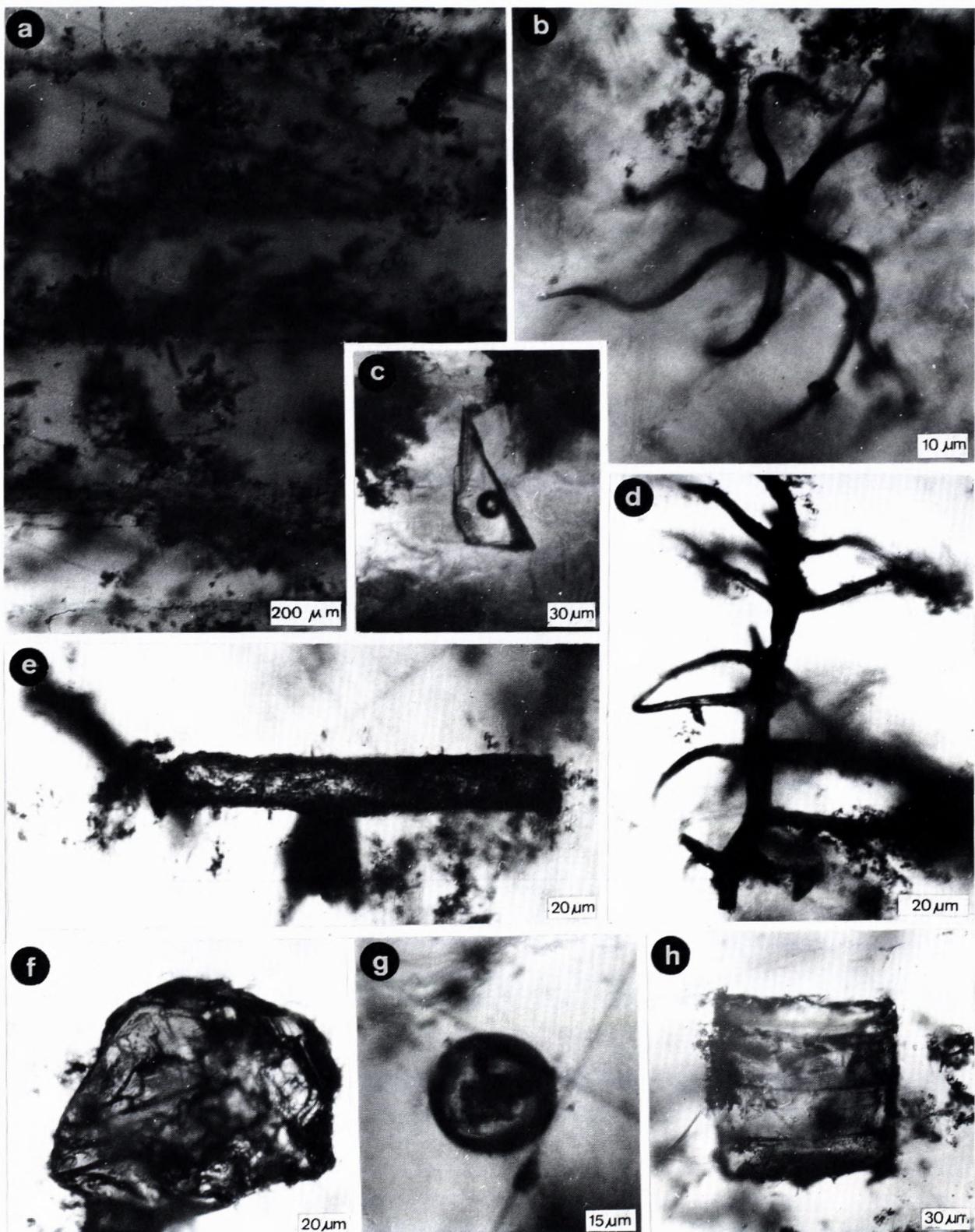


Fig. 11. Inclusions in gypsum crystals.

*a* - Rhythmic pattern of inclusion occurrence in gypsum caused by periodic changes of gypsum crystallization at the bottom of the basin; *b*, *d* - Characean fragments; *c* - Two-phase inclusion; the air bubble may result from dehermetization of the inclusion; *e* - Inclusion originated through coupling of algal segments; *f* - Fluid (brine) inclusion with oily matter; *g* - Coccoid inclusion; *h* - Gypsum inclusion of zoned gypsum in giant gypsum intergrowths. The zoning is regarded to reflect the changes of crystallization conditions during day and night.

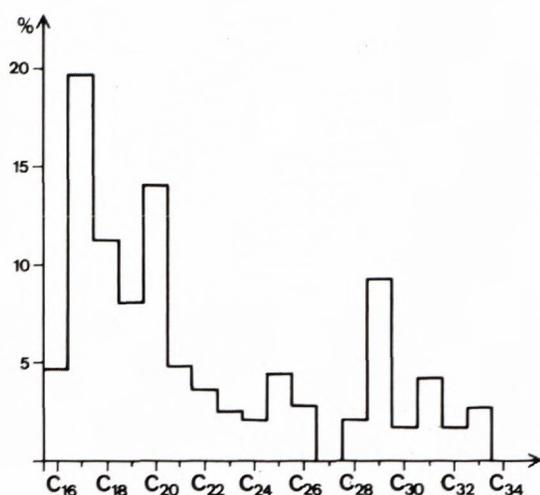


Fig. 12. Composition of n-alkanes in one sample (no. 92-21) of laminated gypsum.

### Discussion and conclusions

As proved by Garlicki (1994), a detailed lithostratigraphic examination of the Badenian salt deposits and the distinction of a number of key horizons within these deposits makes it possible to correlate the Upper Silesia salt sections with those known from Wieliczka even though Upper Silesia and Wieliczka salt basins are separated by sulfate facies. Such a similarity of evaporite facies through the Badenian basin seems to be related to an extrabasinal control that did not obscure important local and regional tectonics. Intrabasinal marker beds occurring in the evaporite sequences record distinct phases of brine body evolution (frequent refreshing episodes) or diagenesis related to subaerial exposure.

In Kobeřice it is possible to distinguish some marker horizons typical of other parts of the northern marginal area of the Badenian sulfate basin:

(1) Unit of giant gypsum intergrowths, forming the basal part of gypsum sequences in southern Poland (Babel, 1987; Kubica, 1992) and West Ukraine (Peryt, 1996). In particular, Kobeřice giant gypsum intergrowths are very similar to a massive-skeletal facies transition that was earlier recorded in the Nida Valley area, southern Poland, and regarded as a deeper-water deposit when compared to other facies of giant gypsum intergrowths (Babel, 1996).

(2) Unit of microcrystalline ("alabastrine") gypsum that can be traced out in the peripheral part of the basin over a distance of almost 700 km from Kobeřice through southern Poland ("unit c" - Kasprzyk, 1993; Peryt *et al.*, 1994) to eastern Galicia in the east (Peryt, 1996). It should be mentioned that in the marginal part of the Badenian gypsum basin there are several alabastrine gypsum beds which can be traced throughout individual exposures or

group of exposures, over a distance of hundreds of meters to kilometers (e.g. Kasprzyk, 1993; Peryt, 1996), and also in Kobeřice there is an "alabastrine" gypsum bed underlying the proper (main) bed of microcrystalline gypsum. However, only one alabastrine gypsum bed is of regional importance. The occurrence of this unit is roughly related to the zone of occurrence of giant gypsum intergrowths and therefore it is not recorded in the nearshore facies of the gypsum (see Peryt, 1996).

(3) Unit of the upper laminated gypsum has many striking similarities to a unit of laminated gypsum occurring in the lower part of unit "n" in Borków, southern Poland (Peryt & Jasionowski, 1994) including the presence of pseudomorphs after halite crystals.

In addition, considering development and position in the sequence, the unit with sabre gypsum is common for Kobeřice and other peripheral northern parts of the Badenian basin (Kwiatkowski, 1972; Babel, 1986; Kubica, 1992; Peryt *et al.*, 1994; Peryt, 1996) although Kobeřice sabre gypsum differs from other sabre gypsum occurrences by its relation to associated claystones that are coeval with gypsum precipitation. A clayey nature of the Kobeřice gypsum is explained by a very important and continual clay delivery to the Upper Silesia evaporite basin. Like other sabre gypsum crystals, those recorded in Kobeřice show very constant orientation that is interpreted by Babel (1986, 1996) as due to directional growth of sabre crystals that was enforced by the inflow of calcium sulfate-saturated brines.

The upper part of the gypsum sequence in Kobeřice shows widespread redeposition phenomena that are also characteristic of the upper part of the Badenian gypsum elsewhere (Peryt & Kasprzyk, 1992; Peryt & Jasionowski, 1994; Peryt, 1996). These redeposition phenomena are related to the existence of a paleoslope. Paleoslopes are rarely observed in the field and their presence is inferred from the analysis of lateral facies changes of evaporite sequences. In particular, the presence of redeposition phenomena is important to determine the existence of slope zones in evaporite basins (e.g. Peryt *et al.*, 1993; Peryt, 1994) although the uncertainty of lateral correlations of evaporite facies is a limiting factor in reconstruction of paleogeographical and facies patterns (see discussion in Sonnenfeld, 1984). In Kobeřice, the presence of paleoslope is well expressed during deposition of the entire gypsum sequence. Amount of clay material in the facies of giant gypsum intergrowths increases eastward, and this increase is accompanied by a change of massive facies to skeletal facies of giant gypsum intergrowths, decrease in frequency of amalgamates of supercones, as well as increase in the thickness of laminated gypsum units and the number and thickness of breccias in the upper part of gypsum sequence. The basin was located east of Kobeřice, and as

recognized by Krach (1958), the basal zone of evaporites in Upper Silesia is characterized by occurrence of laminated gypsum, anhydrite and halite.

Although the evidence of redeposition indicates paleoslope and not necessarily deeper water conditions, it seems that the upper part of the gypsum sequence as well as the major part of the lower part represent deeper water deposits. The presence of planktonic foraminifers throughout the entire section (except in giant gypsum intergrowths and both units of laminated gypsum) indicates that there existed water stratification in which the bottom gypsum-saturated brines were overlain by normal marine waters containing planktonic fauna. Such a water stratification was already suggested by Krach (1956). The surficial water layer was affected by dilution by floods supplying clays as well as terrestrial elements of palynofacies. Accordingly, the salinity in the upper, nearsurface part of the water column was subject to major variation. On the other hand, the occurrence of pseudomorphs after halite in the upper laminated gypsum unit is possibly related to bottom brines that were temporarily saturated with halite (*cf.* Babel, 1996). It is thus difficult to assume that the multiple dilution phases of the surface water could reach concentration that allowed precipitation of halite crystals. The occurrence of pseudomorphs of halite thus would imply the existence of halite-saturated brines overlain by gypsum-saturated brines which in turn were overlain by waters of changing, but usually low, salinity. Accordingly, strongly stratified waters in a relatively small basin exerted an important control on gypsum turbidite deposition (*cf.* Rimoldi *et al.*, 1996).

Summarizing, the major part of the gypsum sequence of Kobeřice originated in rather deeper water conditions in density-stratified waters. The only exceptions to rather deeper water conditions prevailing during gypsum (and related claystone) deposition are exposure episodes following formation of the giant gypsum intergrowths and during the alabastrization phase(s). The same major stages in the basin evolution can be recognized throughout the northern marginal basin (Peryt *et al.*, 1994; Peryt, 1996; Babel, 1996). The peculiarities of Kobeřice gypsum section indicate its more basinward location compared to other gypsum exposures known from Poland and West Ukraine.

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## Relation of sulfur-forming processes to lithofacies and structural features of Badenian chemical sediments in the Carpathian Foredeep (Poland)

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**Abstract.** Sulfur-forming processes in the Carpathian Foredeep were closely connected with Badenian gypsum and anhydrite. The basic sulfur-forming process was an alteration of the sulfates into limestones sustained by hydrocarbons and bacteria. The most intensive sulfate alteration took place in the northern marginal part of the foredeep. This process, though less intensive, also affected sulfates from the deeper parts. The alteration took place especially in uplifted structures which favored accumulation of hydrocarbons. Hydrocarbons were displaced from original and secondary traps when the Carpathians overthrust their northern foreland in the early Sarmatian through the Pliocene. Channels of migration were depressions and troughs filled with sand series. According to rough estimates, the sulfur resources mobilized from sulfates during the alteration processes and contained primarily in limestone pores and cavities, and bound to hydrogen sulfide amounts to 2,000 million Mg. To mobilize 1 Mg sulfur about 730 m<sup>3</sup> natural gas is needed so about 1,500,000 million m<sup>3</sup> natural gas was "consumed" in the foredeep.

**Key words:** Miocene, sulfur, Carpathian Foredeep, hydrocarbons, sulfate metasomatism.

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### Introduction

According to the present state of the art, sulfur-forming processes can proceed through biochemical alterations in the presence of bacteria and under conditions which favor their biological activity, as well as through chemical reactions. The involvement of bacteria in these alterations should not be taken into account due to the presence of disadvantageous environment in which high temperatures (above 100°C) and pressures, and mineralization of waters (above 100 g/l) are prevalent. However, in both cases, hydrocarbons are a decisive source of energy which speed up these processes.

In the Miocene of the Carpathian Foredeep, natural gas and crude oil deposits occur on the foreland side of the zone of sulfur deposits. In addition, native sulfur accumulations were found within sulfates that occur in natural gas deposits located in a deeper part of the Carpathian Foredeep. The sulfur contains trace accumulations of bitumens whose content increases below 300 m depth.

This paper summarizes the research on the sulfur-forming processes, based on data from the eastern part of the Carpathian Foredeep in Poland, and presents an outline of the conditions of sulfate alteration in the less known, western part of the Carpathian Foredeep.

### Chemical sediments - sulfur-rich hostrocks

In the Central Paratethyan Miocene, chemical sediments occur in the Badenian stage M<sub>4</sub> (Fig. 1); in the area of the Carpathian Foredeep it was assigned to the Vieltian substage (Garlicki, 1994).

Chemical sediments are divided into three laterally interfingering lithofacies. They are as follows: originally deposited gypsum lithofacies occurring down a depth of 300 m, secondary diagenetic-recrystallized lithofacies, i.e. dehydrites (somewhat dehydrated sulfates) and anhydrites (Kubica, 1972). The lithogeophysical correlation based on resistivity curves indicated similar cyclic anomalies in all gypsum, dehydrite and anhydrite (Kubica, 1992, 1994a). Aside from a decrease in grain size of most crystals, thinning of the laminae and an increase of density, recrystallization and dehydration did not cause important physical changes in these lithofacies.

The regional analysis indicates that the thickness of sulfates ranges from a few meters to 60 m (Pawłowski, 1965). A complete section of the thickest lithostratigraphic units is about 68 m (Kubica, 1992). In the N-S cross-section, the distribution pattern of the thickness of sulfates from the Carpathian Foredeep allows two zones to be distinguished:

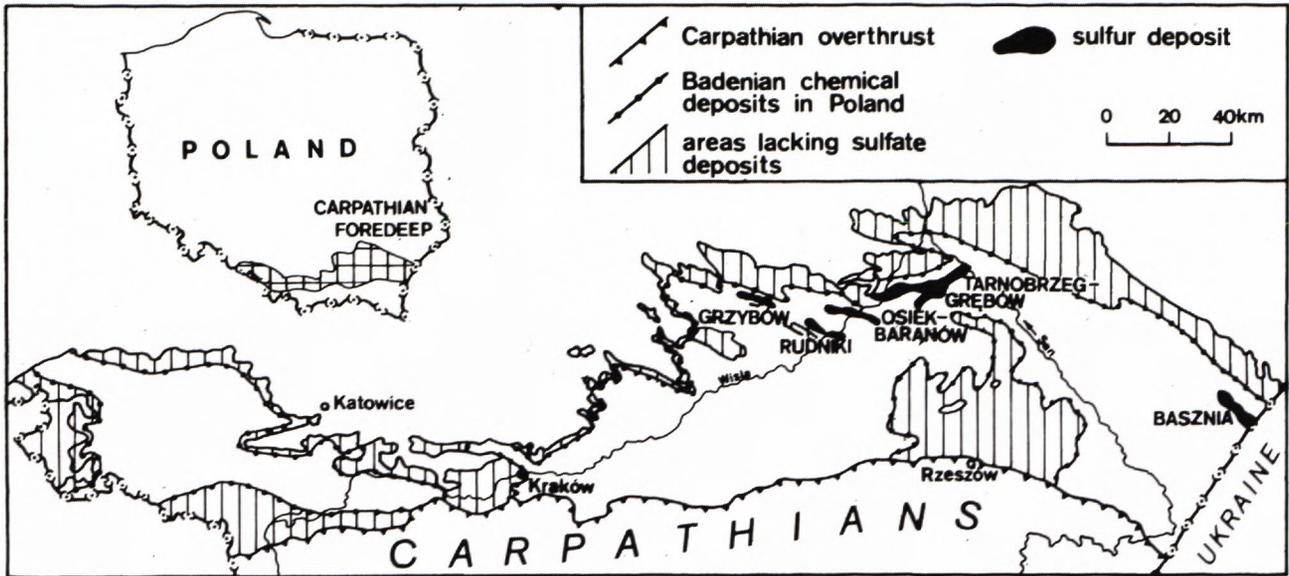


Fig. 1. Miocene sulfur deposits in the Carpathian Foredeep in Poland.

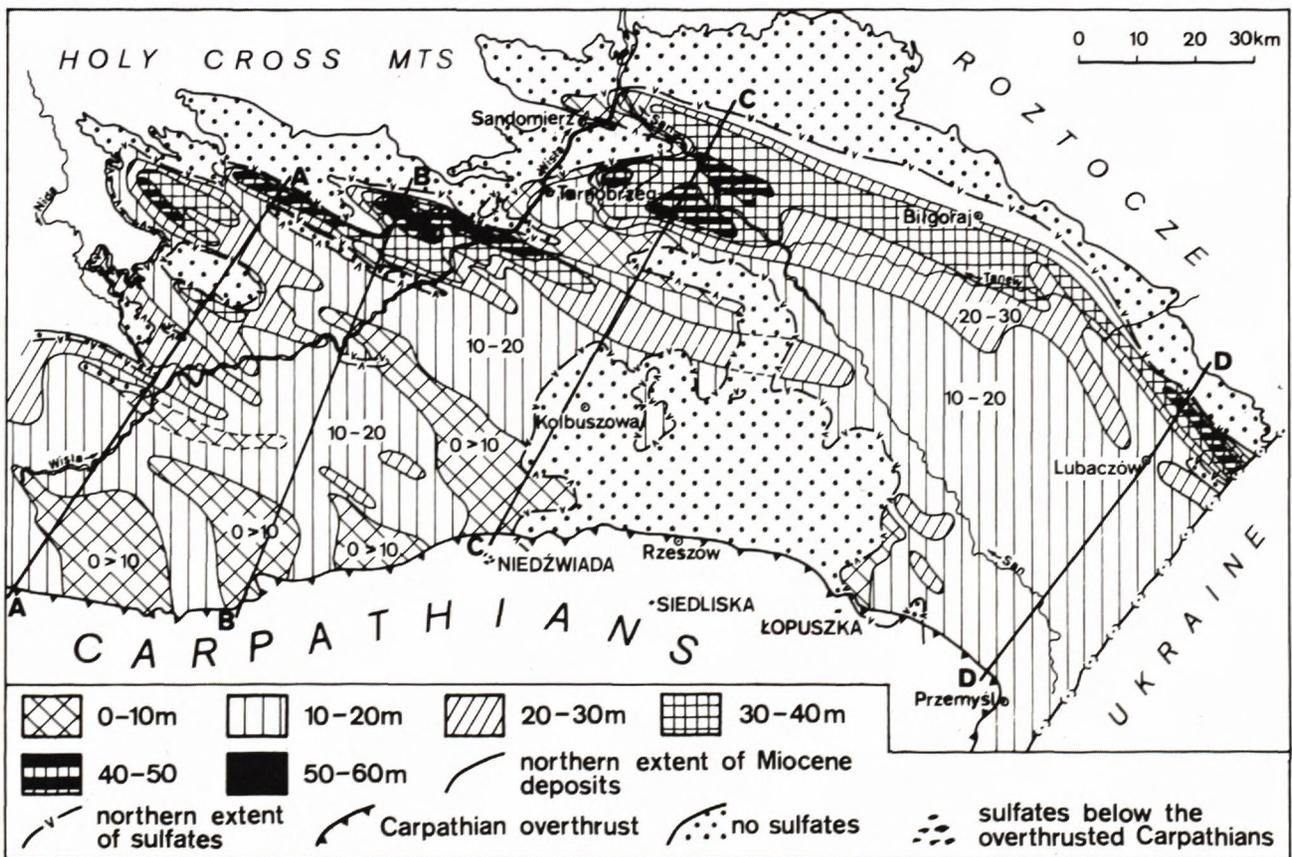


Fig. 2. Thickness of the Badenian sulfate deposits in the eastern part of the Carpathian Foredeep in Poland.

(i) a large, monotonous and uniform zone ranging from 3 to 15 m in thickness. It makes up the southern and central parts of the foredeep around the "Rzeszotary island"; its total area is about 6,700 km<sup>2</sup> which constitutes almost 70% of the area occupied by sulfates,

(ii) a northern zone, split into small basins, and characterized by a distinctly increased thickness primarily of gypsum (40 to 60 m). The elongated basin near the Holy Cross Mts. extending from Chmielnik through Szydłowiec and Baranów Sandomierski to Leżajsk can be distin-

guished here. In turn, a very large basin extends from Tarnobrzeg through Rozwadów to Nisko, and the near-Roztocze basin from Antoniów through Krzeszów, Tarnogród and Cieszanów to Basznia.

### Postsulfate limestones - sulfur-rich lithofacies

The youngest lithofacies within the chemical sediments is represented by postsulfate limestones with prevalent gypsum lithofacies. Its extent is local. As a result of complex processes, metasomatic alteration of sulfates into limestones took place. In some areas these limestones contain native sulfur.

Views on the alteration process of sulfates have a long history. Suszycki (1876) claimed that "hole-like" limestones had been formed as a result of the influence of organic matter on gypsum. Łomnicki (1905) recognized Ratyn cavernous limestones (postgypsum) as a secondary product resulting from chemical alteration of gypsum (see Peryt & Peryt, 1994). Teisseyre (1921) attributed the alteration of gypsum to hydrocarbons. Bolewski (1935) and Krajewski (1935) emphasized the

genetic connection between bitumens, gypsum, calcite and sulfur occurring in the Posządza and Czarkowy deposits. Most researchers (e.g. Pawłowski, 1959, 1963, 1970; Kubica, 1965, 1992; Osmólski, 1972; Pawłowski *et al.*, 1985; Nieć, 1992) emphasized the formation of limestones as an epigenetic process of sulfate alteration triggered by a "motory" factor, i.e. hydrocarbons. They relate the origin of these rocks to chemical-biogenic reactions in the presence of bacteria. These conclusions are also supported by such facts as the similarity of structures and textures of gypsum and carbonate rocks (Pawłowska, 1962), as well as stratigraphically different positions of sulfate relicts and even islands within limestones (Pawłowski, 1970; Kubica, 1992). The comparison of structural features of postgypsum sulfur-rich limestones with their gypsum "predecessors", primarily crystalline layers, did not indicate their complete lateral correlation (Gąsiewicz, 1994). The sections examined in the Osiek-Baranów area contain limestone interbeds not corresponding to structural features of selenite gypsum. Gąsiewicz (1994) claims that the alteration processes of sulfates were more complex than previously assumed.

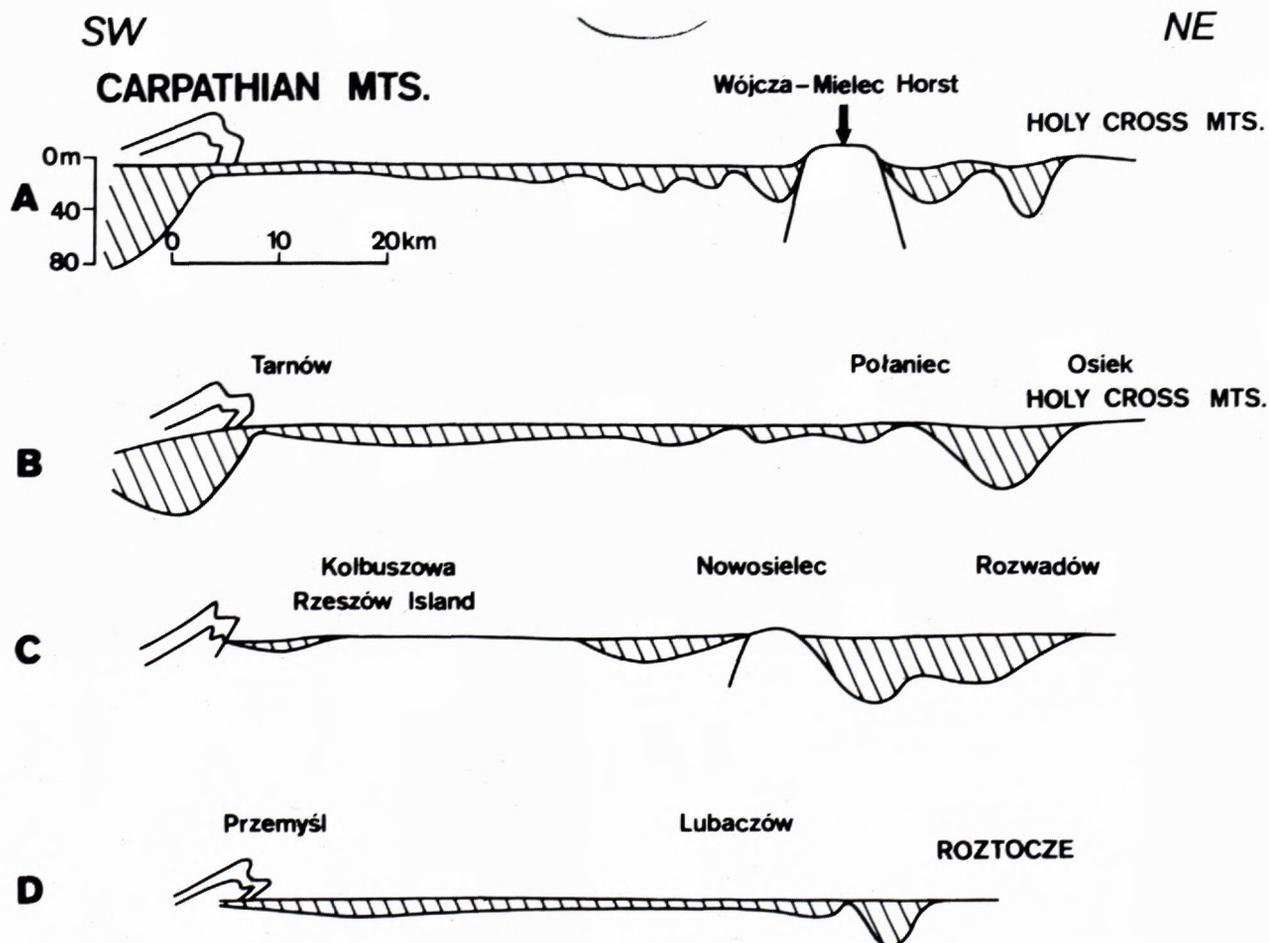


Fig. 3. Thickness changes of sulfate deposits along the lines shown in Fig. 2.

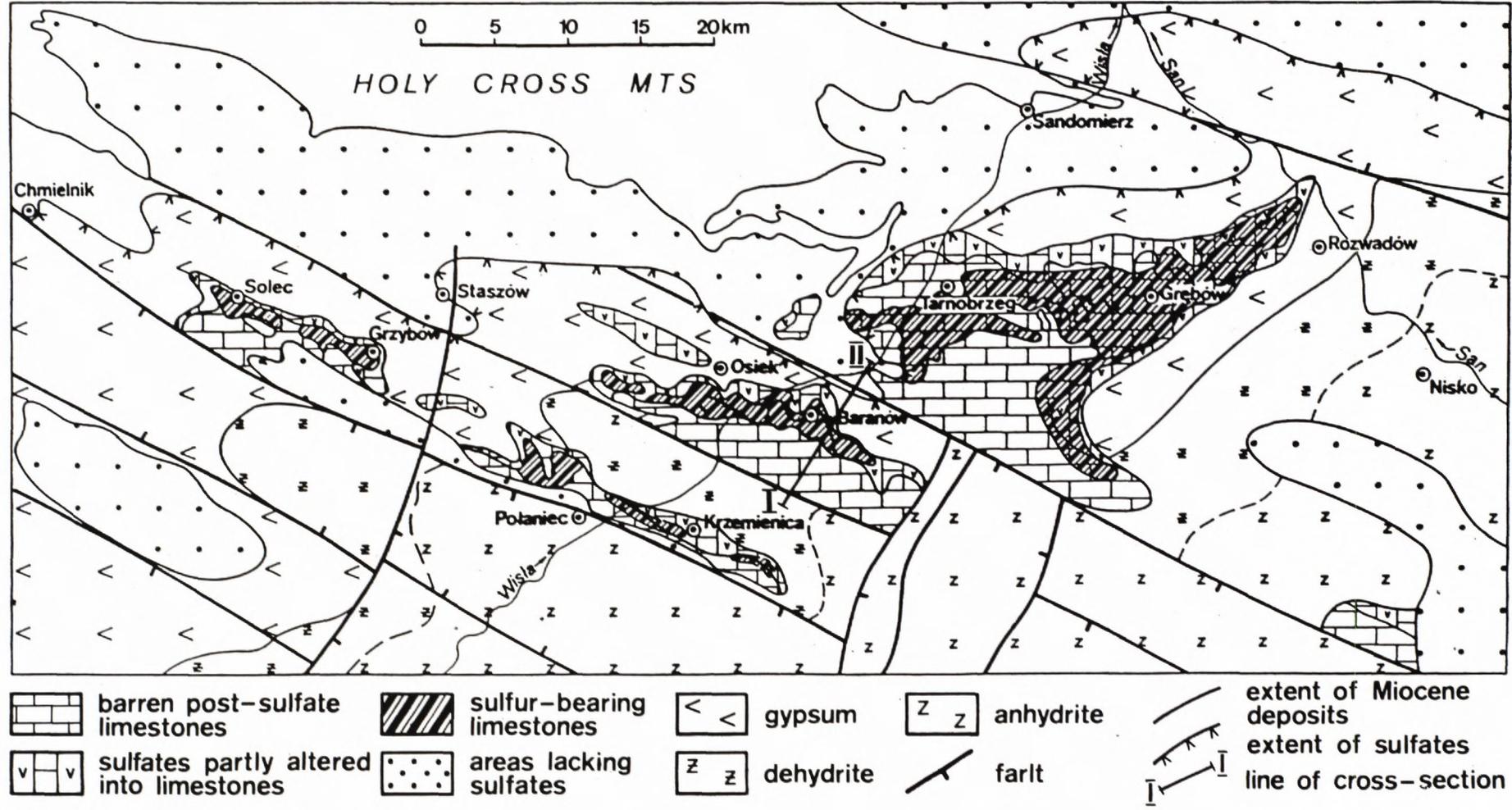


Fig. 4. Map of areas of active metasomatism and sulfate lithofacies.

The activity and intensity of the alteration processes of the sulfates was diverse (Pawłowski *et al.*, 1985; Kubica, 1992). The original stages are represented by local streaks and pods of carbonates. The alteration of some parts of the sulfate was hampered by screens of clayey interbeds; sulfate island relicts, as well as sulfate interbeds occurring within limestones can be observed here (Fig. 4, 5). In places, the whole sulfate complex underwent alteration.

The epigenetic character of postsulfate limestones and the involvement of bitumens in an alteration process is indirectly shown by carbon stable isotope determinations. The  $\delta^{13}\text{C}$  of limestones from Piaseczno and Machów ranges from -18 to -59.9‰ (Czerwiński & Osmólski, 1974), and from the western Ukraine from -32 to -65‰ (Sakseyev, 1972). The  $\delta^{13}\text{C}$  values of natural gas in the Carpathian Foredeep are similar to those from postgypsum limestones and range from -30 to -55‰ (Żuk *et al.*, 1973).

### Sulfur-forming processes in limestones

As a result of metasomatic processes in sulfates, aside from carbonate rocks, previously bound to  $\text{SO}_4^{2-}$  sulfur is also produced. During the first phase of this reaction, except in secondary limestones, a large amount of hydrogen sulfide is produced as a by-product. As a result of oxidation, chemically bound elemental sulfur is then released. It fills the limestone mass whose porosity ranges from 10 to 30%. Because of the mobility of dissolved hydrogen sulfide, sulfur accumulates not only in carbonate rocks and gypsum, but also outside the host bed within cracks and fissures cutting the clayey overburden (Pecten-Spiralis Beds), and within underlying sands, sandstones and siltstones primarily in the form of cement. In addition, some free hydrogen sulfide is dissolved in waters in the Miocene aquifer (chemical sediments and Baranów Beds) far from the sulfur-rich bed.

The distribution of sulfur in limestones within particular ore fields does not correspond to proportions resulting from the metasomatic alteration equation for a specific area; in general, these concentrations exceed two or even three times the primary content of sulfur in the original gypsum. Within a deposit series, interbeds of pure sulfur as much as 1 m thick have been recorded. Taking into account the fact that gypsum is contaminated and that this process involves at least 15% of mobile sulfur, accumulation of sulfur in limestones exceeds twice the value calculated from the metasomatic alteration equation. Depleted zones are commonly associated with slightly narrower enriched zones; the latter reflect optimal conditions for sulfur accumulation in structural highs. In the zone between Szydów-Pońaniec on the west and Tarnobrzeg-Rozwadów on the east, within active

zones of metasomatism, large fragments of barren rocks making up from 20 to 60% of carbonate lithofacies occur (Fig. 5); the remaining, usually smaller, part is composed of sulfur-rich limestones and somewhat altered gypsum.

### Conditions of hydrocarbon accumulation

Most natural gas deposits (40) discovered in the foredeep, occur in Badenian and Sarmatian sediments. The remaining accumulations are in Mesozoic rocks; they include 8 natural gas and 6 crude oil deposits (Karnowski, 1994; Borys, 1996). The principal natural gas accumulations are in sand interbeds within Sarmatian rocks (Fig. 6). Scarce gas accumulations occur in the Baranów Beds. Most of these beds are developed as poorly permeable clayey-sandy shales and siltstones, particularly in the area of the "Rzeszotary island".

As for the generation of bitumens, their source may have been organic matter scattered within Upper Badenian and Lower Sarmatian clayey sediments. Secondary accumulations of hydrocarbons may have been derived from damaged traps present in flysch sediments and para-autochthonous Miocene rocks as a result of overthrusting of the Carpathians on their foreland. The position of natural gas deposits in the foredeep is specific; they form a zone parallel to the Carpathian overthrust ranging from 25 to 35 km wide in the western and central part, and as much as 45 km wide in the eastern part of the foredeep.

In the northern outer part of the foredeep, where principal native sulfur ore deposits occur, no major natural gas deposits have been noted. In addition, the natural gas resources decrease as the distance from the Carpathian overthrust increases. It should be mentioned here, that according to the author's opinion, the natural gas deposits now present are remnant accumulations left in well-preserved isolated traps; these accumulations did not migrate to the sulfur-bearing zone which consumed most of the natural gas.

### Quantitative estimation of alteration processes of sulfates

To qualitatively and quantitatively assess the dynamics of sulfur-forming processes in the Carpathian Foredeep area, the following assumptions were made:

(i) amount of natural gas needed for stoichiometric calculations to mobilize 1 Mg sulfur from sulfates is 730  $\text{Nm}^3$  (Kozlov, 1959). A loss of about 30% as a result of this reaction should be assumed,

(ii) directions of migration and conditions of natural gas accumulations; migration advanced toward north and northwest in the shallow and less compressed parts of the foredeep primarily in post-Sarmatian time. The gas accumulated within alternating sand interbeds present in



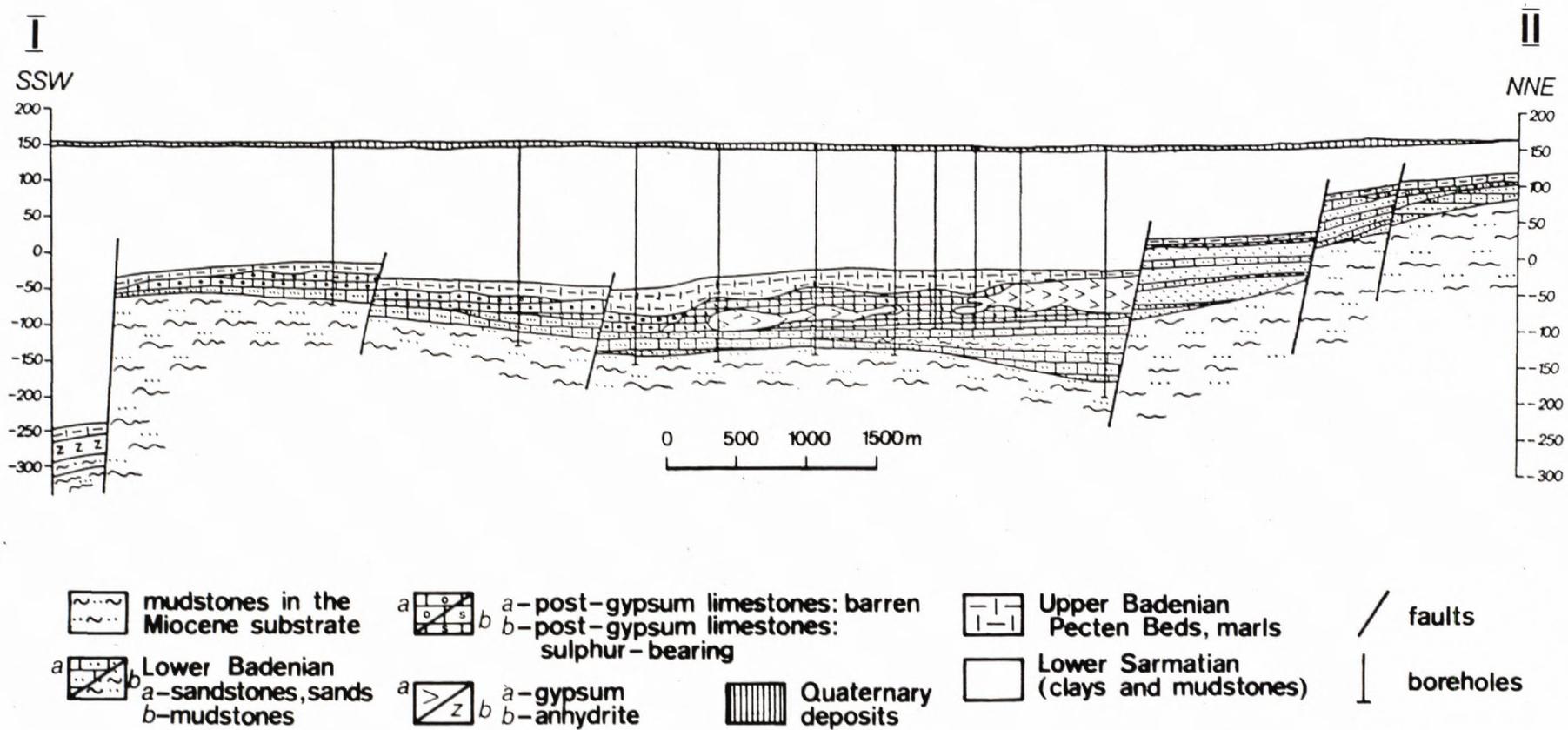


Fig. 5. Cross-section along the line I-II shown in Fig. 4.

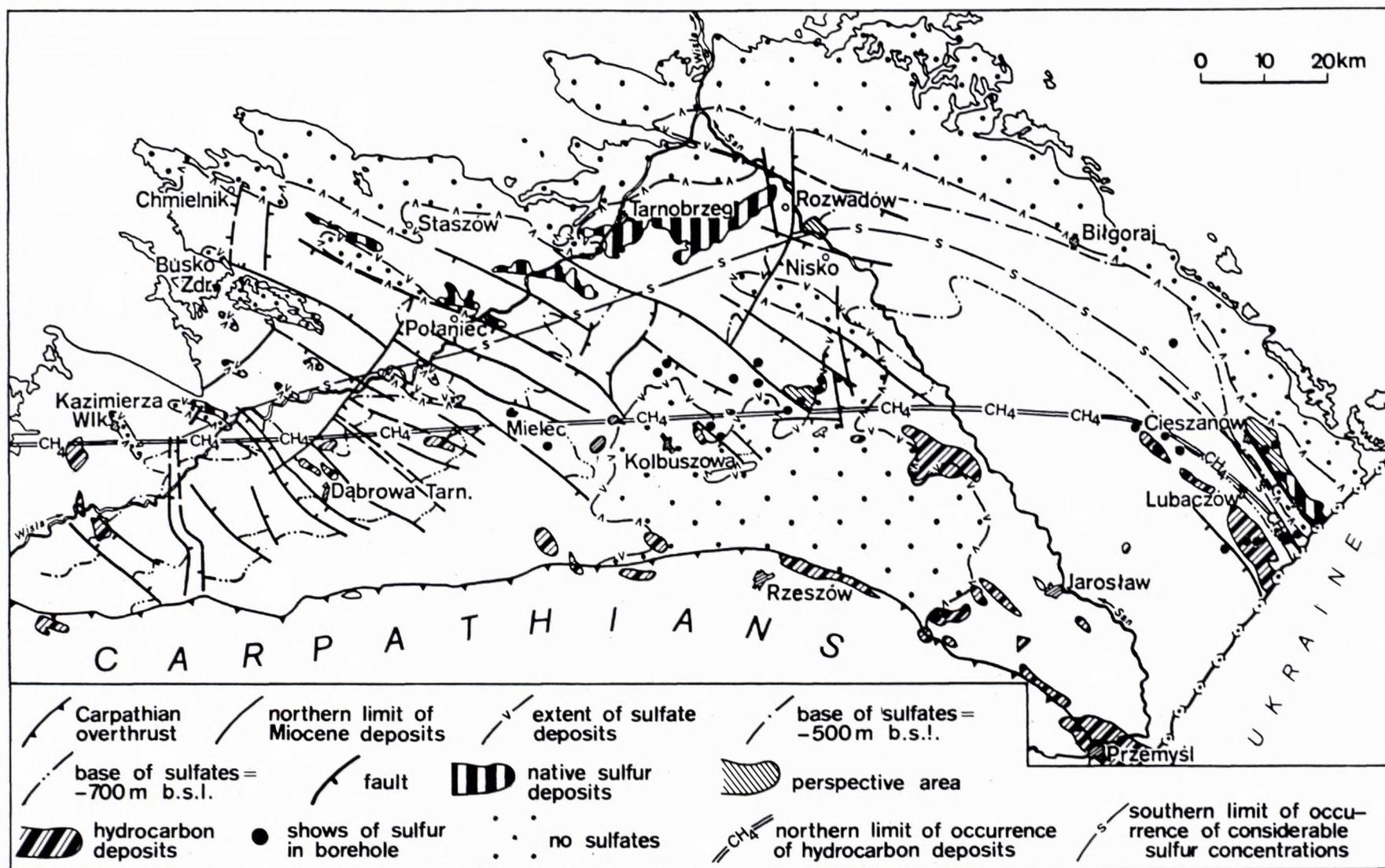


Fig. 6. Relation of occurrence of sulfur deposits and hydrocarbon deposits in the Carpathian Foredeep.

Lower Sarmatian clays, as well as beneath chemical sequences within sands, sandstones and Lithotamnium limestones which occur in the northern margin of the Carpathian Foredeep (and southern margin of the Holy Cross Mts) and in the near Roztocze zone extending from Chmielnik through Biłgoraj to Lubaczów (cf. Fig. 2),

(iii) amount of sulfur mobilized only in the Tarnobrzeg-Staszów district (in the zone of intensive alteration processes of sulfates) was determined to be 1,050 million Mg. Aside from deposit fields documented in detail, this assessment includes subeconomic and potential areas (~15%),

(iv) amount of hydrocarbons (primarily gas) which were involved in these processes was assessed to be about 1,025,000 million m<sup>3</sup> (assuming about 30% of losses derived from this reaction). According to rough estimates, about 300,000 million m<sup>3</sup> of natural gas was taken up by H<sub>2</sub>S, or migrated into the air because of the lack of an impermeable cover and weak trap conditions. This preliminary assessment done for one of the largest sulfur deposits indicates a large resource potential for hydrocarbons in the Carpathian Foredeep. The movement of such amounts of hydrocarbons through a complex system of reservoirs and hydraulic contacts between traps (mainly within fault zones) was possible owing to several phases of thrusting of the Carpathians toward their foreland,

(v) one of the largest areas of hydrocarbon accumulations was the "Rzeszotary island" which did not subside until deposition of sulfates took place; it was a part of the consolidated Małopolska Massif. During Sarmatian time more than 1000 m of subsidence took place. Sarmatian clayey-sandy sediments filling this depression are characterized by high hydraulic conductivity and filtration (Jucha *et al.*, 1990). In the depression, high hydraulic conductivity and filtration in N-S oriented parallel zones have been observed. They laterally enter sulfur ore deposits in the area of: Grzybów-Rudniki-Krzemienica, Osiek-Baranów-Skopanie, Tarnobrzeg-Grębów-Jamnica and Dęba-Gwoździec-Kamień through the Ostrowy-Rozalin Trough. These favorable migration "paths" channelled hydrocarbons in the NW, N and NE directions into elevated (primarily horst) structures, i.e. the Grzybów-Krzemienica, the Staszów-Baranów Sandomierski and the flat Tarnobrzeg, speeding up alteration of sulfates and sulfur-forming processes.

Sulfates make up an area about 18,000 km<sup>2</sup> in the Polish part of the Carpathian Foredeep. They contain a huge amount of sulfur bound to gypsum (18.6% S) and anhydrite (23.3% S); it is estimated to be about 120,000 million Mg sulfur. During the alteration process of sulfates that led to the formation of subeconomic sulfur accumulations and deposits, only 1.6% of this potential, *i.e.* about 2,000 million Mg was apparently formed. Nonetheless, to put into motion such an amount of sulfur, an

adequate quantity of energy for this complex and multi-stage sulfur-forming process was required. According to rough estimates, 2,000 million of sulfur moved required about 1,500,000 million m<sup>3</sup> natural gas. Assuming losses of about 20%, the total reserves of natural gas needed to trigger this process amount to about 1,800,000 million m<sup>3</sup>. This preliminary assessment indicates that both in the area of the Carpathian Foredeep and the northern Carpathians, a huge amount of hydrocarbon resources was concentrated. Thus, so far discovered and inferred deposits of natural gas in the Carpathian Foredeep are about 10% the original accumulations and may be regarded as remnant.

The rough balance of native sulfur enables the following assessment:

- (i) 1,200 million Mg belong to deposit accumulations,
- (ii) 700 million Mg refer to scattered accumulations in the form of inclusions and thin interlayers,
- (iii) 100 million Mg is linked to hydrogen sulfide,
- (iv) losses (20%) connected with oxidation of sulfur, erosion of deposits and dissolution by waters and removal in the form of hydrogen sulfide.

One of the most essential problems connected with the estimate of the dynamics of sulfate alteration, and sulfur-forming processes is that of supply of hydrocarbons into exposed zones. The accumulation and migration of such an amount of hydrocarbons should have taken place over a long period. Rapid accumulation and slow consumption of hydrocarbons have not been shown either by reservoir conditions and capacity of traps, especially within the Baranów Beds (beneath sulfate series). It had to be a diverse pulsative flow, which is indicated, among others, by the varied content of sulfur in sections, and irregular and locally considerable accumulations of sulfur.

#### Conditions of sulfate alteration in the Upper Silesia part of the Carpathian Foredeep

The Miocene Upper Silesia Foredeep occurs primarily on the Paleozoic (Carboniferous) basement. In the northwestern and western parts of the foredeep, the basement consists of Jurassic and Cretaceous rocks, whereas in the southern part it is composed of Tertiary flysch sediments. In the area of the Upper Silesia, the foredeep is nearly oval and has local deep parts. This region has been investigated for a long time now. The first reports come from the XIXth century. In the last five decades, prospecting and development work for coal and hydrocarbon deposits included many boreholes and pits which pierced mainly the Miocene overburden of the Carboniferous productive series. The results of these investigations were presented by researchers working on Miocene sediments (see review by Jasionowski, 1995).

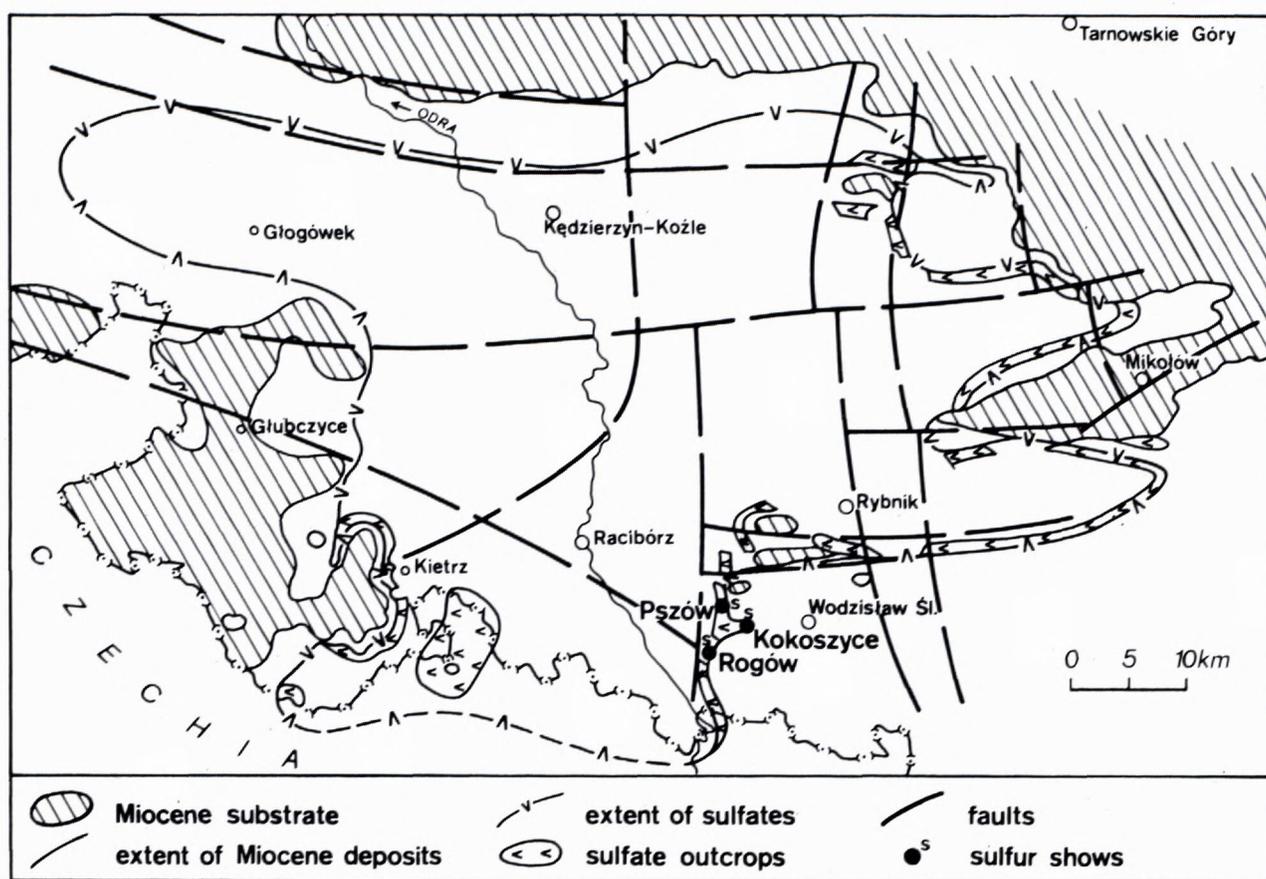


Fig. 7. Badenian sulfate deposits in Upper Silesia (faults after unpublished notes of S. Pawłowski).

Based on the results derived from boreholes and outcrops, the thickness of sulfate sediments ranges from several meters to 54 m (borehole Twardawa IG 1) in the western part of the basin (Bossowski *et al.*, 1969). Materials and archival descriptions indicate that particular layers and sequences are similar to those in the near Holy Cross Mountain part of the foredeep. The only difference is that laminated gypsum layers contain more clay minerals (over 60% in gypsum); the latter form clayey interbeds in halites (Alexandrowicz, 1963). The results obtained may be the basis for distinguishing separate layers of gypsum clays. Clay-rich gypsum beds are characteristic of the Orzesze-Żory Salt Depression. They were one of the main causes of preserving chloride salts because of their relatively small solubility. Crystalline gypsum layers consist of glassy gypsum (giant gypsum intergrowths) observed in outcrops near Czernica (Czarnocki, unpublished notes) and in gypsum mine Kietrz as well as in Kobefice in Czech Republic (Peryt *et al.*, 1997). They are also represented by sabre gypsum.

In the area of the Upper Silesian Carpathian Foredeep, sulfur was found in boreholes in the 19th century (Fig. 7). It occurs in the southern part of the foredeep

between Kokoszyce and Pszów close to the sulfate lithofacies and Carboniferous remnants (sulfate base). Prospecting work for sulfur has not been conducted on a large scale in this part of the foredeep. All the available data come primarily from the period preceding World War I (1878-1910). Recent primarily stratigraphic-lithologic investigations proved the presence of sulfur near fault zones in the vicinity of Rogów (Alexandrowicz, 1965). In Kokoszyce, two layers of sulfur-rich marls: the first 3.9 m thick (at the depth 35 - 38.9 m) and the second 7.0 m thick (54 - 61 m), occur. In Pszów sulfur-rich marls were found (thickness in parentheses) at: 36 - 36.5 m (0.5 m), 48 - 49.25 m (1.25 m) and 104 - 108.7 m (4.7 m). The dip of beds is 4°, whereas the content of sulfur varies from 5 to 30%.

A small amount of sulfur marks initial alteration of sulfates. The main cause that inhibited the course of this process was the lack of adequate screen. In Upper Silesia, the overthrusting of the Carpathians on their foreland was less intensive than in the Tarnów-Przemyśl area (SE Poland); it did not bring about adequate amounts of hydrocarbons to activate the alteration process. Young Alpine faults which cut Carboniferous and Miocene

complexes into blocks formed channels for migration of the hydrocarbons. Methane, as a product of the generation of hydrocarbons in coals, could migrate along these faults and alter sulfates. This fact was indicated by the presence of sulfur in fault zones (Fig. 7).

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## Sulfur- and oxygen-isotope composition as the genetic indicator for celestite from the Miocene evaporites of the Carpathian Foredeep

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**Abstract.** New results of sulfur- and oxygen-isotope analysis of celestite point to two different origins for the celestite in the Carpathian Foredeep. Celestite from the salt mine at Wieliczka has  $\delta^{34}\text{S}$  values ranging from 21.2 to 22.1‰ and  $\delta^{18}\text{O}$  from 9.6 to 15.8‰, values similar to those found in gypsum and anhydrite of Miocene evaporites. In native sulfur deposits, two genetically different groups of celestite have been observed. The oldest generation with  $\delta^{34}\text{S}$  from 55 to 60‰ records residual sulfates strongly enriched by ore forming processes. The younger generation with  $\delta^{34}\text{S}$  from 35 to 40‰ was formed during mixing of residual sulfates and those from leaching of original evaporites.

**Keywords:** Miocene, evaporites, sulfur deposits, celestite, sulfur isotopes, oxygen isotopes.

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### Introduction

Celestite is a relatively common mineral which occurs in Miocene evaporitic sediments of the Carpathian Foredeep (see Parafiniuk, 1989). Attention was paid by various investigators and mineral collectors to nicely developed crystals of celestite which were found in many locations within native sulfur deposits. In a microcrystalline form celestite occurs also in sulfate and halite facies of evaporites (see Kasprzyk, 1989). Its occurrence in the salt deposit in Wieliczka mine has been reported by Prochazka *et al.* (1969).

Here we demonstrate the use of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of celestite as an indicator of its genesis. The isotope data published so far refer to celestite from sulfur deposits only (Hałas & Kurpiewski, 1982; Parafiniuk, 1989). No isotope data have been published for celestite which occurs in evaporitic gypsum or halite, and no experimental data on isotope fractionation between celestite and sulfate ion in a mother solution have been reported so far. For these reasons a comparison of the isotopic ratios of celestite from evaporites and from sulfur deposits should lead to better understanding of some aspects of sulfur deposit formation.

### Mode of occurrence of celestite

As a rule, celestite occurs in Miocene evaporites of the Carpathian Foredeep in the form of scattered, very

irregularly distributed crystals averaging hundredths of millimetres in size. The strontium content in gypsum of the Nida Valley is 0.18 wt% (Parafiniuk, 1987), whereas in the Staszów region it is 0.67 wt% (Kasprzyk, 1989). Gypsum in some localities contains up to 3 wt% strontium. Residual material which results from the karstic solution of gypsum is distinctly enriched in strontium. Celestite present in gypsum forms minute xenomorphic grains, at some places prismatic or tabular crystals, reaching 0.03 mm in size. They occur on surfaces of gypsum crystals or in the interstices around carbonate and clay minerals.

In one of the rock salt varieties in the Wieliczka deposit Prochazka *et al.* (1969) reported up to 2.8 wt% strontium. It was linked to the abundant content of irregular grains or tabular crystals of celestite ranging from 0.03 to 0.06 mm in diameter. Celestite crystals coated carbonate and anhydrite aggregates, forming intergrowths with surrounding halite.

Celestite-rich rock salt constitutes the oldest beds of the Wieliczka deposit, reflecting the view that during seawater evaporation, maximum celestite precipitation occurs before halite precipitation (Usdowski, 1973), or in the final phase of carbonate precipitation and at the beginning of sulfate crystallization (Müller, 1962; Butler, 1973). Such regularities are less visible in the gypsum profiles of the Carpathian Foredeep. The celestite content is more distinctly dependent on the admixture of carbonate and clay minerals what may be connected with the

solution of gypsum rocks and an accumulation of celestite residual material. Nevertheless, the mode of occurrence of celestite in salt or gypsiferous rocks indicates its evaporitic origin. Subsequent recrystallization in the form of idiomorphic crystals sometimes has been observed.

The sulfur-bearing limestones, which were formed from evaporitic gypsum, are particularly celestite-rich rocks. The average content of celestite in Polish sulfur deposits may be only roughly estimated as 1 to 1.5 wt% due to its nonuniform distribution. Celestite forms as tiny grains scattered in limestones or native sulfur and as clusters up to several kilograms in weight which may be found in limestone fissures and caverns. Moreover celestite occurs in a huge diversity of forms and varieties, *i.e.* massive, veined, nested and perfectly shaped crystal druses. Celestite crystals may be totally translucent and colourless, or white and greyish, as well as coloured in various tints of yellow through brown to nearly black. The white and greyish colour comes from numerous liquid inclusions while other tinges are due to an admixture of bituminous substances and/or native sulfur inclusions. Pale blue varieties of celestite have also been found. The crystals commonly have a prismatic habit and range from a couple of millimetres to several centimetres in diameter. More bituminous varieties often yield a more needle-like habit. Several celestite generations can be distinguished here. Their origin was connected either to formation processes of native sulfur deposits or their consecutive transformation. Based upon its development, celestite from sulfur deposits does not seem to have been derived directly from host evaporites, but it has been formed epigenetically.

### Materials and methods

The following set of samples has been selected for this study: 12 samples of celestite from a native sulfur deposit at Machów, 3 samples from an abandoned sulfur mine at Czarkowy and 5 samples from the salt mine at Wieliczka (Fig. 1). Coarsely crystalline celestite from sulfur deposits was powdered in an agate mortar and subsequently treated by HCl to remove traces of carbonates. Finely crystalline celestite from the salt mine was separated from halite and carbonates by dissolution in distilled water and subsequent treatment by HCl. Finally celestite was separated from anhydrite and other minerals by mean of methylene iodide. Attempts at celestite separation from gypsum in the same manner were fruitless, although some gypsum samples contained considerable amounts of Sr.

Splits of prepared celestite samples were melted with a mixture of  $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$  and then dissolved for determination of Ba concentration by the AAS and ICP/IAS methods. Celestite for sulfur isotope analysis

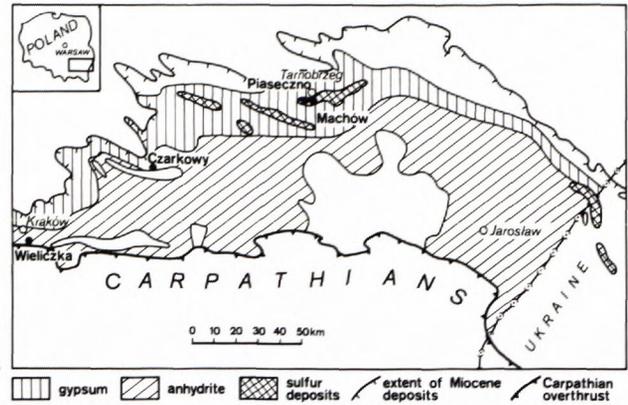


Fig. 1 Location of studied localities in the Carpathian Foredeep

was converted to  $\text{SO}_2$  by means of  $\text{NaPO}_3$  (Hałas & Wołacewicz, 1981). Oxygen isotope analysis was performed on  $\text{CO}_2$  obtained by reduction of  $\text{SrSO}_4$  with graphite (Mizutani, 1971).

### Results

The analysis for barium in celestite demonstrates that no solid solution barite - celestite occurs in the Carpathian Foredeep, though the complete series in the binary system  $\text{SrSO}_4\text{-BaSO}_4$  is known (Burkhard, 1973; Wieser, 1982). Barium content in celestite in the investigation was rather low, from 0.17 to 0.54 wt% (Table 1). Celestite from Wieliczka has a more homogeneous Ba content (at 0.20 wt%) than that from sulfur deposits.

The results of sulfur and oxygen isotopes analysis are listed in Table 1 and plotted in Fig. 2. A major difference in the isotope ratios of celestite from Wieliczka and that from native sulfur deposits is clearly seen. Celestite from Wieliczka is rather isotopically homogeneous in comparison to that from sulfur deposits. Moreover, its isotopic composition is close to that of gypsum (or anhydrite) of Miocene evaporites in the Carpathian Foredeep (Halas & Krouse, 1982).

The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of Miocene evaporites from the Carpathian Foredeep are also summarized in Table 2. From the comparison of these data and  $\delta$  values of celestite from Wieliczka, one may state that during celestite crystallization from sea water in the halite facies the isotope fractionations do not exceed those for gypsum. The experimentally determined fractionations of sulfur and oxygen isotopes during crystallization of gypsum are 1.65‰ and 3.5‰, respectively (Thode & Monster, 1965; Lloyd, 1968). Although there are no data on fractionations for celestite, it seems reasonable to assume that celestite which precipitated in the sulfate facies has similar  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values as gypsum formed in these facies. It should be emphasized that  $\delta^{34}\text{S}$  in gypsum

Table 1. Isotopic compositions and Ba contents of celestite

Sample	Ba content [wt.%]	$\delta^{34}\text{S}$ CDT [‰]	$\delta^{18}\text{O}$ SMOW [‰]
Wieliczka:			
W-1001	0.19	22.1	9.6
W-1003	0.19	21.3	10.5
W-1011	0.20	21.4	13.2
W-1012	0.21	21.2	15.8
W-1013	0.20	21.4	11.3
Czarkowoy:			
CZ-21	0.30	39.8	20.7
CZ-22	0.27	40.3	18.3
CZ-23	0.26	40.4	19.6
Machów:			
CM-1	0.31	58.6	23.6
CM-5	0.40	53.1	27.0
M-50	0.54	38.8	22.1
M-51	0.31	59.3	24.6
M-52	0.54	38.7	19.2
M-53	n.d.	56.8	22.6
M-54	0.42	51.4	26.1
M-55	0.34	35.4	19.1
M-56	0.22	56.4	24.0
M-57	0.27	45.1	24.7
M-58	0.43	39.7	18.5
M-59	0.17	37.2	18.1
TS-7a *	n.d.	41.7	18.5
TS-7b *	n.d.	35.9	16.7
TS-8 *	n.d.	35.9	17.0
TS-9 *	n.d.	36.9	17.0
Piaseczno:			
S-1 *	n.d.	47.4	19.0
S-2 *	n.d.	57.7	23.6

n.d. not detected

\* data from Hakas &amp; Kurpiewski (1982)

Table 2. Isotopic composition of  $\text{CaSO}_4$  from the Miocene evaporites from the Carpathian Foredeep.

Sample	$\delta^{34}\text{S}$ CDT [‰]	$\delta^{18}\text{O}$ SMOW [‰]	Data source
Wieliczka:			
W-1002	22.2	12.9	3
W-1005	21.9	10.6	3
W-1008	22.7	14.2	3
W-1010	22.8	14.2	3
29664-1	21.8	12.9	1
29664-2	21.9	10.8	1
29664-3	21.6	12.9	1
Gacki:			
BS-9	23.0	13.9	2
BS-10	22.9	13.0	2
BS-11	22.4	13.1	2
Piaseczno:			
T-30a	24.6	14.4	2
T-31	22.4	13.6	2
T-39	23.6	13.3	2
T-40	23.0	13.6	2
Horyniec:			
H-5	23.2	12.9	2

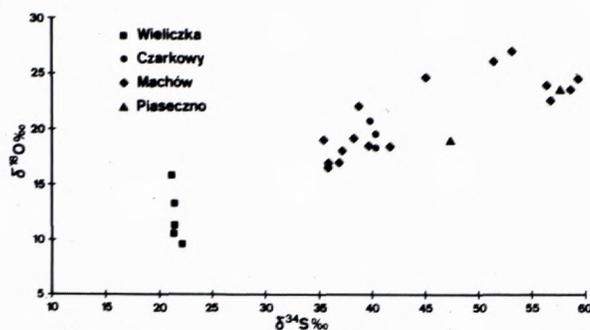
Data source: 1. Claypool *et al.* (1980), 2. Halas & Kurpiewski (1982), 3. This paper

Fig. 2. Spread of isotope data for celestites from the Carpathian Foredeep.

that crystallized at the beginning and at the end of the sulfate facies differed by less than 1‰ (Raab & Spiro, 1991).

Celestite from native sulfur deposits has significantly higher  $\delta$  values than evaporitic sulfates, what has been noted by Parafiniuk *et al.* (1994). The  $\delta^{34}\text{S}$  values determined for this celestite vary from 35.0 to 59.3‰, the  $\delta^{18}\text{O}$  from 17 to 27‰. Two diverse groups of celestite can be noted from Fig. 2, one with  $\delta^{34}\text{S}$  from 55 to 60‰ and the other with  $\delta^{34}\text{S}$  from 35 to 40‰. Only a few samples have  $\delta^{34}\text{S}$  values between these ranges. These groups also can be distinguished with respect to the oxygen isotopes ratio, although differences in  $\delta^{18}\text{O}$  values are smaller. There is no correlation between habit and size of celestite crystals and their isotopic composition.

The most likely lanation of the two groups of celestite seems to be linked with different generations of this mineral. The first generation with higher  $\delta^{34}\text{S}$  values was related to the conversion of gypsum to native sulfur. A strong isotope fractionation during bacterial reduction of sulfate results in high  $\delta$  values of the remaining sulfate in the solution. That remnant sulfate has been fixed predominantly in the first generation of celestite.

The second generation probably contains sulfate ion fixed later, most likely during processes of transformation of the native sulfur deposits. A trend in increased  $\delta^{34}\text{S}$  values with age was observed directly. In two specimens in which a celestite cluster subsequently grew on another we noticed  $\delta^{34}\text{S}$  values of 45.4 and 44.4‰ for the older, while 41.7 and 35.9‰ for the younger cluster, respectively.

### Isotopic composition of celestite and the formation of sulfur deposits

The isotopic composition of sulfur and oxygen in celestite seems to be a valuable indicator of the conditions in which sulfur deposits were formed. The isotopically heavier (older) celestite represents compositions of

SO<sub>4</sub><sup>2-</sup> ion of residual sulfates. Its isotopic composition can be used for estimation of sulfur isotope balance and hence of the capacity of the gypsum reduction process (Parafiniuk *et al.*, 1994). A large enrichment in <sup>34</sup>S implies that the ore forming process went on with limited mass exchange, at nearly closed system conditions, excluding supply of hydrocarbons. The estimated capacity of reduction did exceed 75 to 77% (see Parafiniuk *et al.*, 1994).

The younger generation of celestite with lower δ values seems to be a product of various processes which have gone after formation of the sulfur deposit, including recent processes. Although recent crystallization of celestite was not reported, investigations of recently formed barite were reported by Parafiniuk *et al.* (1994). Its δ<sup>34</sup>S values vary from 42.2 to 36.3‰ close to values of the younger generation of celestite. Recent barite precipitation has been noted within the pipe of the Machów mine drainage system as well as in sulfur bearing limestones. Also sulfate dissolved in formation waters shows residual feature with δ<sup>34</sup>S from 31.5 to 33.8‰ (Parafiniuk *et al.*, 1994).

It seems that a drop of δ<sup>34</sup>S values which is observed between two generations of celestite may be interpreted as a record of evolution of the ore water composition due to influence of ambient water containing sulfate from freshly dissolved gypsum. Such an interpretation is suggested by correlation between the isotopic composition of sulfur and oxygen in celestite from evaporites and sulfur deposits (Fig. 2). Contrary to sulfur isotopes, oxygen isotope ratios do not depend on the degree of sulfate reduction but on the isotopic composition of water in which the reduction took place (Fritz *et al.*, 1989).

The intensity of crystallization of younger celestite was probably controlled by a growing sulfate concentration which came from dissolution of surrounding gypsum. In the Machów mine conditions one may estimate from the isotopic compositions of both generations of celestite that sulfates of the deposit waters are a mixture of residual and primary evaporitic sulfates in proportion *ca.* 1:1. The isotopic ratios of sulfates in recent deposit water have been found to be remarkably lower than that in younger celestite. The main reason for the decrease of δ<sup>34</sup>S of dissolved sulfates may be reoxidation of isotopically lighter native sulfur.

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## Resedimented salt in the Northern Carpathians Foredeep (Wieliczka, Poland)

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**Abstract:** Examination of sedimentary structures of the Middle Miocene salt (halite) deposits of the Wieliczka Salt Mine (Carpathian Foredeep) indicates that a part of the salt was deposited through the action of gravity currents and a resultant fan-like distribution of facies can be distinguished. The response to apparent continued tectonic movements was an increase in the rate of the redeposition processes. The development of the salt basin in this area ended with mass movements of marly-clay sediments containing halite olistoliths.

**Key words:** Miocene, salt, redeposition, foreland basin, Carpathians.

### Introduction

In the Wieliczka mine, situated near Kraków (Poland), within the salt layers there are unique sedimentary structures that show that most of the halite layers have been formed from redeposition by gravity mass movements (Kolasa & Ślącza, 1985; Ślącza & Kolasa, 1987). While resedimented gypsum occurrences are well known (e.g. Kwiatkowski, 1972; Parea & Ricci-Lucchi, 1972; Schreiber et al., 1976; Meier, 1977; Catalano et al., 1978; Peryt & Kasprzyk, 1992) resedimented halite deposits are less common (cf. Schreiber, 1986) and therefore deserve particular attention.

To distinguish salt deposited by precipitation from resedimented salt, the term saltstone is proposed for salt layers that consist of redeposited salt grains: cf. sandstone or dolostone, and the term pebbly saltstone for layers that consist of fine grained redeposited salt that contains rock fragments: cf. pebbly mudstone.

### Geological setting

Salt Rocks (mainly halite) occur in a narrow zone below and in front of the Carpathian flysch nappes (Tołwiński, 1956, Gaweł, 1962, Garlicki, 1979) (Fig. 1). They are strongly folded (with 3 principal folds) and are also thrust over the autochthonous Middle Miocene deposits of the European Platform.

The salt deposits of the Wieliczka Mine were formed during the salinity crisis that affected the region of the Carpathian Foreland (Fig. 2) in the Early Serravalian ( $\pm$

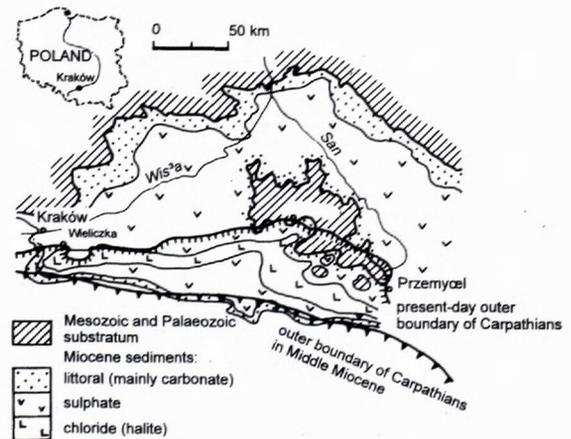


Fig. 1. Facies map of the Middle Miocene evaporites in the Northern Carpathian Foreland.

15 My; Hamor, 1988). These evaporites accumulated within the Carpathian Foredeep and Foreland basins along the northern margin of the evolving Carpathian orogen (Alexandrowicz, 1965, 1971; Garlicki, 1979; Łuczowska, 1978). The halite was deposited in a marine, euxinic (Garlicki, 1979) basin which was asymmetric in bathymetric profile (deeper to the south and shallow in the northern part). In the south, the basin was bordered by the active Carpathian orogen and towards the east it was connected with the ancestral Mediterranean by a narrow strait (Fig. 2). Deposition of halite was dominant in the southern part of the basin, while further

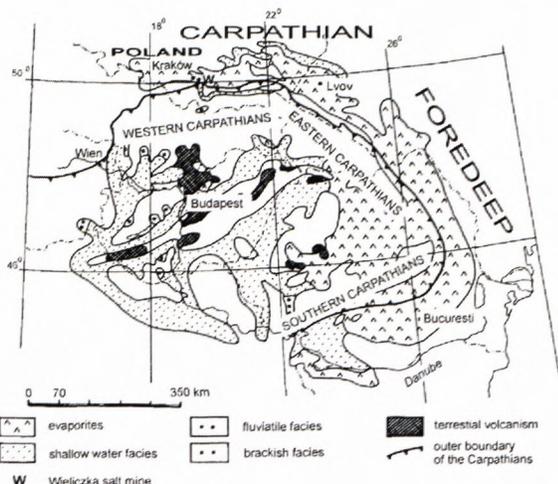


Fig. 2. Distribution of facies in the Carpathians during the Middle Miocene. Based on Hamor (1988).

north apparently only sulphate facies were deposited. The sulphate facies presumably also occurred along the southernmost margin of the basin, as indicated by the sulphate fragments redeposited in the adjacent sequences. The near shore sequences formed along the southern margin of the depositional basin are characterized by clays that contain bivalves, echinoderms, Lithothamnion, and individual corals (*Caryophyllia* sp.) (Kowalewski, 1935; Morycowa & Roniewicz, 1988).

Plant fragments, abundant within the salt sequence, are typical of the continental, so-called younger mastixioid floras, known from the European Miocene (Mai, 1964). There are also some palaeotropical species (Łańcucka – Środoniowa, 1984). This association of plants derived from different climatic zones may be attributed to the morphology of the bordering land area and/or to long-distance transport.

During Late Miocene tectonism, the salt deposits, together with a part of the substratum, were detached, folded, and overthrust toward the north onto the autochthonous Miocene deposits of the European Platform. The lateral displacement of the overthrust Middle Miocene rocks exceeds 10 km but it is difficult to calculate this distance more precisely because postdepositional tectonic deformation has obliterated much of the evidence.

**Wieliczka salt deposits**

The main halite sequence of the study area is underlain by siltstones, anhydritic claystones and siltstones, together with sandstones containing anhydrite and/or halite cement (Pp on Fig. 4). There are sporadic intercalations of conglomerates and pebbly mudstones containing boulders derived from the Carpathian flysch rocks. The salt-bearing sequence comprises two members (Fig. 4): the Stratified Salt Member (SSM) and the overlying

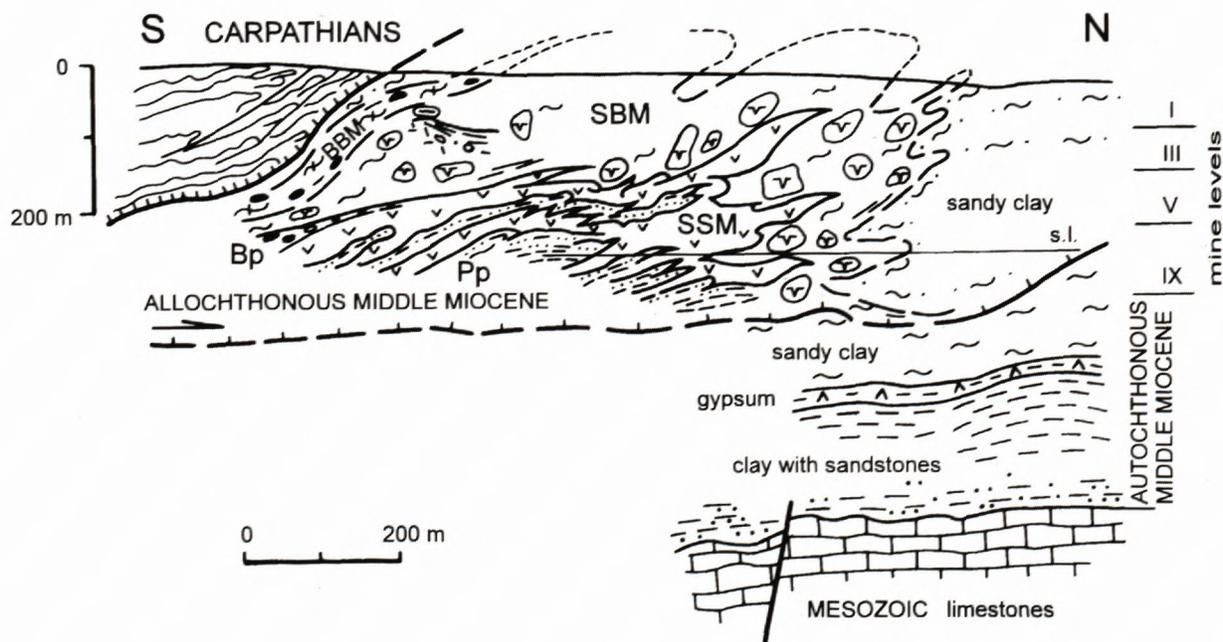


Fig. 3. Structural cross-section of the Wieliczka Salt Mine (after Gawel, 1959, modified). Explanation of letter symbols: P<sub>p</sub> – clay and sandstones below the salt-bearing sequence; SSM – Stratified Salt Member; B<sub>p</sub> – lens of halite conglomerates in upper Spiza; SBM – Salt Breccia Member; BBM – Barren Breccia Member.

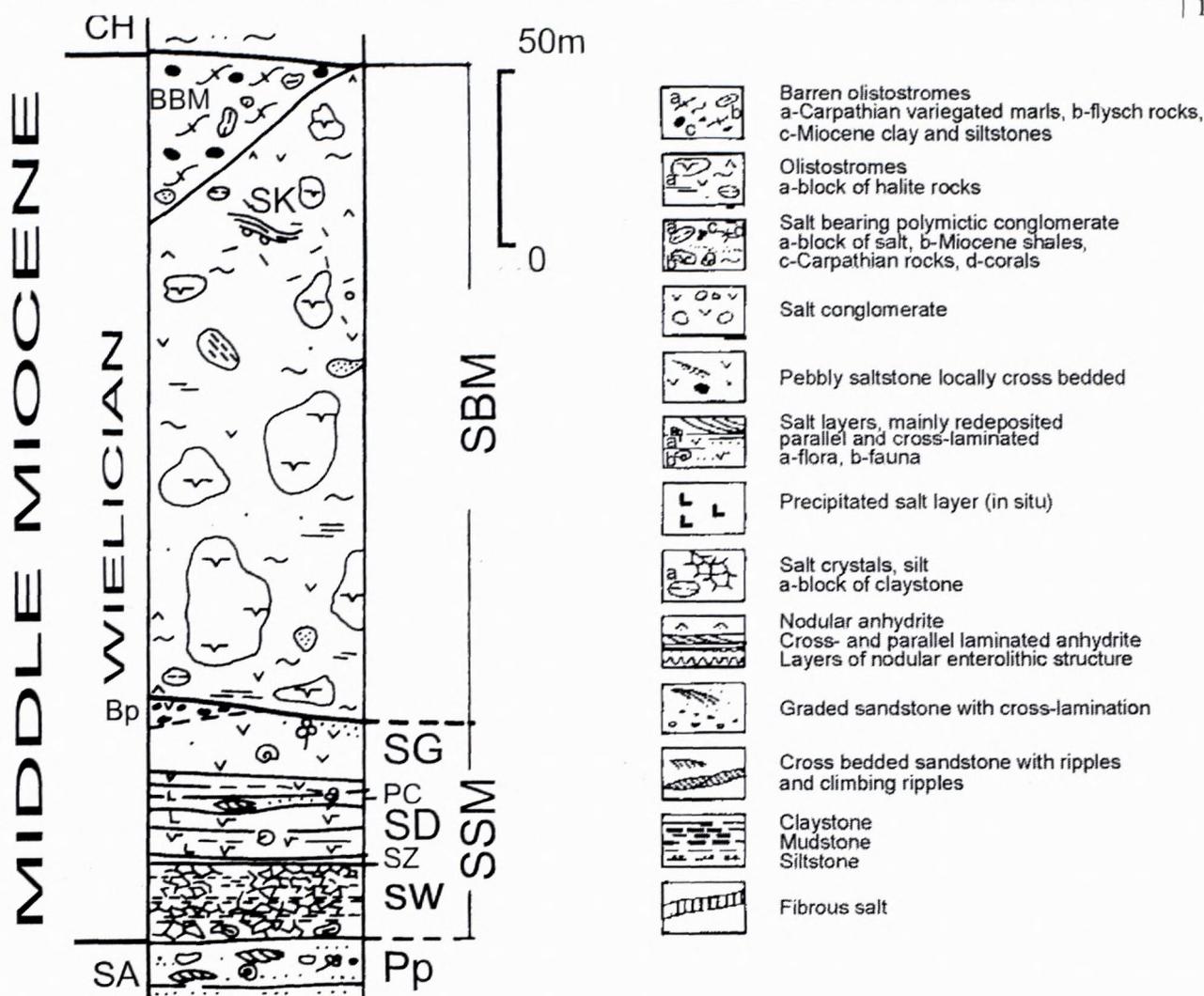


Fig. 4. Generalised litho-stratigraphic column of the Wieliczka salt deposits.

Explanation of letter symbols: Pp, SSM, SBM, BBM, - see Fig. 3; SA - marine clays and sandstones (Skawina Beds); SW - Green Salt; SZ - Shaft Salt; SD - Lower Spiza Salt; BP - pebbly saltstones and conglomerates; SK - intercalation of saltstones (Klęczki); CH - marine clays and sands (Chodenice Beds).

Salt Breccia Member (SBM) (Niedźwiecki, 1883, 1884; Gaweł, 1962). The lower member is made of stratified, partly redeposited salts (halite) together with "barren" rocks. The upper member is composed of olistostromes (Kolasa & Ślaczka, 1985) with huge halite blocks and grains chaotically distributed within a finer grained matrix of halite grains and clay. This type of deposit is known in mining nomenclature as the Zuber. The evaporitic sequence is overlain by tectonically deformed marine claystone and sandstone (CH on Fig. 4).

### 1. Stratified Member

The Stratified Member consists of three units: A) Green Salt, B) Shaft Salt, C) Spiza Salt.

A) Green Salt Unit (SW on Fig. 4).

The Stratified Member begins (Figs 4 and 5) with several layers composed of primary coarse halite crystals that originated from direct precipitation (Garlicki, 1979).

These crystals are enclosed in clay material (Fig. 6), the Green Salt of mining nomenclature. Within some of the salt layers there are sporadic single pebbles and cobbles of Miocene marl and anhydrite and the layers resemble pebbly mudstones. These features suggest that resedimentation processes occurred during sedimentation of the Green Salt Unit. The salt layers are intercalated with thin rock layers devoid of salt crystals. These intercalations generally thin towards the north. They are composed of sandstones, cemented by salt and anhydrite, and mudstones. There are also anhydrite-rich layers that commonly occur in thin cyclic sequences. Such cycles consist of massive and laminated sandstones overlain by mudstone and then by anhydrite (Figs 6 and 7A). Commonly, the lower portion of the cycles is absent. The sandstones contain numerous anhydrite grains and nodules and a smaller quantity of biogenic debris. Part of the anhydrite layers are characterized by very thin laminations, probably indicating a quiet depositional environment.

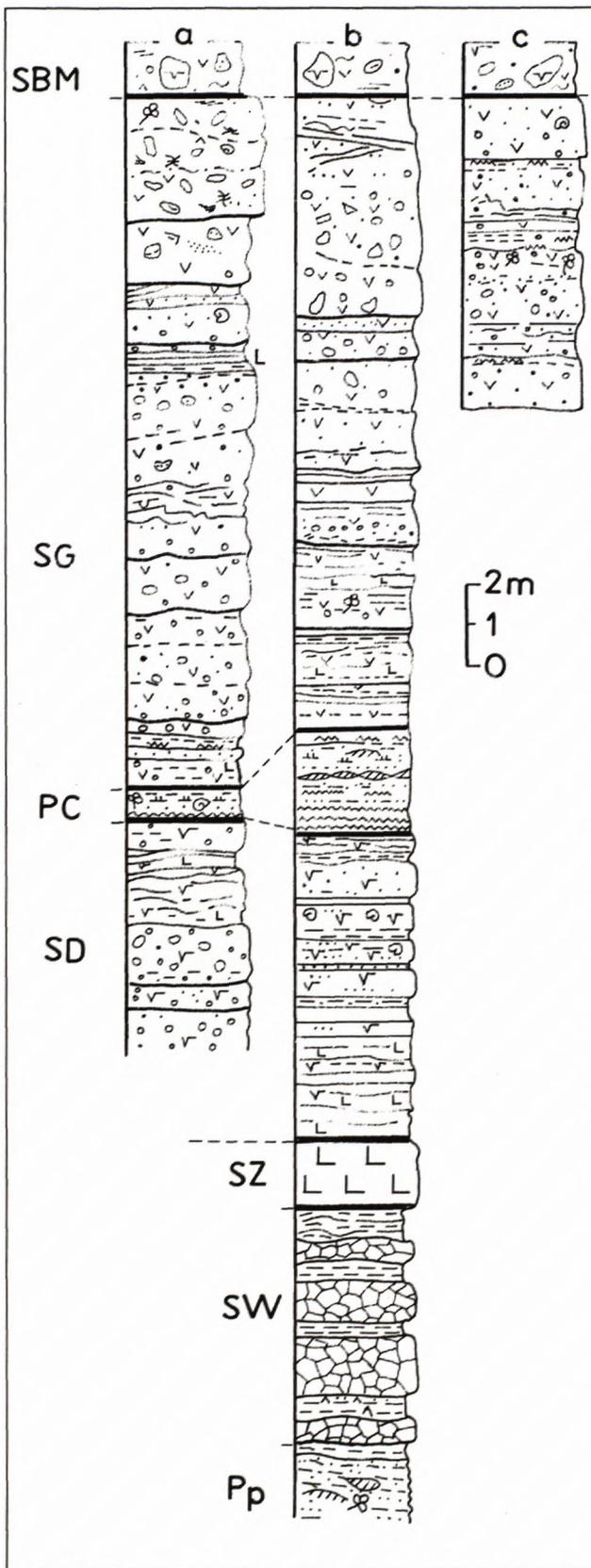


Fig. 5. Lithostratigraphic columns of the Layered Salt Member in the southern (a), central (b) and northern (c) part of the Wieliczka Salt Mine. (Explanation of lithological symbols as in legend to Fig. 4).

B) Shaft Salt Unit (SZ on Fig. 4)

The Green Salt Unit is overlain by about 2 metres of pure halite (Figs 4 and 5) which includes abundant primary cubic crystals. This salt represents a period of quiet deposition by precipitation. There is no evidence of redeposition within the salt layers.

C) Spiza Salt Unit

The Shaft Salt is overlain by salt layers formed partly by precipitation and partly by redeposition. The Unit can be divided into two parts: Lower Spiza (SD in Fig. 4) and Upper Spiza (SG on Fig. 4), separated by the Central Barren Intercalation (Figs 4 and 5).

The Lower Spiza sub-unit consists of layers of pure halite intercalated with thin laminae composed of quartz arenite material and anhydritic grains and nodules, banded white and grey pure halite, and layers of halite with fragments of Miocene marl and sandstone. There are also thin intercalations of mudstone and very fine sandstone.

The Lower Spiza salt is overlain by a few metres of the barren unit (Central Barren Intercalation - PC, Figs 4 and 5). In the central part of the Wieliczka salt succession the barren unit attains its maximum thickness (Fig. 7B) and becomes thinner both towards the south and north (Kolasa, 1990). Generally the barren unit is composed of sandstones (siliciclastic) but locally in the southern area it is dominated by homogeneous mudstones. In the area where the barren unit is clastic, the lower part is composed of several lithologies similar to those described from the stratified member. Commonly the individual cycles start with sandstone and pass upwards into marly mudstone, clayey shale, and terminate in anhydrite and sporadic salt layers (upper part of column PC A on Fig. 7B). In the upper part of the section, the number of evaporitic intercalations decreases. The lower parts of the sandstones are occasionally graded and often the sandstones and mudstones display current ripples (Fig. 8) and convolute laminations. The azimuth of the ripple-foreset planes is generally stable and directed towards the east and northeast.

Above the Central Barren Intercalation lies the main unit of redeposited salt (Upper Spiza salt - SG on Fig. 4, Fig. 5). In the lower part of this unit there are layers of transparent halite, sometimes with dark and white bands, made up of medium sized salt crystals mixed with quartz grains and fragments of reworked fossils from different environments and of different ages. In the middle portion of the sequence, layers of precipitated salt are intercalated with layers of redeposited salt. Thin intercalations of marls containing scarce, autochthonous foraminiferal assemblages occur sporadically. In the higher part of the section, most of the halite is reworked and forms layers composed of halite clasts, together with sandstones and

conglomerates. The lateral and vertical distribution of the lithofacies is shown on Fig. 5. The pebbly saltstones and conglomerates (Figs 4 and 5) occur in the uppermost part of the salt sequences in the southern part of the basin (Fig. 9B). Salt-clast rudites (Figs 9A and 11A) prevail in the central area; saltstones prevail in the northern area.

Some of the layers are strongly folded (Figs 10 and 12). These structures may represent synsedimentary slumps although some of them may have a tectonic origin.

*Petrographic composition of redeposited material in the Upper Spiza Subunit*

Redeposited layers consist mainly of grains and fragmented crystals of halite. Large halite grains, up to a few centimetres across, are coated sporadically by thin layers of clay and gypsum. Besides the halite grains, there are anhydrite and gypsum grains or crystals, quartz grains, clay minerals (illite, kaolinite and less common montmorillonite, Pawlikowski, 1978), organic detritus (Spiculae, foraminifera, fragments of shells) and lithic fragments (micritic limestone, shale, sandstone). Minor accessories include feldspar, calcite, glauconite, micas,

Fe-minerals, zircon, and titanite. The content of non-vaporitic material varies from less than one percent to more than 60 percent.

Locally there are zones enriched in fragments of carbonized flora (fruits, seeds, leaves and wood), preserved in the form of lignite (Unger, 1850; Zabłocki, 1928, 1930; Łańcucka-Środoniowa, 1984).

The grain size of the halite varies from fine to very coarse. The grain shapes are generally angular; cubic and ellipsoidal halite shapes are less common. Some of the cubic crystals evidently grew by displacement after sedimentation. The pebbles, mainly angular, range in size from 3 to 8 cm, and sporadically reach 1 m (boulders). They are composed of laminated salt, quartzitic sandstone, graywacke of Carpathian origin, Miocene clayey marls and smaller amounts of individual coral fragments, Bryozoa, Lithothamnion, molluscs and snails (Reuss, 1867; Niedźwiecki, 1883, 1884; Kowalewski, 1935; Kulka, 1980; Morycowa & Roniewicz, 1987). The laminated halite blocks generally differ from the laminated salt found *in situ* in the lower part of the salt sequence in the Wieliczka mine. The laminae in the blocks are wavy and often are similar to stromatolitic structures.

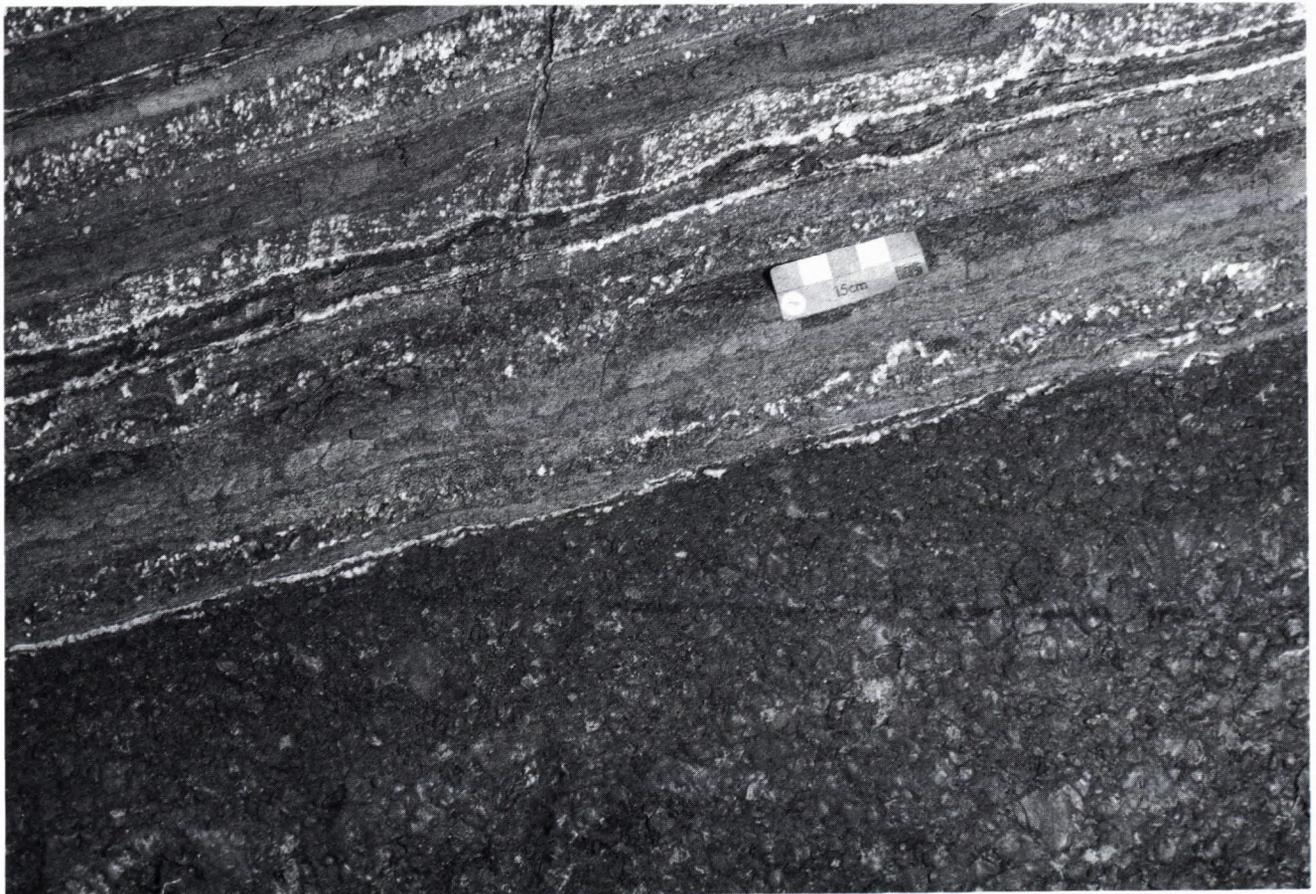


Fig. 6 Lithologies of the lower part of the Stratified Salt Member. Contact of barren layers (A - sandstone, mudstone and anhydrite beds) with underlying Green Salt (B), where halite crystals are embedded in clay. Rittinger Gallery.

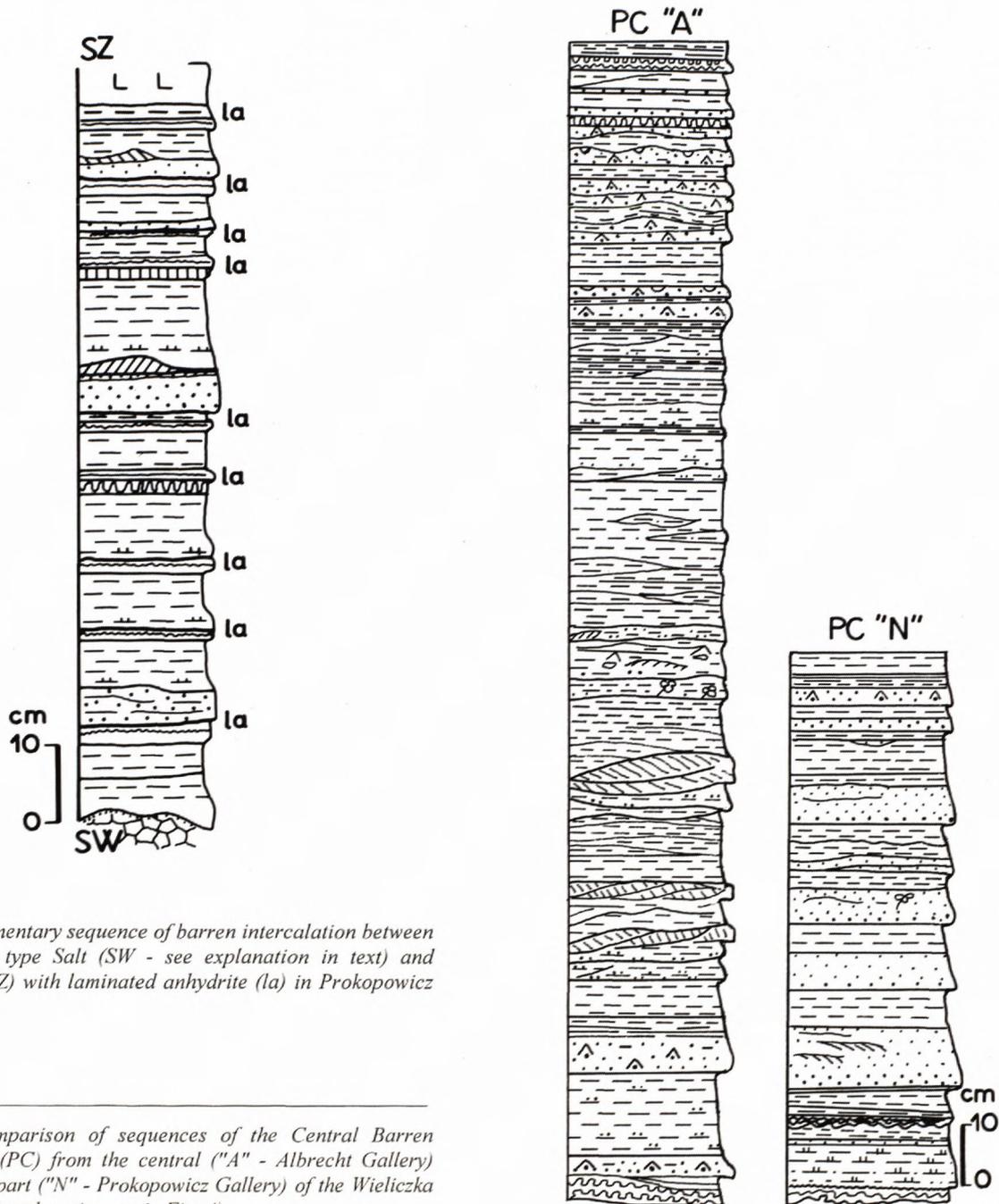


Fig. 7A. Sedimentary sequence of barren intercalation between Stained-glass type Salt (SW - see explanation in text) and Green Salt (SZ) with laminated anhydrite (la) in Prokopowicz Gallery.

Fig. 7B. Comparison of sequences of the Central Barren Intercalation (PC) from the central ("A" - Albrecht Gallery) and northern part ("N" - Prokopowicz Gallery) of the Wieliczka Mine. (Symbol explanations as in Fig. 4).

#### Characteristic of resedimented salt

##### Laminated and graded saltstones

This lithofacies is represented by medium to very coarse grained, partly conglomeratic strata which commonly show parallel laminations (Figs 10 and 11B) or gradation and consist mainly made of salt particles.

Laminated saltstones occur either as individual beds or they form the upper part of graded beds. They consist of alternating grey and white laminae. Grey laminae are composed of a mixture of halite grains, clayey material

and anhydritic sand. White laminae are composed mainly of halite. Sporadically there are siliciclastic laminae composed of quartz grains and clay. The thickness of individual beds varies from 0.5 to 1.5 m.

Parts of the saltstones infrequently display cross-lamination. Some layers are markedly structureless, almost homogeneous in grain size, and lensiform (Fig. 10B). The bases of these beds are sharp and flat.

*Interpretation.* The graded and laminated saltstones show many features characteristic of sediments deposited by debris flows, turbidity currents. The structureless beds might have been formed by grain flow or fluidised flow

mechanisms. Most of the structures observed correspond to those in the A, B, and C divisions of the Bouma turbidite sequence; the structureless beds resemble the fluxoturbiditic sequences (F division according to Ślaczka and Thompson, 1981). Some salt layers with crudely parallel lamination do not provide evidence of redeposition and might have been deposited by precipitation.

### *Conglomerates*

These are composed of pebbly to bouldery salt clasts (Fig. 11A) scattered within a matrix of coarse- to medium grained salt (matrix-supported conglomerates). They contain occasional shaly clasts. Conglomerates form sheet-like and lens-like bodies that range in thickness from a few decimetres to 6 meters (Fig. 10a). The base of the conglomeratic beds is sharp, usually flat, but occasionally displays flame and load structures (Fig. 13) or scour marks. Wavy basal contacts, visible in some beds, are probably an effect of the sliding movement of already deposited beds, caused by depositional and post-depositional deformation. The majority of these conglomerate beds fine upwards and pass into horizontal- and cross-laminated saltstones. They can also show crude inverse grading.

In the southern part of the salt mine there are polymictic conglomerates. These are characterized by the occurrence of numerous unsorted or poorly sorted clasts, mainly poorly rounded blocks of different salt rocks as much as 1 m in length, broken halite crystals and grains, together with blocks of Carpathian flysch sandstones (as much as 50 cm in diameter) and Miocene marls (Figs 14, 15 and 16). Locally there are many fragments of corals. These polymictic conglomerates display cross bedding (Fig. 16A). The thickness of the layers is as much as 80 cm and contacts between them are usually indistinct (Fig. 14A). In sections perpendicular to the direction of sediment transport, the conglomerates are lenslike (Fig. 16B). In the central part of the lens, clast-supported conglomerates are common; towards the margins, they pass into matrix-supported conglomerates.

*Interpretation.* The features described indicates that the conglomeratic rocks were transported by high-density debris flows. However, those conglomeratic layers containing angular clasts might be storm deposits.

### *Pebbly saltstones*

These rocks consist of thick (as much as 2 m) beds of medium to very coarse, poorly sorted salt grains together with irregularly scattered, subangular to rounded, sometimes imbricated, pebbles and boulders (< 1m) of Carpathian sandstones and Miocene marls (Figs 17B and 17A). In some beds the matrix contains clay. Locally, layers rich in anhydrite fragments can be found. The



Fig. 8. Central Barren Intercalation. Rippled and cross-laminated siliciclastic sandstones, siltstones and layers of nodular anhydrite, some having enterolithic structures. Albrecht Gallery.

pebbly saltstone beds are sheet-like and extend over distances of tens of metres. They are generally structureless, although some units display crude cross-laminae which dip up-current. In some cases the layers of the pebbly saltstones are terminated by a parallel-laminated section.

*Interpretation.* The observed structure suggests that pebbly saltstones similar to normal pebbly mudstones, represent sediments deposited by subaqueous debris flows or incoherent slump which passes into high density turbidity currents. That process best explains the sedimentation of layers containing chaotic mixture of multisized clasts (comp. e.g. Friedman & Sanders, 1978).

## 2. Salt Breccia Member

The Salt Breccia Member (SBM in Fig. 4) is an unsorted mixture of pebble-, boulder- and block-size clasts scattered in a finer grained matrix and is about 150 m thick (Fig. 4). The occurrence of sporadic intercalations of saltstone suggests that this complex was not formed in

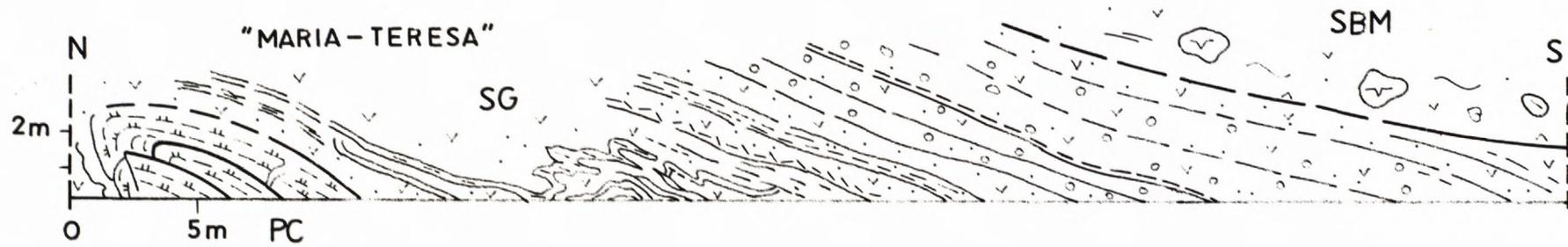


Fig. 9 (A) Cross-section through the folded Upper Spiza (SG) unit with salt conglomerates and contact with the overlying unit - Salt Breccia Member (SBM). Thrust-faulted Central Barren Intercalation rocks (PC) occur in the core of an anticline to the north. Maria Teresa Gallery.



Fig. 9 (B) Cross-section through the uppermost part of the Upper Spiza (SG) unit in the southern part of the Wieliczka Mine with pebbly saltstones and polymictic conglomerates. Salt Breccia Member (SBM) at the top. Gruszczyn Gallery. Symbol explanations as in Fig. 4



A



B

Fig. 10 Lithologies in the Upper Spiza unit (Gallery west of Kościuszko shaft): (A) laminated saltstones, strongly deformed in the lower part of the photograph; polymictic breccia in the upper part with halite and flysch blocks intercalated between laminated salt deposits. Scale is 1 meter long; (B) Laminated, bar-form saltstones overlain by pebbly saltstones.

one depositional episode. The known extent of this member is about 15 km in length and 4 km in breadth.

The contact with the underlying Stratified Member is sedimentary in character (Kolasa & Ślącza, 1985), although the Salt Breccia Member is regarded by some authors as an overthrust tectonic breccia (Gaweł, 1962; Poborski & Skoczylas-Ciszewska, 1963; Garlicki, 1979). However, the contact has local irregularities caused by erosional processes (Fig. 18). Tectonic effects along that contact are only local and are mainly related to fold crests. On the fold limbs there is generally a lack of slickensided surfaces or other tectonic features.

Halite blocks are the chief component of the Salt Breccia Member (Fig. 19), forming more than 90 per cent of the clasts. The salt clasts are angular, subangular, and rounded. The sizes of the blocks range from a few cubic meters to 12,000 cubic meters, but several blocks have very large volumes, as much as 100,000 cubic meters. They consist of different salt lithologies, such as wavy laminated salt, layered salt, structureless salt, dolomitic salt, or the "stained glass" type of salt (a local name for a rock composed of irregular salt crystals separated by thin layers of clay). The structure of the salt in the clasts is usually different than the structures in the Stratified Member. Some of the salt blocks are enveloped by a thin layer of anhydrite, gypsum or salt of secondary origin which is usually connected with radial secondary veins. Large blocks are commonly imbricated, with their c-axes parallel to the trend of the Carpathian border. In the lower part of the complex the blocks commonly rest in horizontal attitude.

Less common within Breccia M. are much smaller fragments (as much as a few metres across) of Miocene rocks (marls, claystones and sandstones that are contemporaneous with or slightly older than the enveloping salt sediments). Other constituents include variegated Late Cretaceous marls, black Albian shales, and various Cretaceous sandstones of Carpathian provenance. Usually these clasts are angular or subangular and their lengths range from a few to about a dozen centimeters. They are insignificant in volume and commonly are concentrated near the base of the Breccia Member. Occasionally there are also large (as much as 30 cm in length) single crystals of halite that are covered by a thin film of gypsum-bearing mud.

The matrix contains varying proportions of calcareous mudstone and claystone, together with halite crystals and grains (Fig. 19), many of which display hopper structure. Less common are grains (fragments and crystals) of anhydrite and gypsum. Halite crystals and grains can form as much as 75 per cent of the Breccia matrix but in the uppermost part of the sequence they are scarce. The matrix also contains redeposited foraminifera from different stratigraphic units of the Middle Miocene,

Palaeogene, and Cretaceous. Redeposited shallow water faunal elements are minor constituents. The breccia matrix is marly in the lower part of the sequence and more clayey in the upper part. Locally, the amount of matrix diminishes, and the rocks described above pass into clast supported conglomerates. At one locality between two layers of sedimentary breccia an intercalation (Fig. 20) of graded salt conglomerate was observed. In the upper part of the layer the conglomerate passes upward into coarse grained, cross-laminated (Fig. 21) and parallel-laminated saltstone.

*Interpretation.* From the foregoing descriptions, based mainly on studies of the breccia, including the blocks of different provenance imbedded in fine grained material and the sedimentary structures, it seems clear that the Breccia Member is essentially a product of submarine debris flows and might represent "mega-debrites", which could result from earthquakes caused by Mid-Miocene tectonic movements.

### 3. Barren Breccia Member

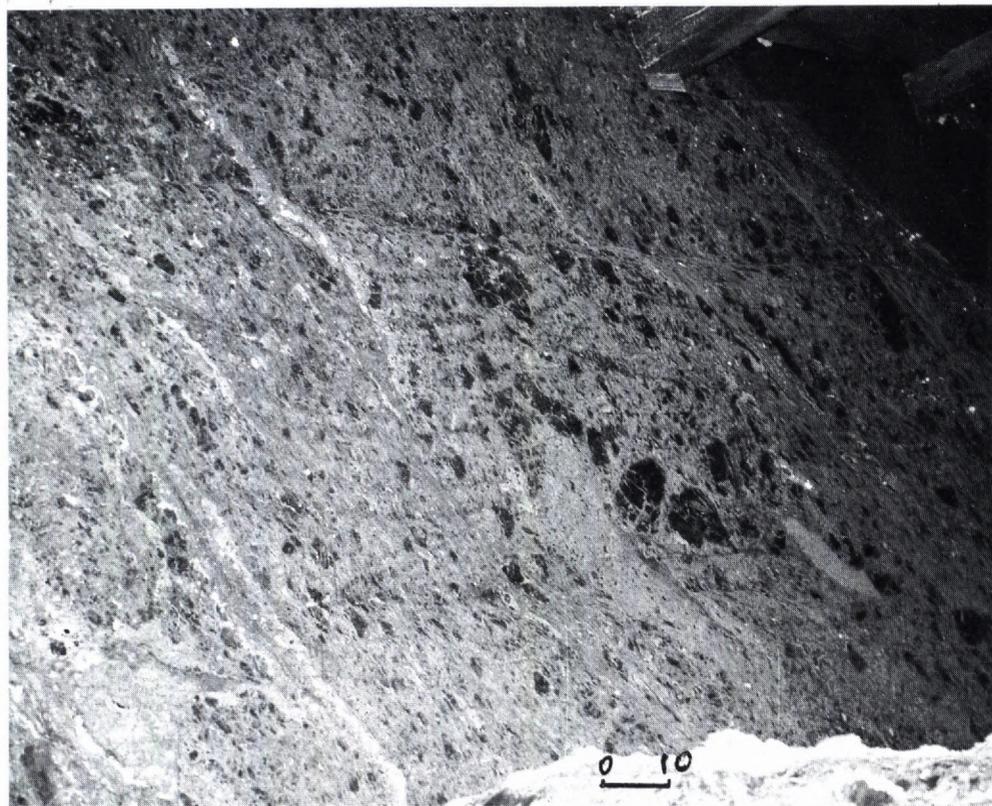
In the southern part of the Wieliczka mine, the Salt Breccia Member is overlain by a sequence of debrites (Reading, 1986) (60 m thick) that are devoid of salt particles and clasts. The sandy, marly and clayey matrix of these debrites hosts abundant dispersed clasts of various Carpathian rocks (variegated marls, black shales, sandstones), together with Miocene marls that are older than the salt deposits (Alexandrowicz, 1975). Clasts of anhydrite and Miocene sandstones are less common. The Carpathian clasts are angular to subrounded and can reach 1 metre in diameter. The size of the Miocene clasts is usually greater, attaining several metres. Part of the Barren Breccia Member has been strongly affected by tectonism associated with overthrusting of the Carpathians.

*Interpretation.* Similar to the Salt Breccia Member, the Barren Breccia Member is also essentially a product of submarine debris flow - it is thick bedded, poorly sorted, internally structureless and is composed of fine grained, mudstone matrix that contains rock fragments which range in size from pebbles to boulders.

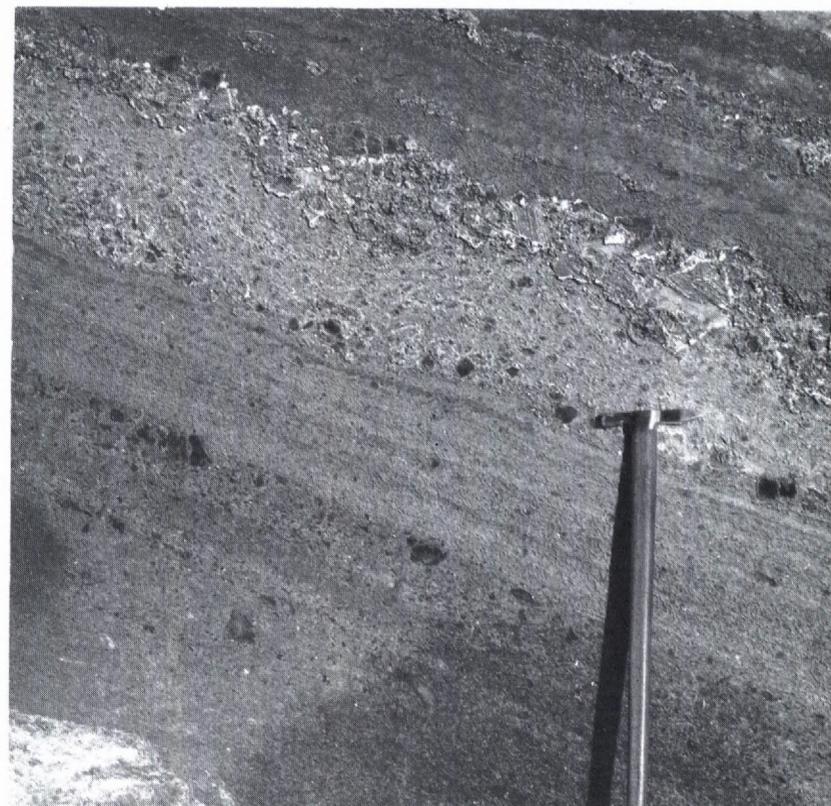
The Salt and Barren Breccia Members are overlain by marine claystone containing gypsum crystals and sands (CH on Fig. 4).

#### *Depositional setting*

The development of the Wieliczka salt basin was closely related to vertical tectonic movements and the northward advance of the Carpathian nappes. At the beginning of salt sedimentation (Fig. 22), when tectonic activity was slow, halite and sulphates were precipitated throughout the basin. However, in the southern part of



A



B

Fig. 11. Lithologies in the Upper Spiza unit:

(A) Conglomerate composed entirely of salt particles and pebbles. Warszawa Chamber.

B) Coarse-grained and conglomeratic saltstone, structurless in the lower part and laminated in the middle part of the photograph. Gallery west of Kościuszko shaft.

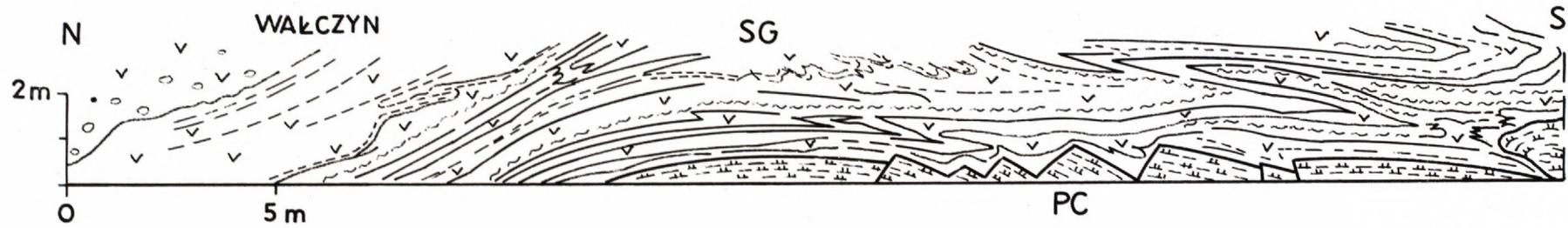


Fig. 12. Cross-section along the Walczyn Gallery showing ductile folds in the Lower Spiza unit, probably of tectonic origin. In contrast, the Central Barren Intercalation (PC) displays more brittle deformation with faults. Symbol explanations as in Fig. 4.

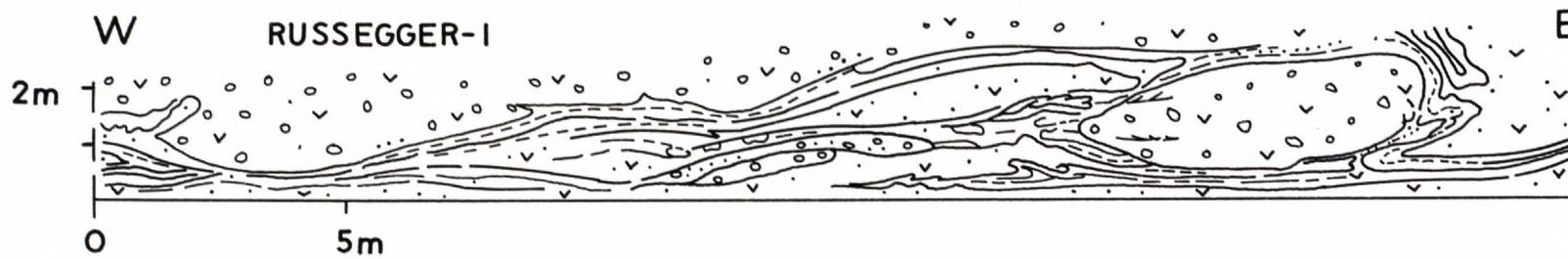
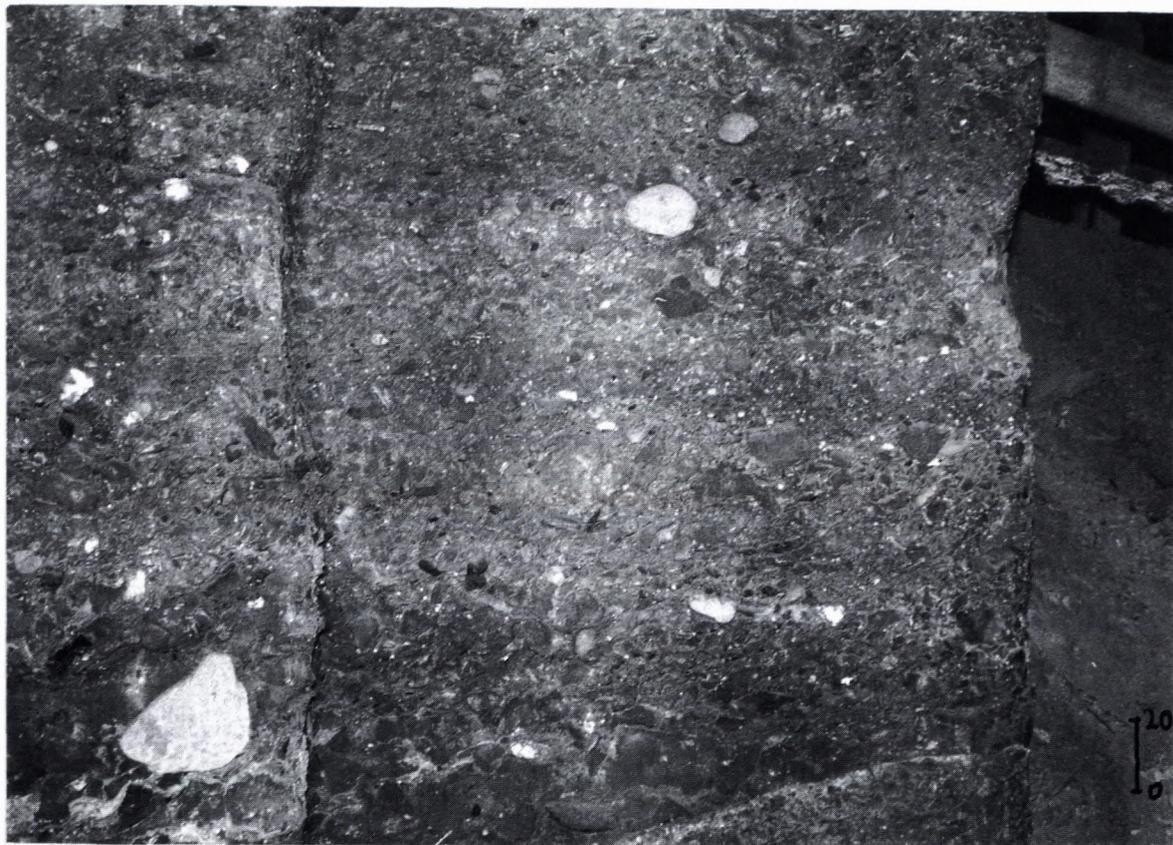


Fig. 13. Cross-section along the Russegger Gallery showing salt conglomerate beds in the Upper Spiza unit with giant load structures. Symbol explanations as in Fig. 4.



A

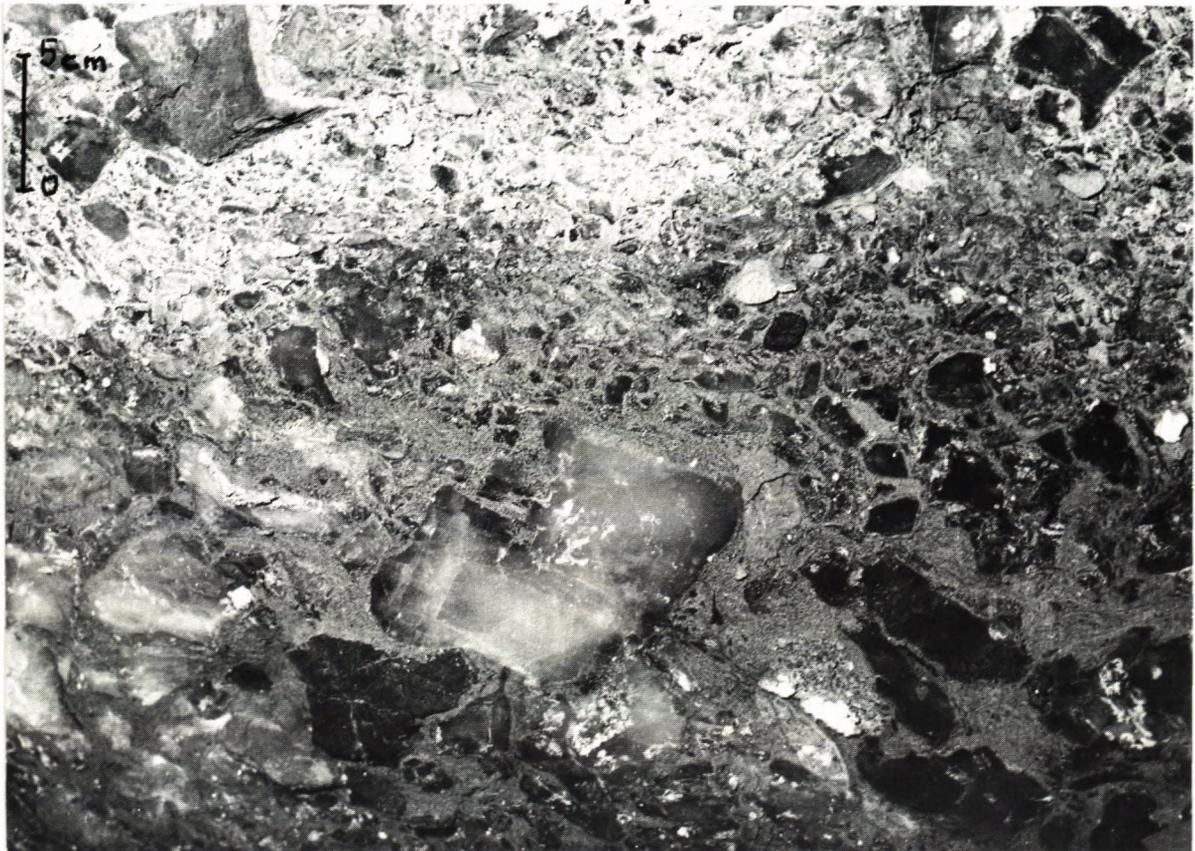


B

Fig. 14. Lithologies in the Upper Spiza unit from the Gruszczyn Gallery: (A) Polymictic, clast-supported conglomerate with crude lamination. Scale bar is 20 cm; (B) Cut slab of unit shown in (A). Fragments of halite crystals, clast of marls (grey, rounded) and sandstones.



A

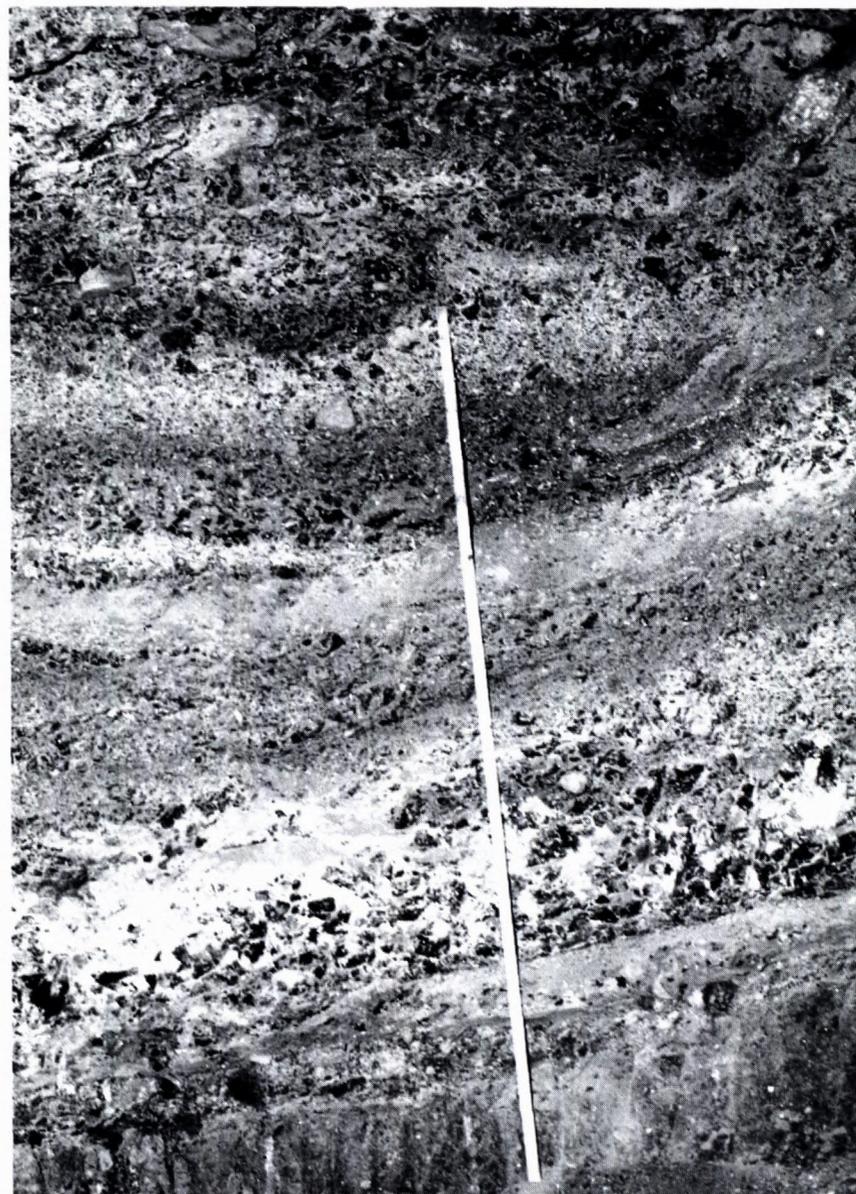


B

Fig. 15. Lithologies in the Upper Spiza unit: (A) Matrix supported, graded conglomerate with fragments of halite crystals and single clasts of angular to well rounded Carpathian and barren Miocene rocks. Secondary gallery of the Gruszczyn Gallery. Scale bar is 10 cm; (B) Close-up view of the unit shown in (A).

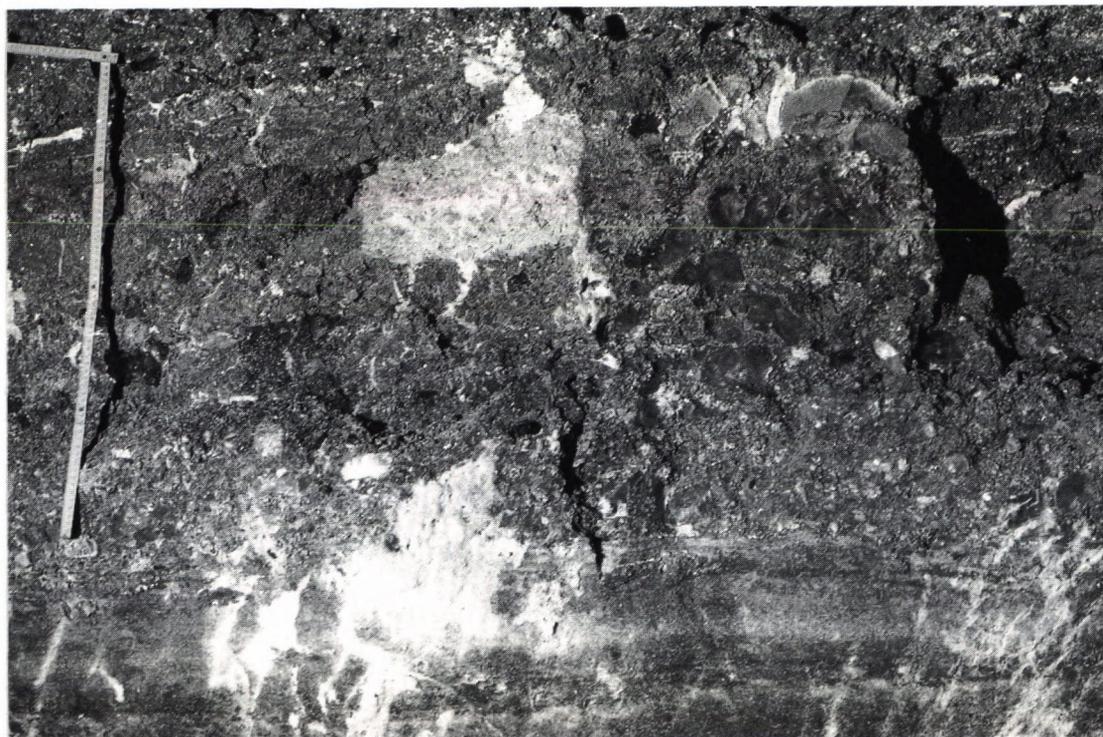


A



B

Fig. 16. Lithologies in the Upper Spiza unit: (A) Profile in terminal part of the Gruszczyn Gallery parallel to the direction of transport of detritic material, showing progradational, cross-bedded polymictic conglomerates; (B) Profile in the secondary gallery of the Gruszczyn Gallery showing polymictic conglomerates, perpendicular to the direction of transport. Note the pinch out of several layers and the contact with underlying pebbly saltstones (A). Length of measuring rod is 200m.



A



B

Fig. 17. Lithologies in the Upper Spiza unit:

(A) Polymictic conglomerate with a salt-rich matrix, transitional to pebbly saltstone. In addition to Carpathian and barren Miocene clasts fragments of large halite crystals are observed. Coral is visible at the lower end of the 80 cm. long scale. The conglomerate is underlain by laminated salt. Gallery west of the Kościuszko shaft.

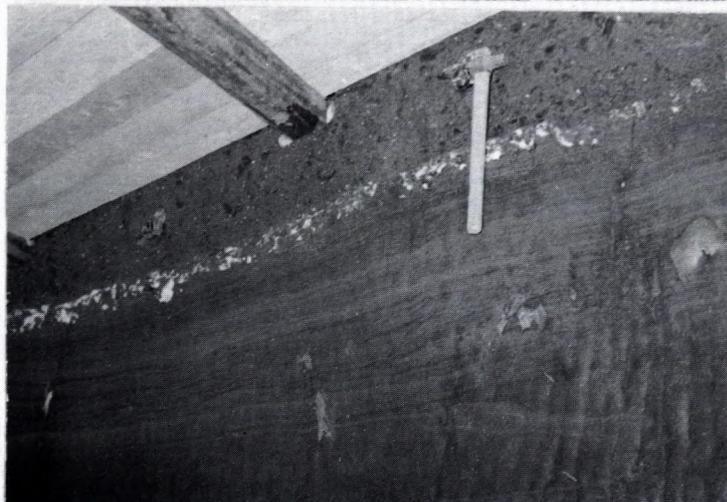
(B) Thick-bedded pebbly saltstone. Pebbles and cobbles of Carpathian sandstones are scattered in salt matrix. The basal part of the polymictic salt conglomerate shown in (A) forms the top part of this photograph. Length of hammer is 40 cm. Thinfeld Gallery.



A

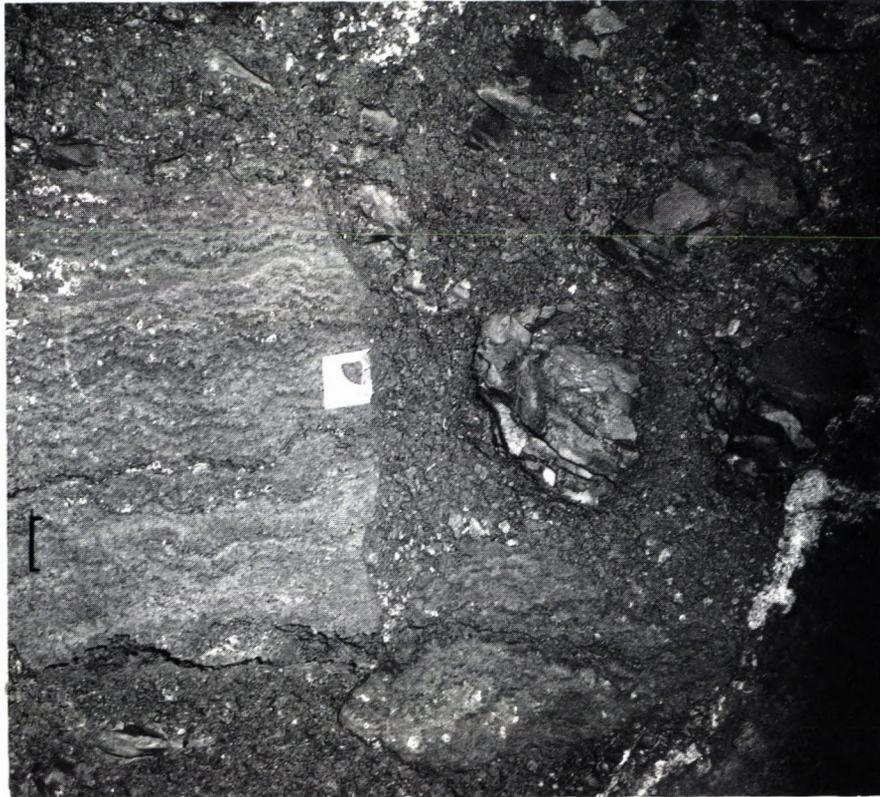


B



C

Fig. 18. Varied nature of the contact between the Stratified Salt Member and the overlying Salt Breccia Member.  
 (A) Upper contact of the Stratified Salt Member, as represented by coarse saltstones, and the Salt Breccia Member represented by clay rich matrix with halite crystals. Wessel Gallery.  
 (B) Similar contact as in (A) but here the Salt Breccia Member is rich in clasts. Lichtenfels Gallery.  
 (C) Uppermost part of the Stratified Member here shows parallel laminations and slump-like structures. Russeger Gallery. Length of hammer is 40 cm.



**A**



**B**

*Fig. 19. Lithologies in the Salt Breccia Member:  
(A) Clasts of laminated salt and Miocene marls imbedded in clay-rich matrix. Kunegunda Gallery. Scale bar is 10 cm. long.  
(B) Salt clasts (dark) set in halite-rich matrix. Lichtenfels Gallery. Length of hammer is 40 cm.*

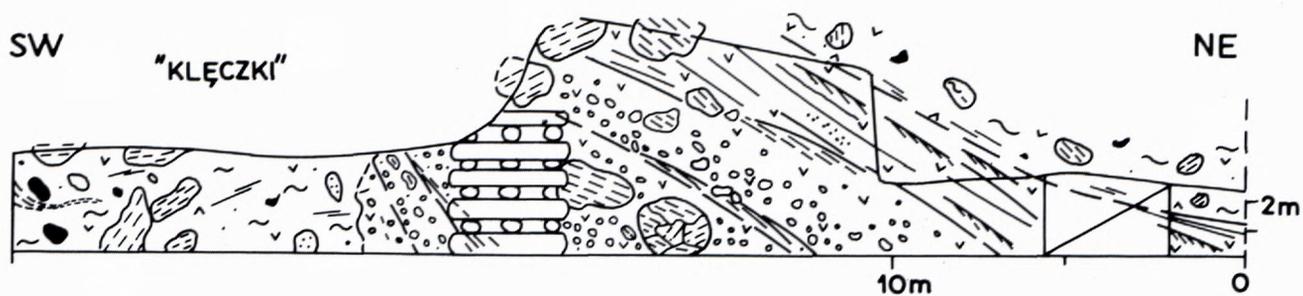


Fig. 20. Cross-section in the Kłęczki chamber showing the nature of the unit intercalated between two mega-debrites in the Salt Breccia Member. The intercalation here comprises graded salt conglomerates terminated by cross-bedded saltstones.

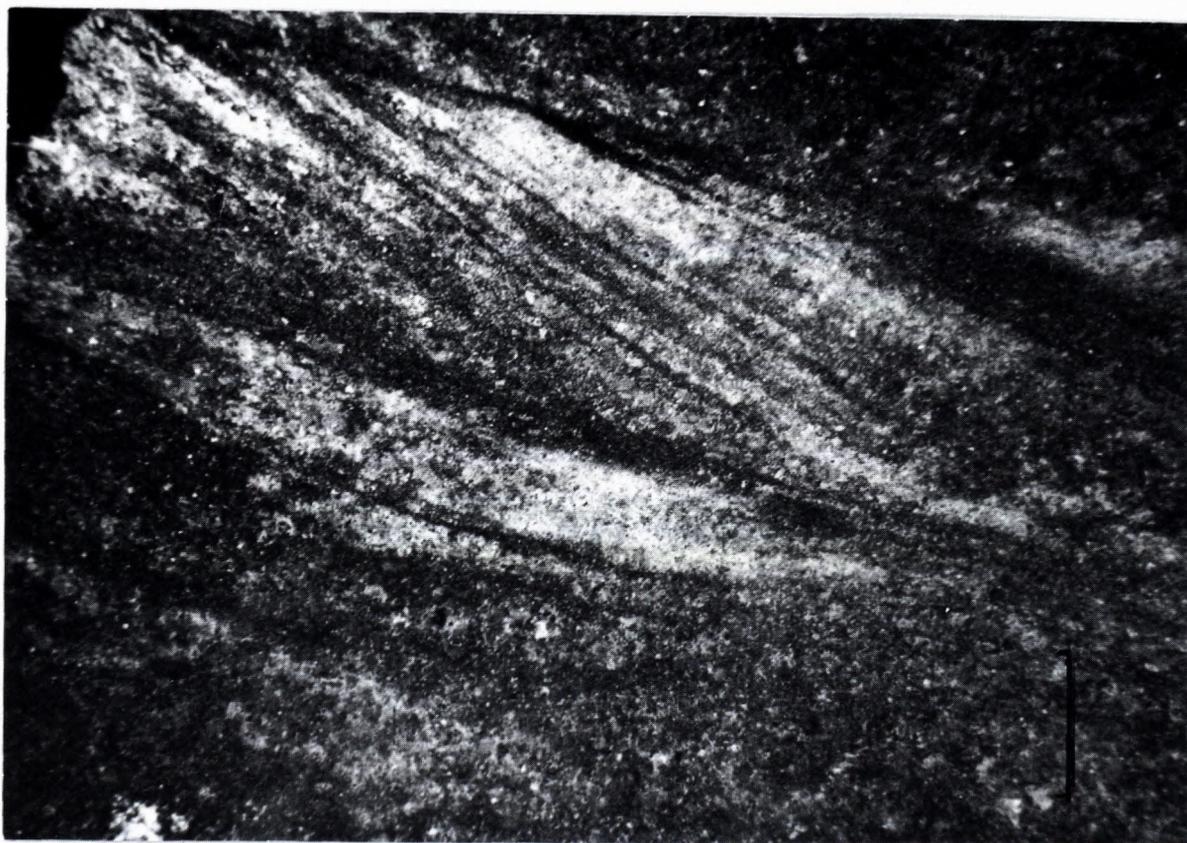


Fig. 21. Salt Breccia Member: cross-bedded, coarse grained saltstone in the intercalation between two mega-debrites. Kłęczki Chamber. Scale bar is 10 cm.

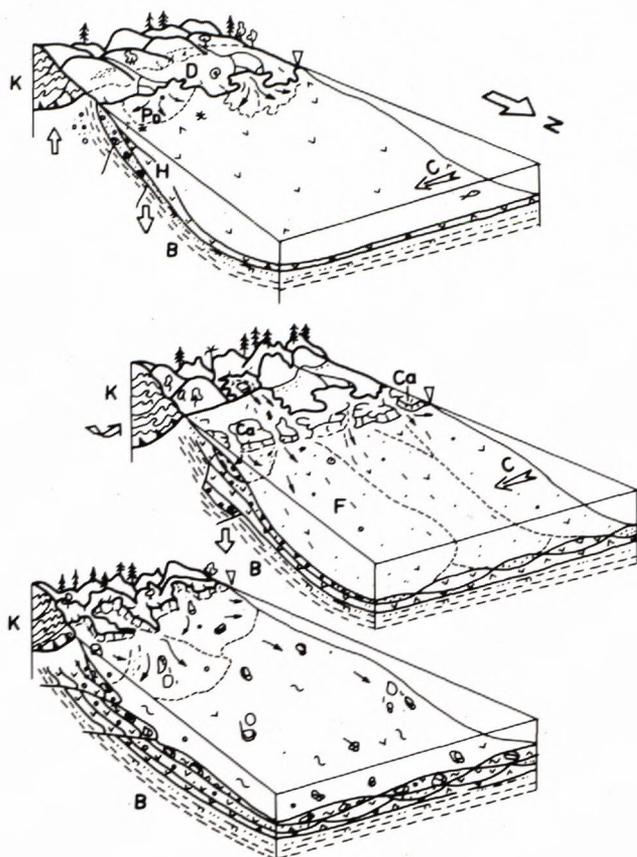


Fig. 22. Schematic diagrams illustrating the sedimentary evolution of the southern and central part of the Wieliczka salt basin. The transition towards the sulphate facies is omitted.

I. Initial stage: widespread precipitation of salt. FD-local fan-deltas; D-shallow water siliciclastic and carbonate deposits with fauna; H-evaporitic, mainly halite deposits; C-main current direction; K-Carpathian Thrust sheet; B-lower Badenian deposits.

II. Beginning of resedimentation of salt in response to tectonic movements in marginal area. Ca-?partially karstified older salt deposits; F-submarine fans P-polymictic conglomerates.

III. Final stage of salt basin development, with widespread mass movements. O-olistoliths.

the basin, the accumulation of halite was more rapid than in the central part, and resulted in the formation of thick layers, which can be inferred from the size of the salt blocks within the Salt Breccia Member. In the more northern, central, and probably deeper part of the basin, the precipitated salt layers were thinner (Green and Shaft Salt, Fig. 22-I). There was also sporadic deposition from density currents.

An increase in tectonic activity led to the accumulation of layers of redeposited salt (Spiza Salt). The siliciclastic sediments observed within the central barren complex can be ascribed most plausibly to a temporary lowering of sea level and an increasing supply of terrigenous material. However, even during this period the

sea remained relatively deep, as can be inferred from the lack of desiccation marks, wave ripples, and a shallow water fossil fauna.

During deposition of the central barren complex, permanent longshore currents prevailed and moved in an overall W-E direction. Deposition from traction currents was followed by redeposition from density currents and subordinate debris flows (Upper Spiza, Fig. 22-II). In the area described, there were several depocentres of coarse material. This suggests the development of a system of small submarine fans that spread from the southern border of the basin. These fans were fed mainly from the southern flank of the Carpathian Foredeep and later also from the Carpathian orogen, although some of the Carpathian rocks also might have been recycled. Simultaneously the southern part of the salt basin was disrupted. The subsequent reworking of the salt clasts and blocks presumably was affected by several processes, such as the transport of loose crystals by wave action, and by marine erosion following uplift of the seafloor, with destruction of the earlier deposited salt beds. The latter process might have been facilitated partly by dissolution of the salt beds. The clastic products of such mechanisms accumulated near channel heads and eventually were displaced downslope by density currents and/or slumping. Additional sediment input might have been generated by erosion of the substrate by the density currents. The redeposited material formed lenslike bodies which can be interpreted as small submarine fans. This interpretation is based chiefly upon bedding characteristics, the vertical and lateral arrangements of sedimentary structures, and the petrographic composition of the blocks. However, the Middle Miocene and later tectonic deformations have obscured much of the evidence required for detailed reconstruction of facies and their relations to the source area. The available data does, however, allow the fans to be divided into several parts: 1. the southern, internal part, which is characterized by polymictic conglomerates, pebbly saltstones, and breccias containing abundant material from the Carpathians; 2. the middle part, composed of conglomerates and coarse-grained saltstones, which can be massive, graded, and laminated, and are almost exclusively composed of salts; 3. the distal part, characterized by a general decrease in the clast-size and in the thickness of beds. The outermost margins of the fans are not exposed.

During the next stage (Fig. 22-III), strong orogenic movements gave rise to huge slumps which, in turn, were transformed into debris flows and olistostromes (Salt Breccia Member, Fig. 22C). In the latter phases of this stage, that part of the salt deposits which previously provided the material for mass flows was removed. Thus the latter redepositional processes involved only barren material (Barren Breccia Member).

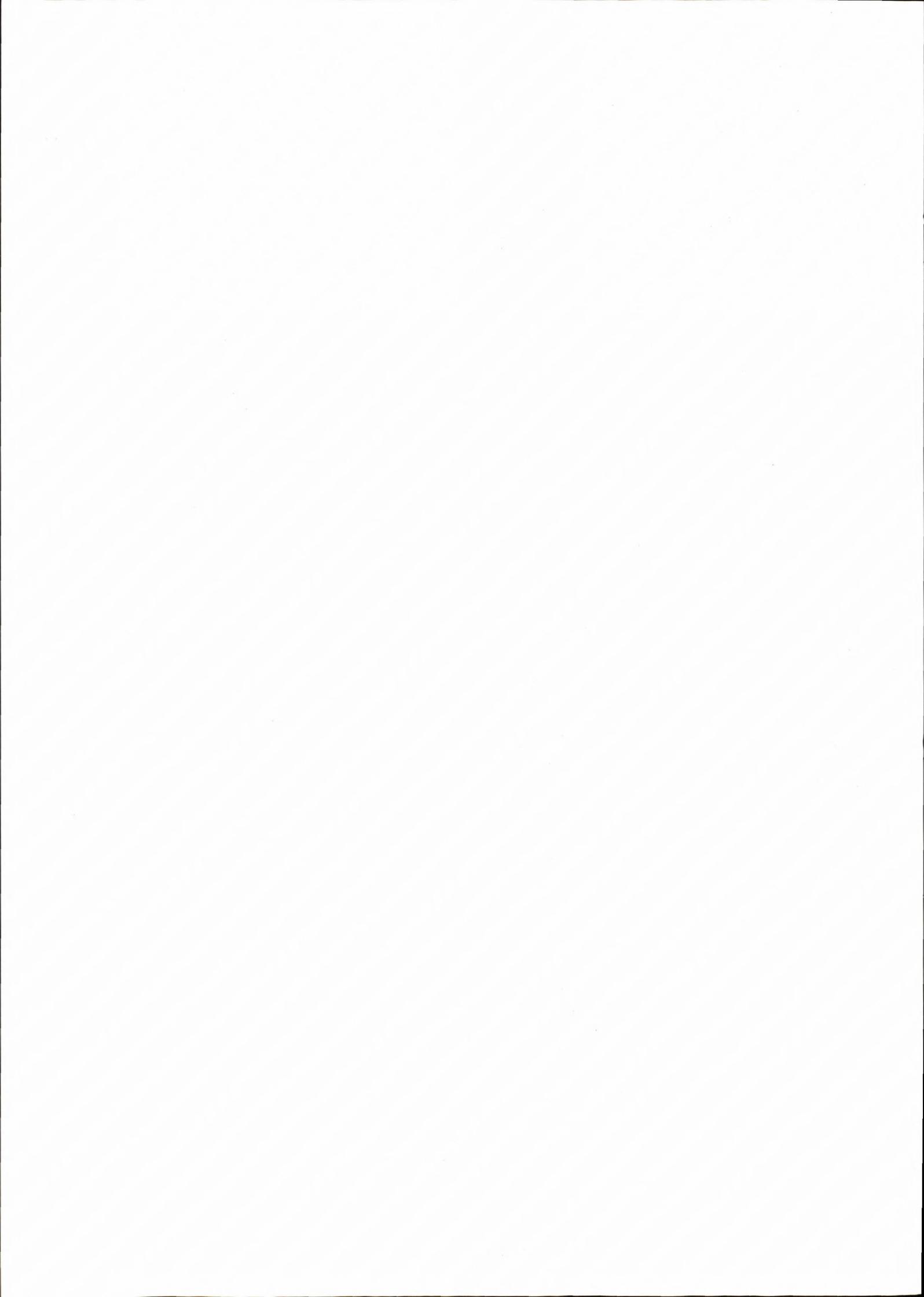
The gravity-induced mass movements discussed in this paper occurred also in the other region of the Polish Carpathian Foredeep, and are evident from sequences in the nearby Bochnia salt mine. In the East Carpathian Foredeep, deposits similar to the Breccia Member have been described by Sandulescu et al. (1980), from the Pyrenaen Foredeep by Ślącza (1994), and in the Upper Permian salt deposits of the Halstatta Salt Mine by Schauburger (1953).

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## Sedimentation of clastic strata associated with Miocene salts in Wieliczka (Southern Poland)

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**Abstract.** The Miocene salt-bearing strata in the Carpathian Foredeep near Cracow in Wieliczka, southern Poland, contain intercalations of conglomerates, sandstones and claystones. These rocks show the facies variability and sedimentary structures characteristic of turbidites. The sediments accumulated near the shores of an evaporite basin and thereafter were transported by turbidity currents into deeper parts in the basin.

**Key words:** Badenian, Miocene, clastic sediments, evaporites, sedimentology, Wieliczka, Carpathian Foredeep.

### Introduction

A Miocene salt-bearing formation, that extends as a narrow strip north of the folded and overthrust Carpathian massif, was deposited in the Late Badenian, *i.e.* about 12.5-13.5 Ma ago (Fig. 1). Paleobotanical investigations show that the associated climate was characterized by dry and hot summers and rainy winters (Zabłocki, 1930). Evaporites accumulated in the foreland of uplifting mountains which coincided with increasing tectonic activity in the Carpathians. Contemporaneous recurrent volcanic eruptions produced pyroclastic deposits (tuffites) whose thickness is as much as 1,000 m in the Transcarpathian basin of West Ukraine (Kityk *et al.*, 1983). The accompanying earthquakes caused landslides and submarine slumps, and initiated turbidity currents, which formed deposits characterized by rapid facies changes and a relatively small extent.

The evaporation basin of Wieliczka was situated far from eruption centers but it contains traces of volcanic material. Tuffite layers occur in the beds both underlying and overlying the evaporites (Kamiński & Glińska, 1966; Wiewiórka, 1979; Parachoniak, 1954, 1962). These rocks are related to with submarine flows and slides interpreted in the Wieliczka mine (Kolasa & Ślęczka, 1985; Ślęczka *et al.*, 1986; Ślęczka, 1994). Their facies variability indicates substantial changes in the water depth and in the configuration of the shore line (Garlicki, 1979; Bukowski, 1994) which reflect dynamic processes connected with the tectonic remodelling of the Carpathians. The aim of this paper is to consider the deposits from the lower part of the

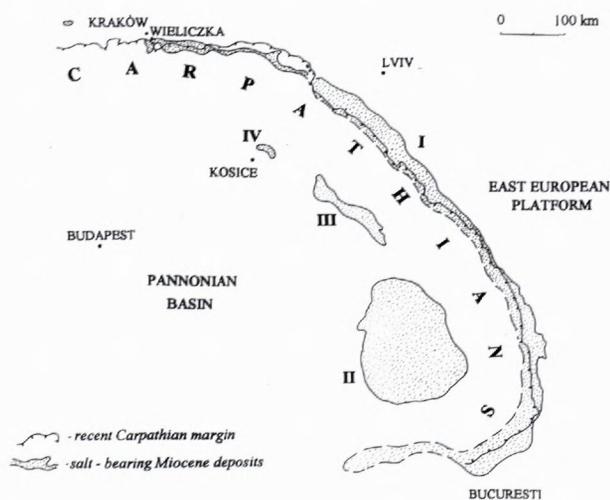


Fig. 1. Distribution of salt-bearing Miocene rocks in the Carpathian zone.

I - Carpathian Foredeep; II - Transylvanian Basin; III - Transcarpathian Basin of West Ukraine; IV - East Slovakian Basin

Wieliczka salt series as a source of information on the depositional environment and processes which took place during the early stages of salt sedimentation.

### The mode of development and extent of the clastic rocks

The clastic-pelitic rocks in the lower part of the Wieliczka strata separate two levels of rock salt, the level

of the oldest salts from the level of the stratiform "green" salt (see Galamay *et al.*, 1997, Fig. 4). In the literature, these rocks were called the "sub-salt sandstone" as they were considered to be a member that initiated deposition of the salts.

Beds at the base of this series are grey and dark-grey claystones and mudstones containing intercalations of anhydrite 1 mm thick. These rocks represent an extension of the vanishing deposition of the oldest salts and were formed probably as a result of opening a connection with more distant parts of the basin and of an influx of waters undersaturated with NaCl. Overlying the claystones and mudstones are coarse-grained sandstones and conglomerates with a gypsum cement (Charysz & Wiewiórka, 1976) which originated under different conditions. The latter are characterized by abundant carbonized plant fragments, grains of anhydrite, fragments of light-coloured limestones and flysch rocks (light-grey and brown-tan siliceous sandstones and variegated shales). The size of the clasts usually varies from several to twenty centimeters in length but can reach 50 cm. The sorting is relatively poor, and the top and the bottom of the layers are uneven and jagged. If the conglomerates occur only in the central part of the deposit, the overlying coarse-, medium-, and fine-grained sandstones are developed as a regular level, observable over the distance of several kilometers. They are grey-greenish, contain small admixtures of disseminated grains of nodular anhydrite (visible in hand specimens), linear thin layers of plant detritus, and numerous disseminated clay partings. The characteristic features of these rocks include graded bedding, ripplemarks, horizontal bedding and cross-bedding, and complex displacements resembling load casts where coarse- and fine-grained fractions are mingled (Fig. 2, 3). The sequence of these textures corresponds best with the Bouma sequence Tabcde (Bouma, 1962). Such a sequence is re-



Fig. 2. Convolute bedding in coarse-grained sandstones. The Galicja gallery, level IV-V.



Fig. 3. A fragment of sandstone with a gypsum-halite cement (the graded bedding is visible). The Galicja gallery, level IV-V.

peated several (at least four) times within the series, but is not always fully developed. Away from the axis of the basin, the content of sandstone decreases and the sequen-

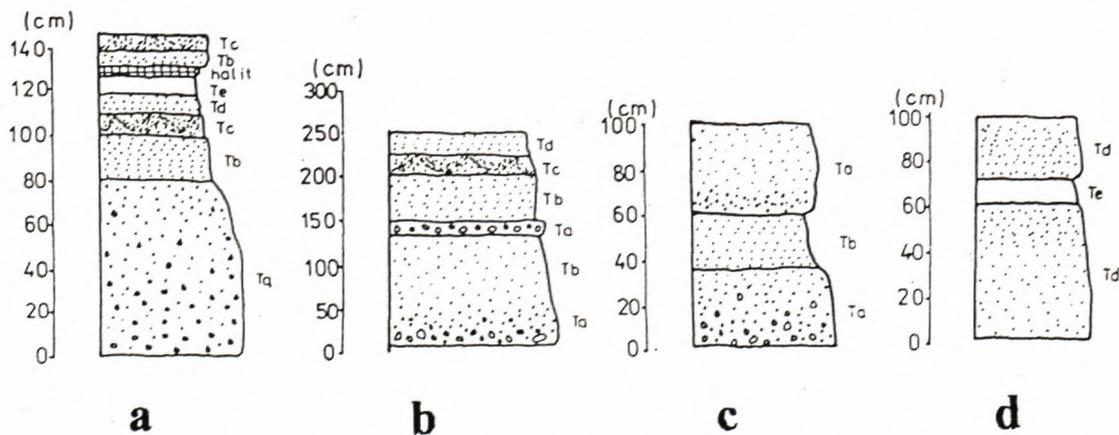


Fig. 4 Examples of Bouma sequences within the "sub-salt" sandstone of the Wieliczka Formation. a - the modified sequence Tabcde with an additional evaporite layer - the central part of the deposit, the Galicja gallery; b - the Tabcd sequence - the central part of the deposit, the Mina gallery; c - the Tab sequence - the eastern part of the deposit, the F. Miller gallery; d - the Tde sequence - the western part of deposit, borehole no. 962 (Barycz).

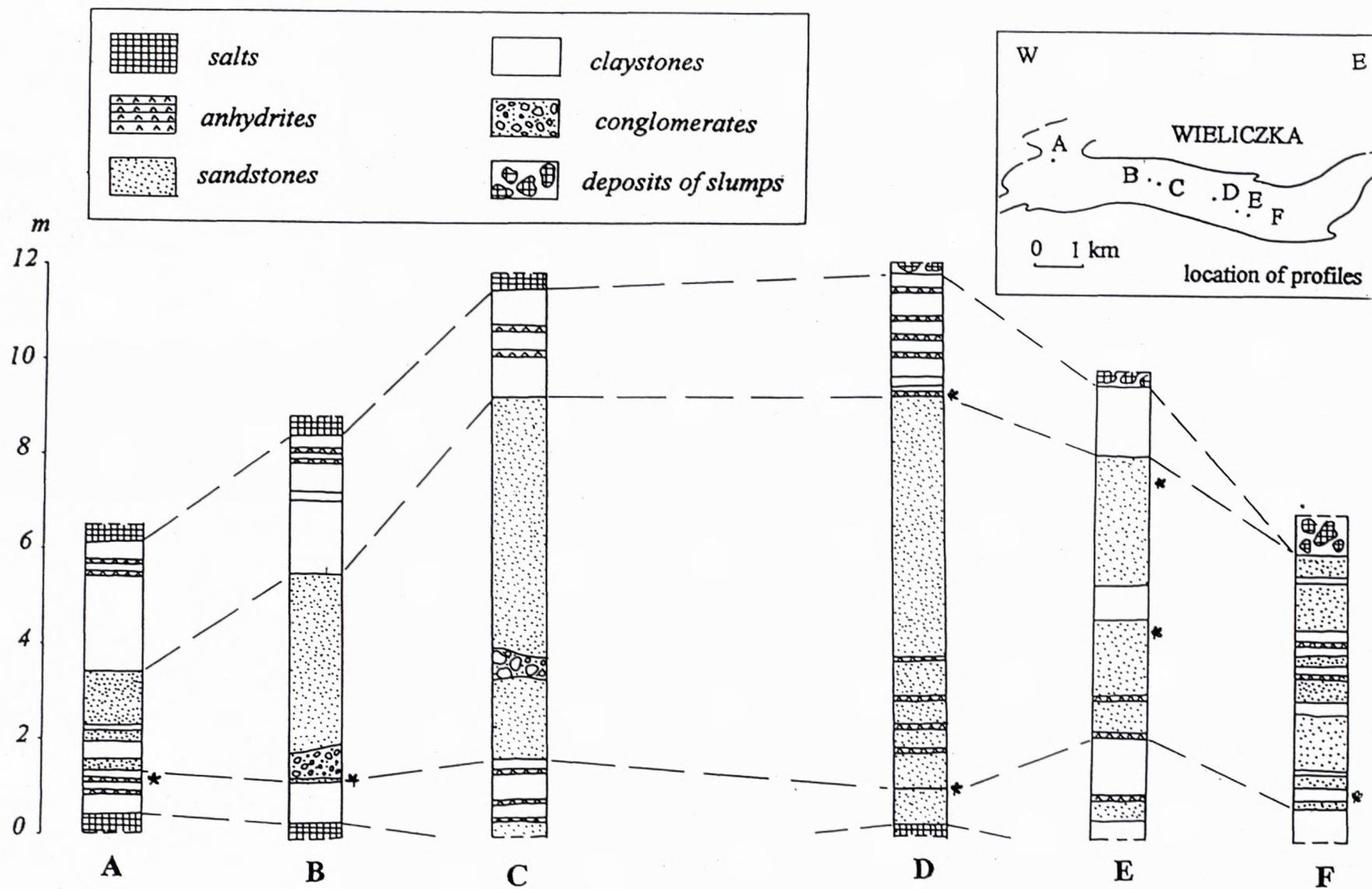


Fig. 5. Lithostratigraphic correlation of "sub-salt" sandstone in the Wieliczka mine.  
 Location of profiles: A - borehole no. 962 (Barycz); B - Mina gallery; C - Galicja gallery; D - August gallery; E - Ilka gallery; F - F. Miller gallery.

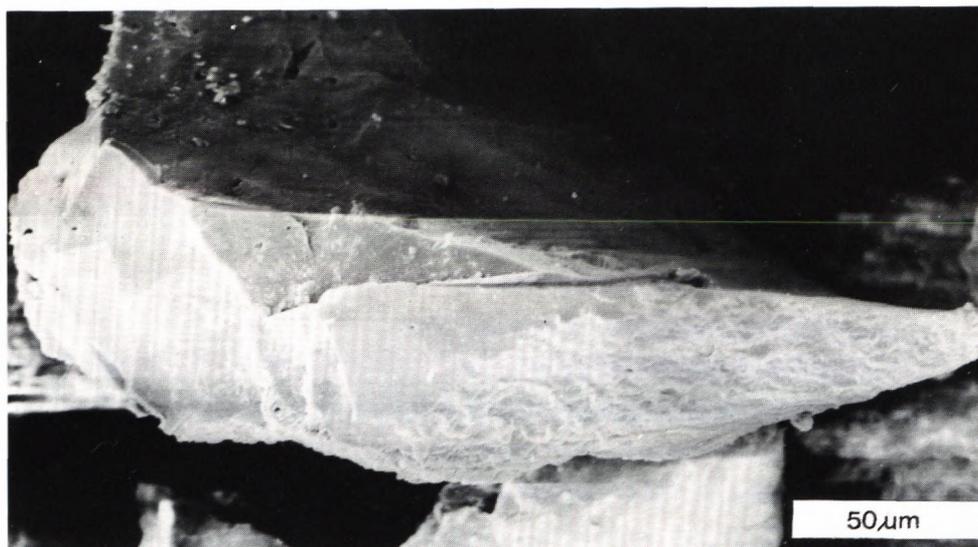


Fig. 6. Angular grain of quartz with a fresh fracture. The sample was taken from sandstone underlying the tuffite insert WT-2. Borehole no. 963.

ces are limited to the Tab (Fig. 4c), Tabcd (Fig. 4b) or Tde (Fig. 4d) members. A modification of the Bouma sequence is caused by the presence of an evaporite layer, tens of centimeters thick, composed of anhydrite or halite. In this case, the sequence takes the form of Tabcdef (Fig. 4a). Plant fragments, which occur most often as a fine dispersed detritus, are sometimes concentrated and include remains of needles, fruits and leaves. The bigger fragments of plants are very rare in the sandstones; they include a carbonized log that was found within the inter-level Kołobrzeg (presently at the collection in the Museum of the Wieliczka Salt Mine).

During geological mapping in the mine, attention was paid to the spatial differentiation of these rocks. Such changes exist west and east of the central part of the deposit and are expressed as the decreasing thickness of the whole series, lower content of coarse-grained deposits, and confining the conglomerate layer only to the center of the basin. Figure 5 illustrates profiles of these sediments at several localities in the basin. The data given by Pawlikowski (1975) to the north seem to confirm this tendency. Simultaneously, towards the top of the whole distinguished series, the coarse-grained sediments disappear and grade into mudstones and claystones, with more abundant intercalations of gypsum and anhydrite. The total thickness of these rocks ranges from 6 m in the marginal parts of the basin to ca. 12 m in its center.

#### Volcanogenic material

In these clastic sedimentary rocks, two layers of tuffites, designated with the symbols WT2 and WT3, were found (Wiewiórka, 1979). They are thin, up to 5 cm, inserts of a pyroclastic material cemented by halite (WT2) or gypsum (WT3) (Pawlikowski, 1975). They were de-

posited probably in waters with an elevated concentration of NaCl. Such an environment is indicated by weak bentonitization of the volcanic ash; this process must have been slowed by the crystallization of gypsum or halite in intergranular spaces of the rocks (Kamieński & Glińska, 1966; Pawlikowski, 1975).

The volcanogenic material is not confined to the tuffite layers. Observations of the detrital fraction of the clay-sandy rocks underlying the tuffites indicated numerous (up to 40%) angular, transparent quartz grains, often of elongated habit and with fresh fractures (Fig. 6). The lack of rounding and luster in these grains indicate their similarity to pyroclastic quartz, described in many papers (e.g. Mišik, 1954; Salat, 1955; Alexandrowicz, 1957). Simultaneously, within the same rocks, the pyroclastic quartz is accompanied by equally numerous quartz grains with leached and corroded surfaces. This advanced corrosion could only be due to the temperature and chemical action of a lava (M. Chandij, pers. com.).

So, the following conclusion can be drawn: the sedimentation of volcanogenic material could have continued for a longer time, also in the clay-sandy deposits, and the tuffite layers were formed only when the volcanogenic material was not diluted by the clastic sediments (comp. Alexandrowicz, 1957). This relationship explains the difficulties faced by some authors during attempts to correlate the tuffite layers. Volcanogenic beds might be continuous but of variable thicknesses or even discontinuous.

#### Evaporite minerals

Anhydrite occurs most often in the form of oval aggregates, defined in the literature as nodular anhydrite, and continuous deformed layers, which resemble tectoni-

cally folded strata (the so-called enterolithic textures). The nodules (concretions) are usually from several millimeters to several centimeters in diameter. They were formed probably by the alteration (dewatering) of gypsum. Although examples of the primary crystallization of nodular anhydrite from a solution are known, that process is limited to dry and very hot sabkha areas, where the temperature reaches 50°C and concentrated brines tend to rise due to capillary phenomena (Kinsman, 1966; Shearman, 1966). The sabkha environment has not been recognized in the salt-bearing basin of Wieliczka.

The origin of enterolithic textures has not been fully explained. They could have been formed by the sliding of unconsolidated sediment on a slightly inclined sea floor (Garlicki, 1980) or by the deformation of a primary sediment during a post-depositional alteration of gypsum into anhydrite. In the second case, the loss of water and increase in the volume of initially deposited gypsum by ca. 38% (Shearman, 1985) could be a major mechanism for these alterations and caused by a rise in temperature during folding of the sediments. Enterolithic anhydrite is commonly found in the described rocks, where it occurs either in form of continuous layers that separate sequences of mudstone and claystone in the uppermost member of the turbidites (Fig. 4a) or as secondary infillings of discordant veins and fractures.

In thinly laminated clay-rocks the anhydrite was formed during diagenesis *in situ*. In coarsely clastic beds, the grains and concretions of anhydrite were brought - similar to other grain components - by currents from other parts of the basin or from the land (Fig. 7, 8).



Fig. 7. A clast of anhydrite with a diameter of 20 cm from within a layer of salt conglomerate. The Lilienbach gallery, level III.

Gypsum occurs with anhydrite in the cement of sandstones and conglomerates, and as fibrous vein fillings.

Halite is less abundant, it occurs in cements mainly in the top and bottom parts of the sequence. The first distinct intercalations of halite herald the onset of the proper chemical sedimentation, *i.e.* the formation of stratified



Fig. 8. A core of sandstone with graded bedding (white grains of anhydrite show the gradation from bigger to smaller ones towards the top of the layer, similar to the other components). Borehole no. 963.

"green" salts. Additionally, redeposited rounded fragments of rock salt and of halite crystals occur in the conglomerate, and locally in coarse-grained sandstone.

#### Rock fragments

During microscopic investigations, about 10 varieties of rock fragments were distinguished, mainly of sedimentary and metamorphic rocks. The most abundant are fragments of claystone and mudstone with a clay cement, sandstone with a calcareous cement, and marls and variegated shales. These fragments are usually well rounded, with a roundness of 3-4 according to Powers (1953). They are accompanied by less numerous fragments of limestone, most often micritic and finely crystalline, and also by rounded polymorphic clasts composed almost entirely of sutured quartz grains, derived probably from quartzites and gneisses (Pawlikowski, 1975). Single quartz grains show variable rounding and microrelief.

Apart from the angular and corroded quartz grains described above, rounded quartz grains have been distinguished by features pointing to an eolian origin or with evidence of beach abrasion (Fig. 9; also E. Myciel-ska-Dowgiałto, pers. com.). Numerous mica flakes are disseminated throughout the rocks, particularly in the claystone.

The rock fragments in the detrital sediments were transported from the land surrounding the Wieliczka basin. They were derived partly from the Skawina Beds, as indicated by the microfauna in the accompanying ball clays and sandstones (Pawlikowski, 1975), and from the flysch rocks of the Carpathian land (fragments of sandstones and variegated shales). Clasts of metamorphic

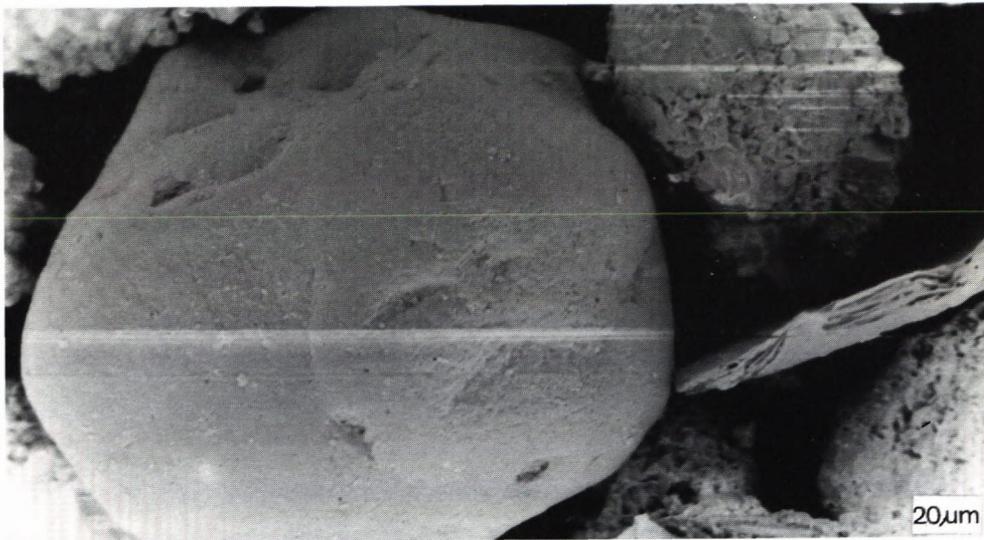


Fig. 9. Quartz grain of beach origin. On the surface of the grain there are half-moon indentations, signs of abrasion. Sandstone sample collected in the Prokopowicz gallery, level III.

rocks (gneisses and quartzites) were probably derived from coarse-grained, older flysch rocks, which had been formed by erosion of the metamorphic cover of a cordillera (Unrug, 1968). The limestone clasts could be derived from both the older rocks of the basement and penecontemporaneous carbonate rocks deposited in marginal parts of the basin.

#### Sedimentary environment

The clastic sedimentary rocks, deposited between sequences of evaporites, display a fan-like form, a range of thicknesses, and various sizes of detrital grains (Fig. 3). The poor sorting of grains in the coarser fractions, facies variability, grain diameters that decrease with distance from the basin axis, and sedimentary structures indicate that the clastic rocks were deposited by turbidity currents. The currents transported detrital material onto the floor of the basin, where the water was saturated with  $\text{CaSO}_4$  and almost saturated with  $\text{NaCl}$ , as indicated by experiments on the crystallization of salts (Jänecke, 1915; Friedrich, 1924). This environment favoured the crystallization of sulfates, either as the cement of sandstones or as regular layers of gypsum. Clasts of rock salt, which occur in conglomerates, were not dissolved under such conditions, and wood fragments have been preserved without signs of decay (Kolasa, 1988). The clastic material accumulated as a vast fan, whose central part is represented by outcrops situated between the "Kościuszko" and "Daniłowicz" shafts. The presence of the submarine alluvial fan in Wieliczka was proved earlier Ślaczka *et al.*, 1986).

In the upper part of the profile, a distinct slackening of the sedimentation rate can be interpreted. At this stage, currents were moving slowly and only fine detrital mate-

rial could be deposited. The presence of pyrite, which occurs within dark-grey claystones, suggests euxinic conditions during deposition. It is probable that such conditions prevailed only in deeper parts of the basin. In shallow waters organisms could proliferate, which is indicated by the fossil fish, found in sandstone (Kolasa, 1981), and by the laminae of fine plant detritus which probably are algal fragments (Kolasa, 1988). The gradually lessening transport of terrigenous material combined with the progressive concentration of stagnant brine resulted in saturation of the water with  $\text{NaCl}$ , followed by the crystallization of rock salts within clayey sediments. The formation of the regular layers of green salts, which overlie the sequence in question, seems to be complex and its explanation will require separate studies.

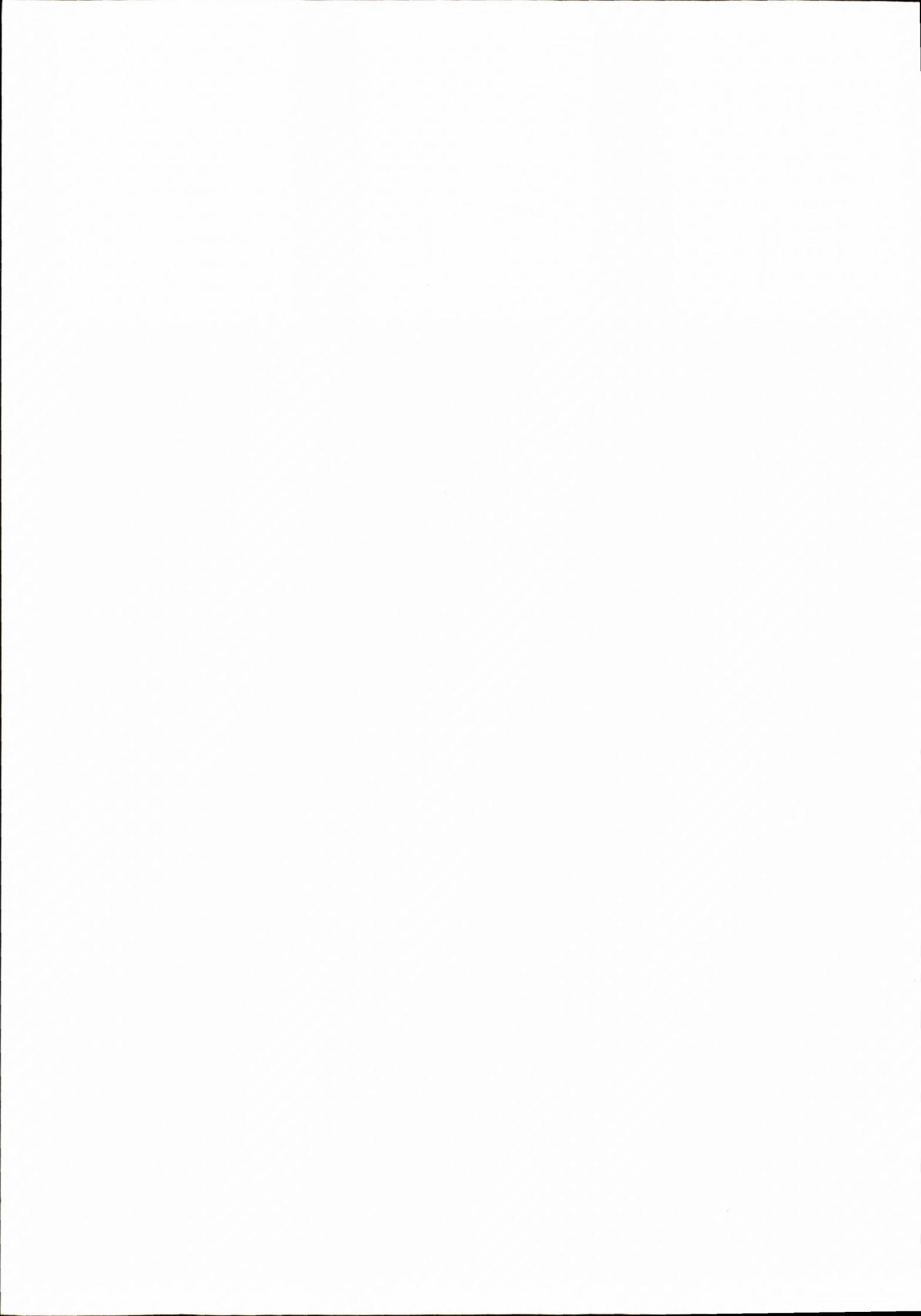
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## Chemical composition and origin of brines in the Badenian evaporite basin of the Carpathian Foredeep: fluid inclusion data from Wieliczka (Poland).

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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

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### 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

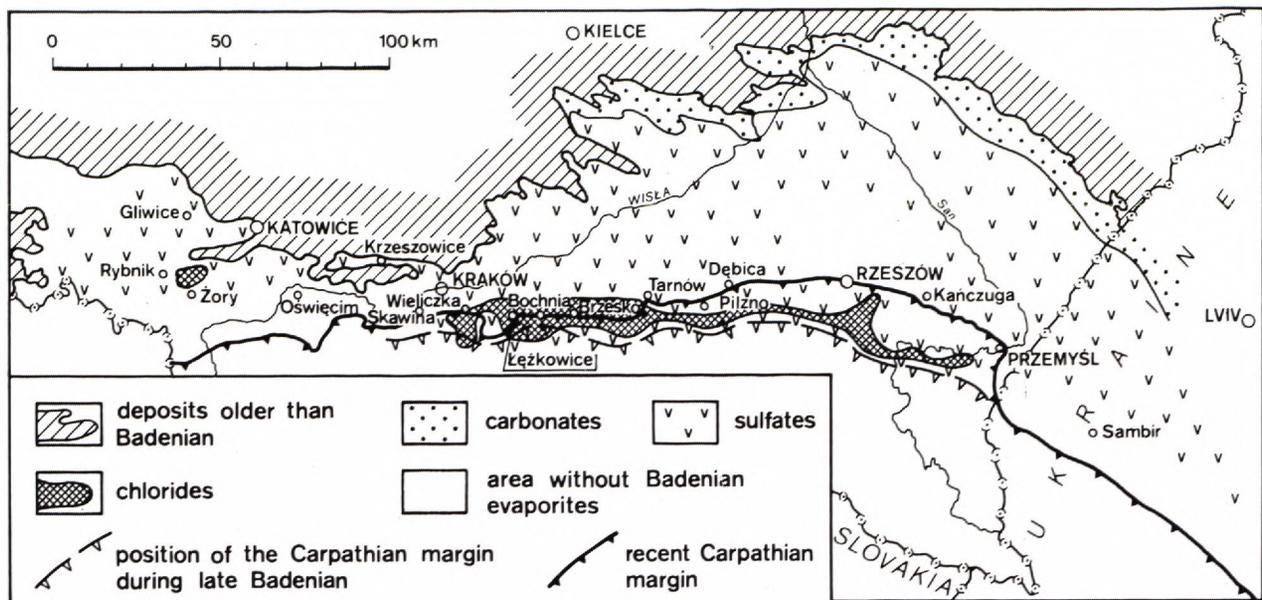


Fig. 1. Distribution of the Upper Badenian evaporites in the Carpathian Foredeep (after Garlicki, 1979).

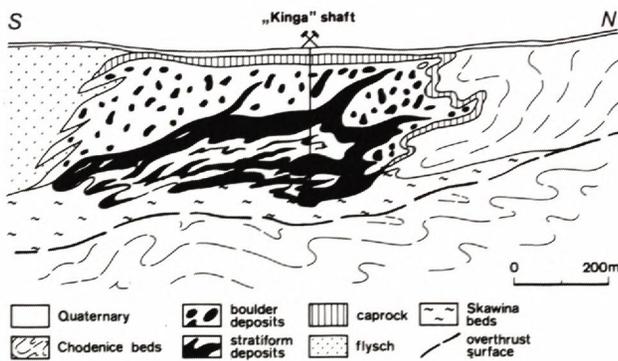


Fig. 2. Transverse cross-section through the Wieliczka salt deposit" (after Poborski & Skoczylas-Ciszewska, 1963, modified).

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" (Gaweł, 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

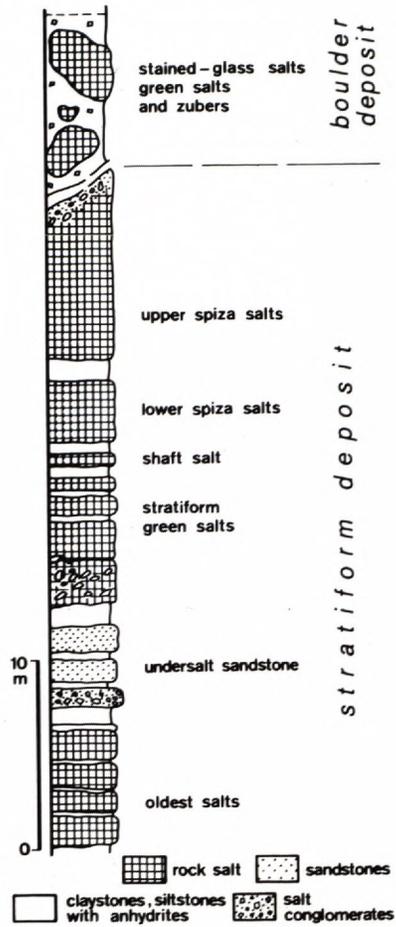


Fig. 4. Lithostratigraphic profile of the salt deposits at Wieliczka.

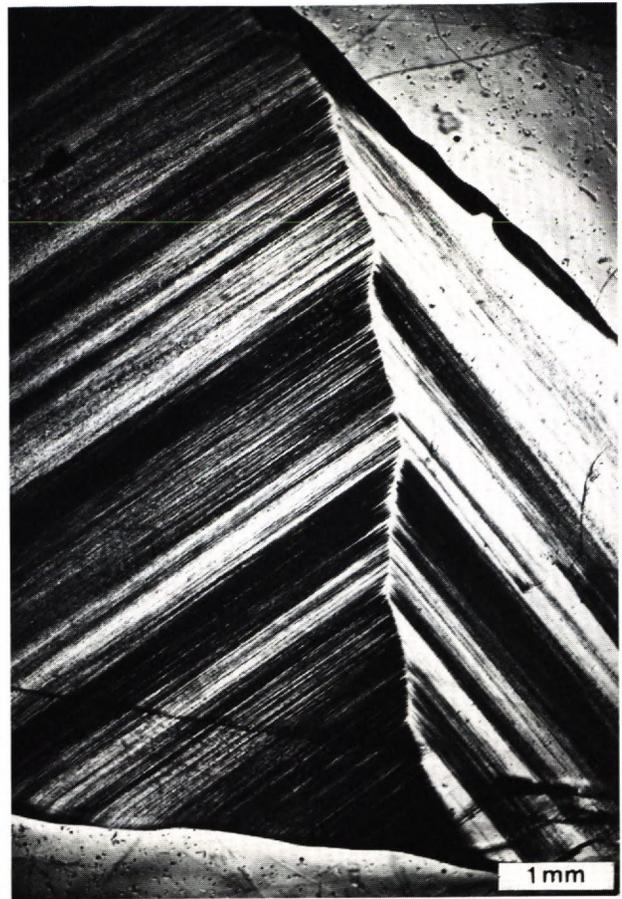


Fig. 5. Zonation (with elements of rhythms), formed by minute fluid inclusions.

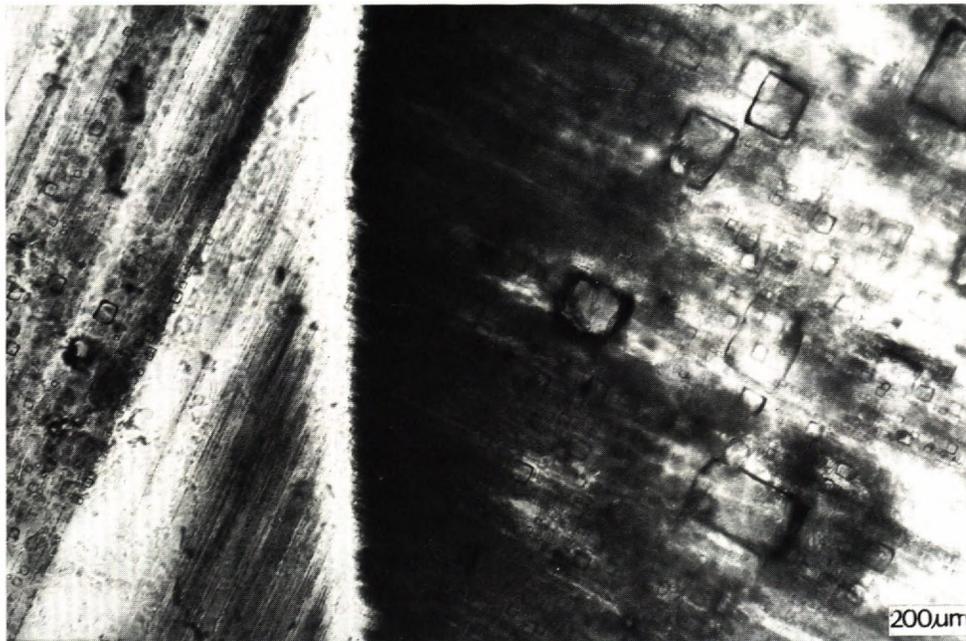


Fig. 6. Asymmetric construction of chevron halite. In right part of structure large fluid inclusions are present.

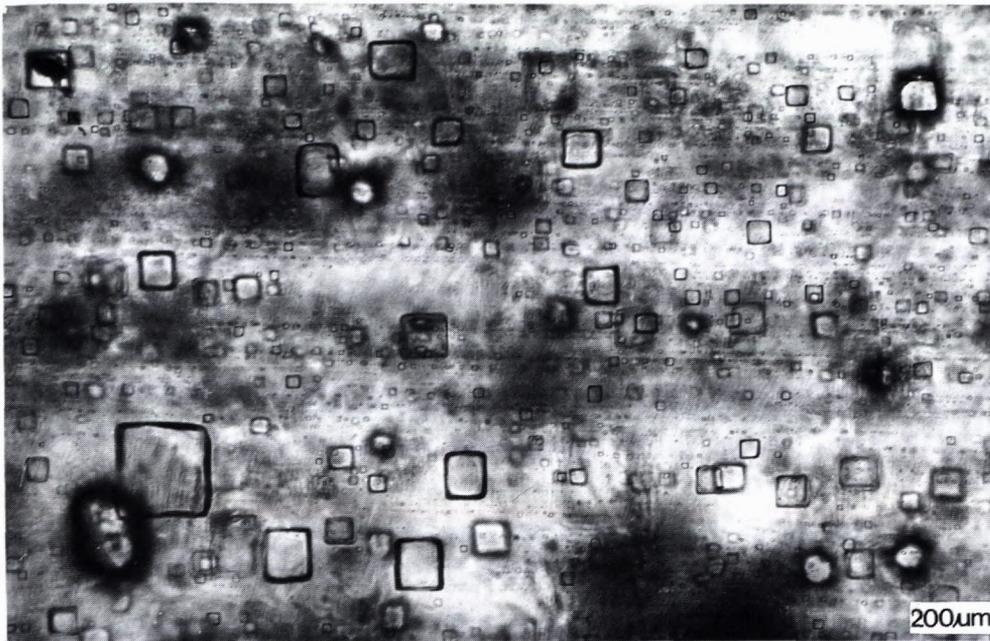


Fig. 7. Fragment of zonal halite with relatively large one-phase fluid inclusions

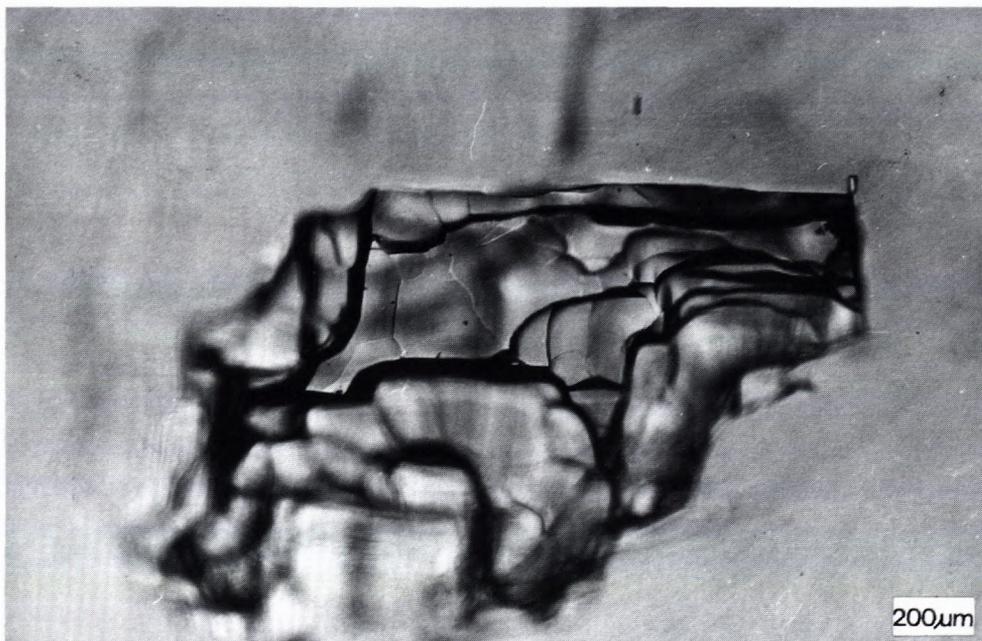


Fig. 8. The structure of the walls of a large fluid inclusion with irregular shape in transparent halite.

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

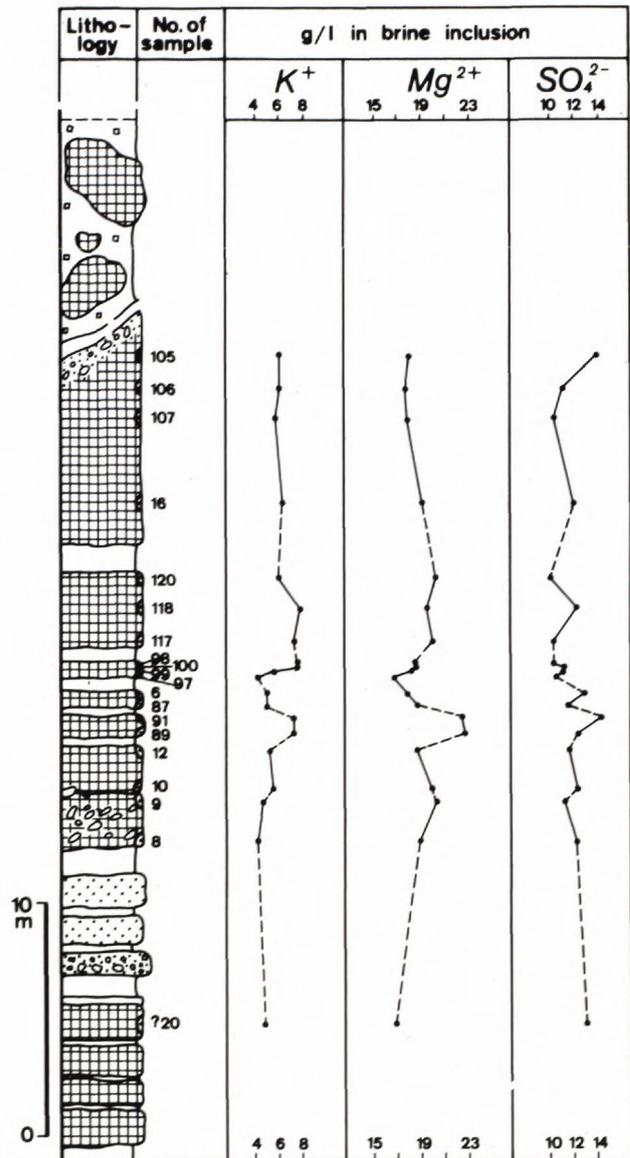


Fig. 9. The changes of K<sup>+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> content in brine inclusions in sedimentary halite. See Fig. 4 for explanation.

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.

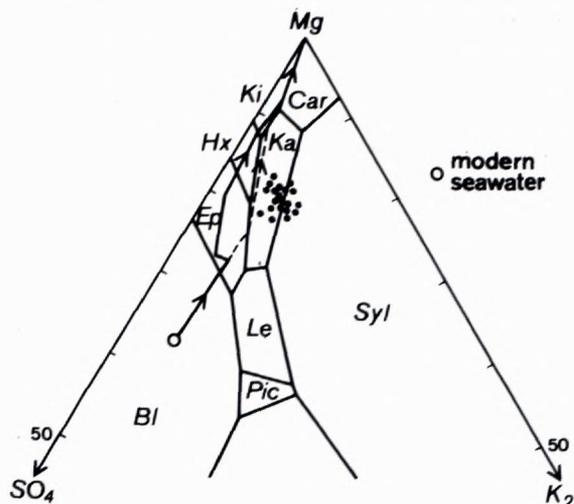


Fig. 10. Analyses of brine inclusions from Wieliczka halite plotted on the Jänecke projection of the quinary system  $\text{Na-K-Mg-SO}_4\text{-Cl-H}_2\text{O}$  saturated with respect to halite at  $25^\circ\text{C}$  (Eugster et al., 1980). The stability fields of Bl, bloeditite; Car, carnallite; Ep, 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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