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^3 natural gas is needed so about 1,500,000 million m^3 natural gas was "consumed" in the foredeep.

Key words: Miocene, sulfur, Carpathian Foredeep, hydrocarbons, sulfate metasomatosis.

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_4 (Fig. 1); in the area of the Carpathian Foredeep it was assigned to the Vielician substage (Garlicki, 1994).

Chemical sediments are divided into three laterally interfinging 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:

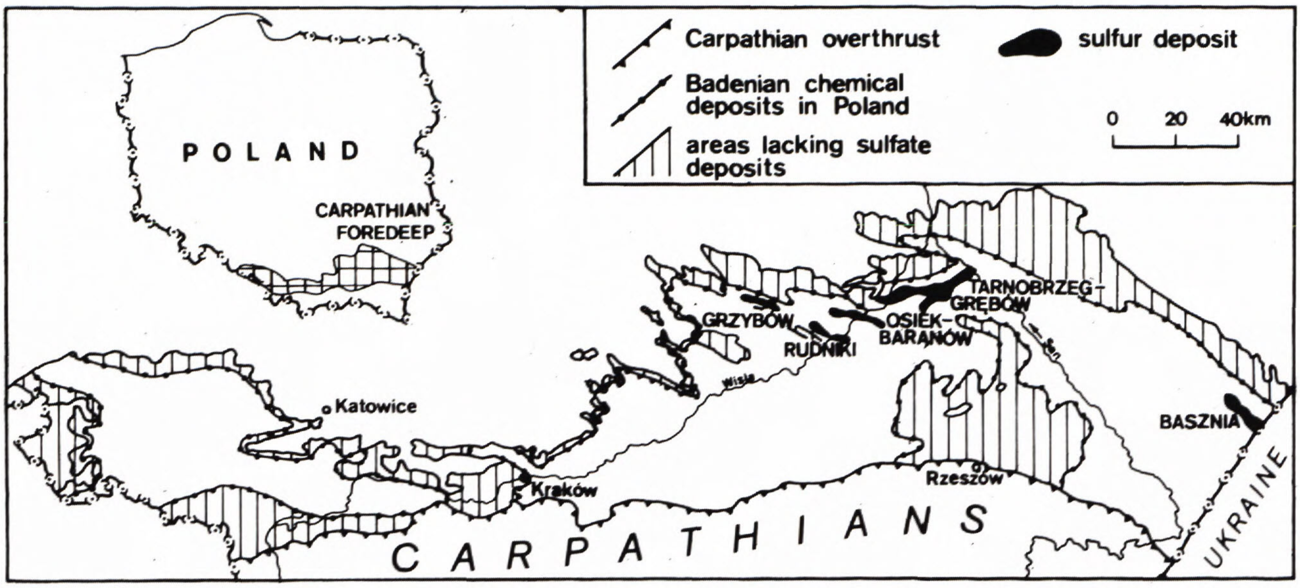

Fig. 1. Miocene sulfur deposits in the Carpathian Foredeep in Poland.

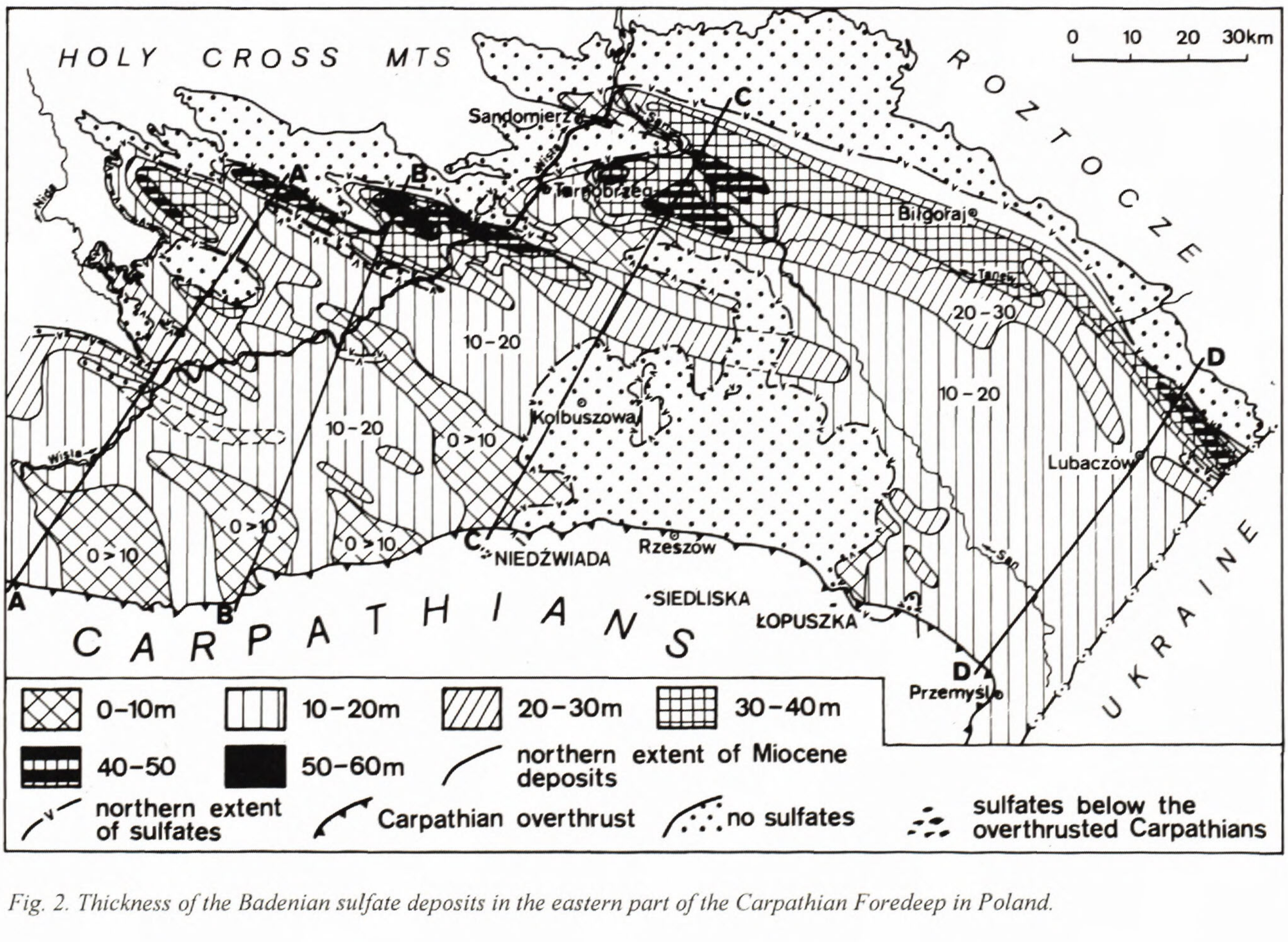

Fig. 2. Thickness of the Badenian sulfate deposits in the eastern part of the Carpathian Foredeep in Poland.

(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^2 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 distinguished 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 Posądza and Czarkowy deposits. Most rearchers (*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 "predecesors", 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.

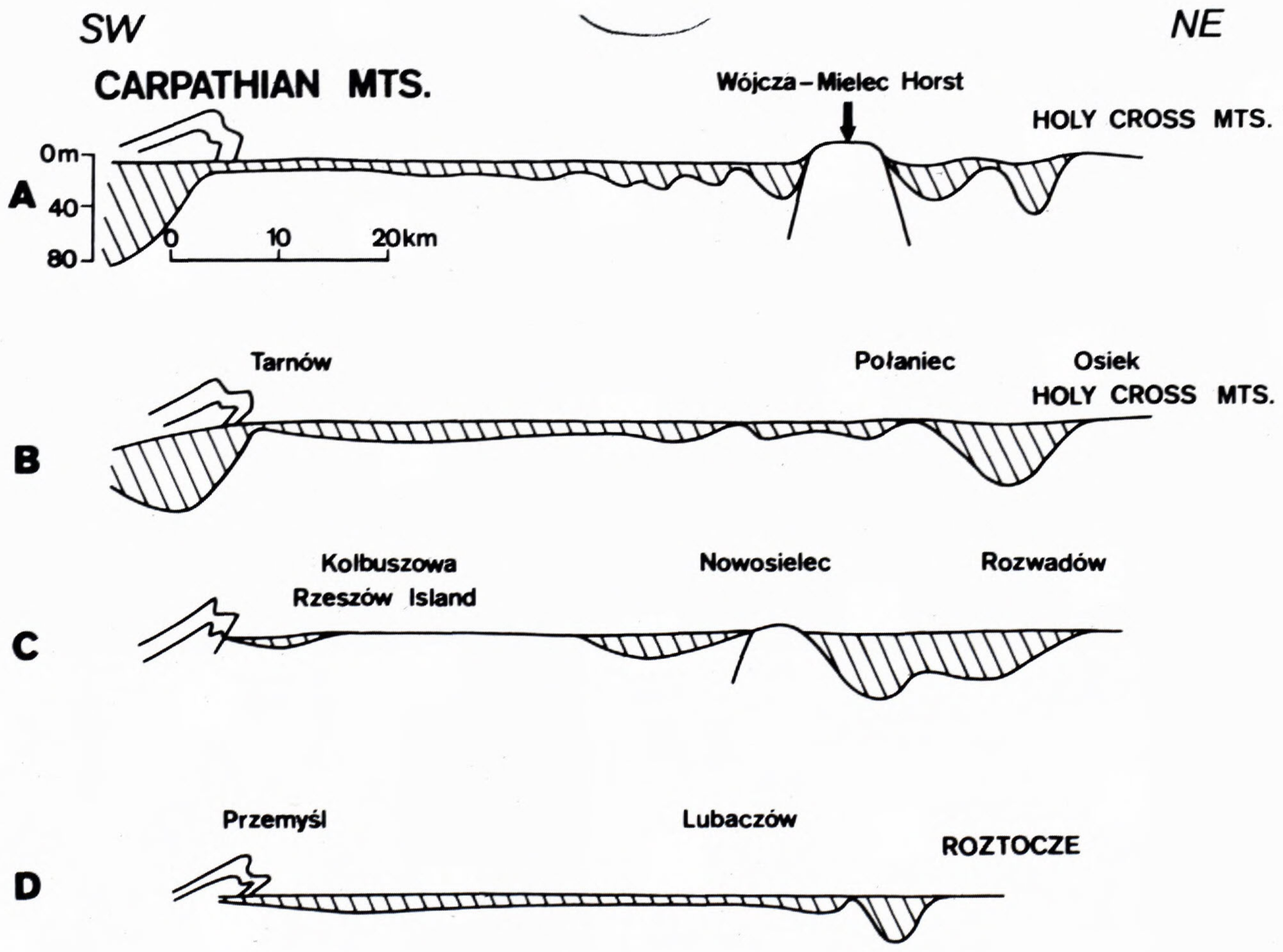

Fig. 3. Thickness changes of sulfate deposits along the lines shown in Fig. 2.

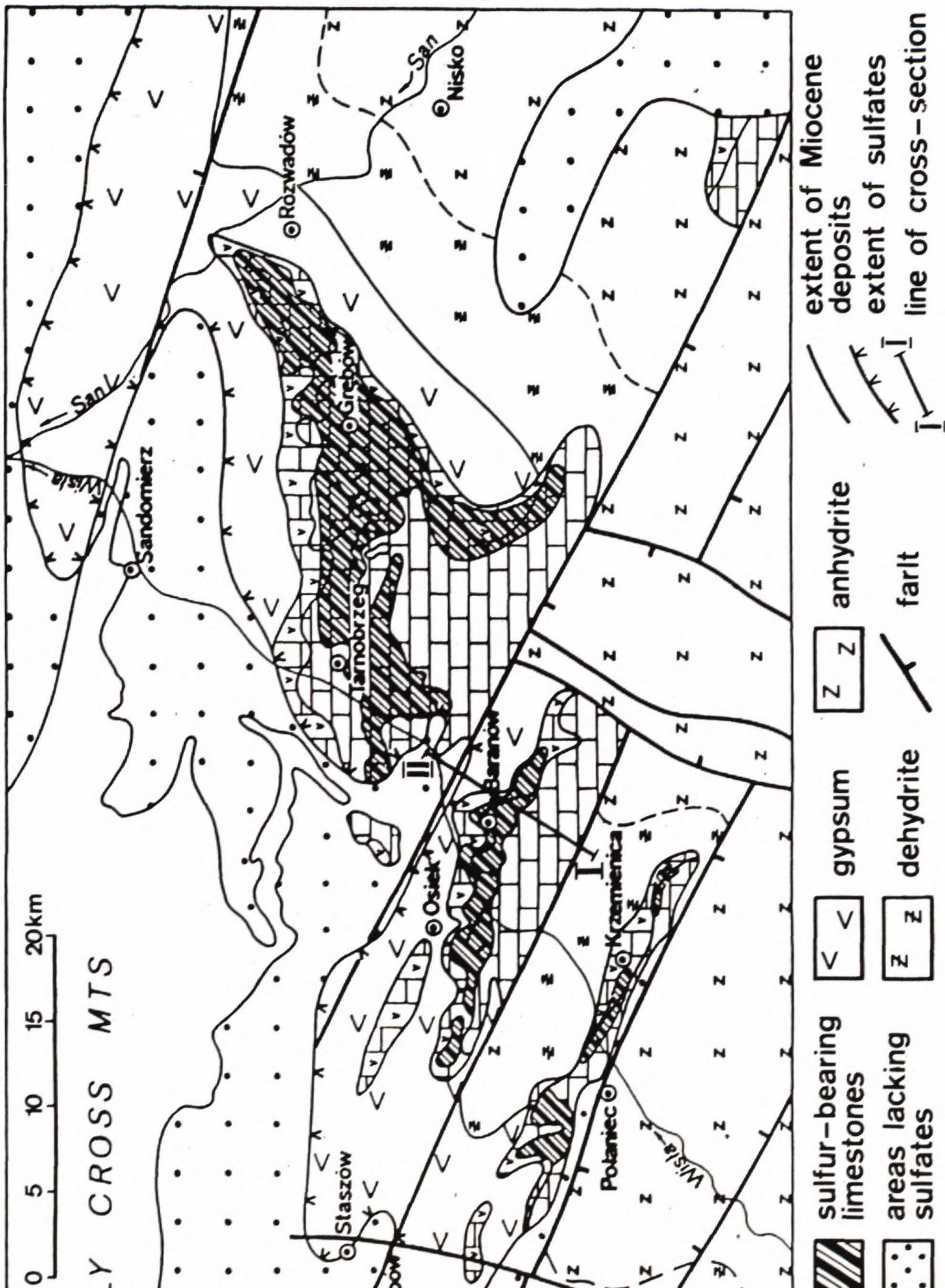

Fig. 4. Map of areas of active metasomatosis and sulfate lithofacies.

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 $\delta^{13}C$ of limestones from Piaseczno and Machów ranges from -18 to -59.9‰ (Czermiński & Osmólski, 1974), and from the western Ukraine from -32 to -65‰ (Sakseyev, 1972). The $\delta^{13}C$ 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 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-Spirialis 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 Szydłów-Połaniec 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 (Karnkowski, 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 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

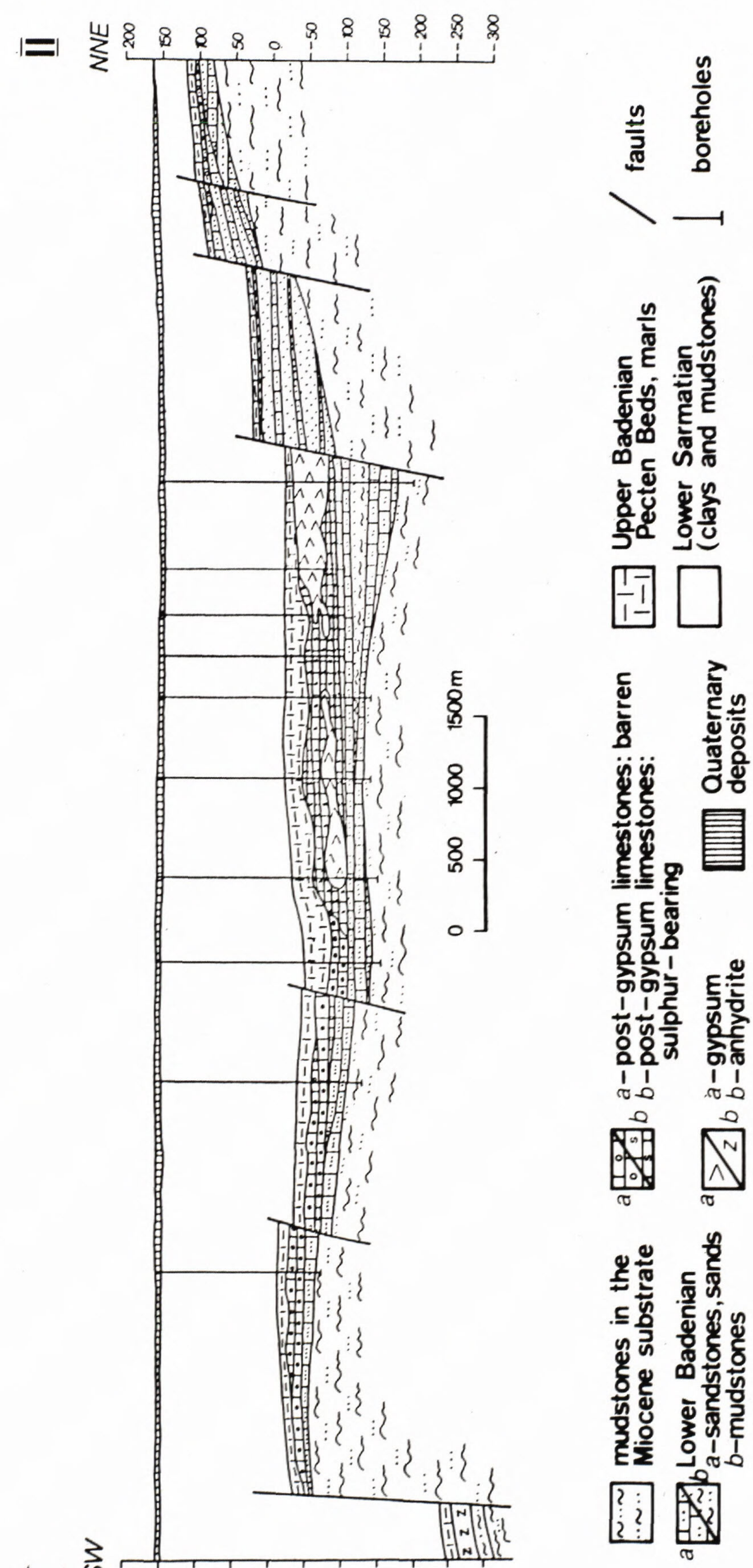

Fig. 5. Cross-section along the line I-II shown in Fig. 4.

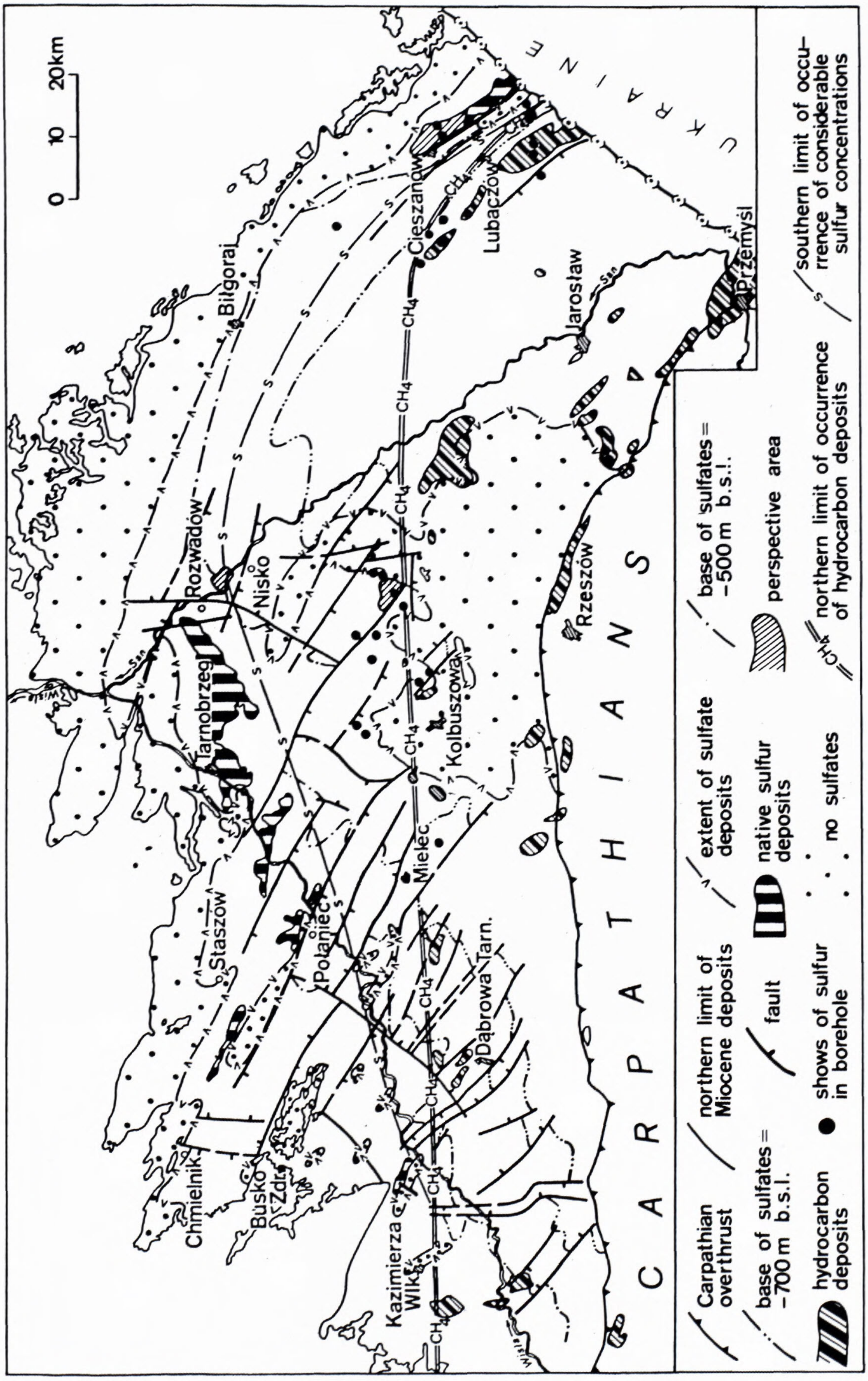

Fig. 6. Relation of occurrence of sulfur deposits and hydrocarbon deposits in the Carpathian Foredeep.

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^3 (assuming about 30% of losses derived from this reaction). According to rough estimates, about 300,000 million m^3 of natural gas was taken up by H_2S, 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^2 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 multistage sulfur-forming process was required. According to rough estimates, 2,000 million of sulfur moved required about 1,500,000 million m^3 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^3. 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).

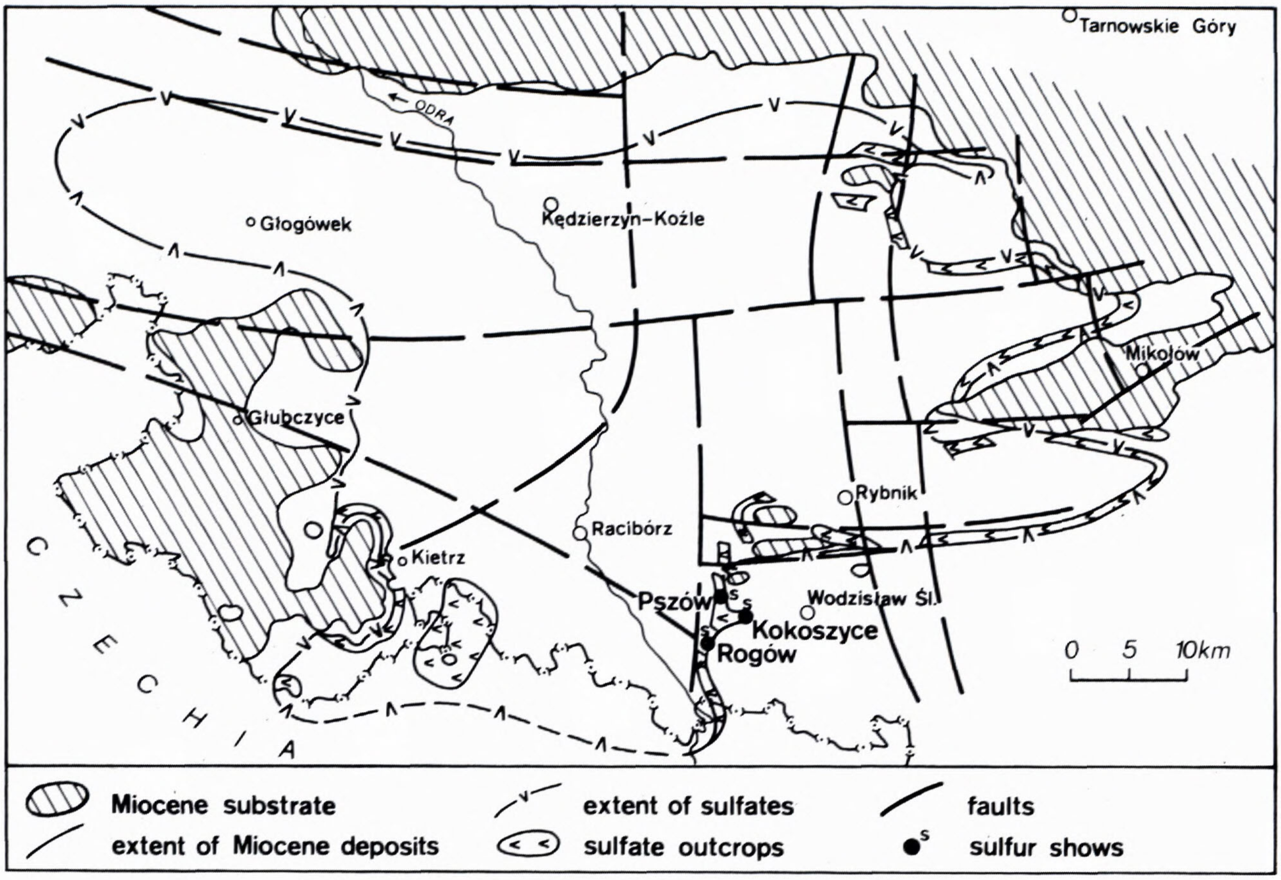

Fig. 7. Badenian sulfate deposits in Upper Silesia (faults after unpublished notes of S. Pawłowski).

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 Kobeřice 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 proceding 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 parantheses) 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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