

Geological Quarterly, Vol. 38, No. 3, 1994, p. 395-414

Bolesław KUBICA

Metasomatism of Badenian sulphates of the Carpathian Foredeep and its palaeogeographic conditions

The Miocene (Badenian) sulphate (gypsum and anhydrite) deposits in favourable structural conditions have undergone metasomatic transformation into limestones closely associated with native sulphur. The transformation process mobilized originally stable sulphate ions into highly mobile sulphide ions followed by their oxidation to elemental sulphur. It is possible to distinguish three stages of metasomatism which include (1) initial metasomatism (locally developed, often as crystal etching), (2) selective metasomatism (activated in the most susceptible parts of the sulphate deposits, e.g. along fractures, faults systems), and (3) complete metasomatism (the full alteration of a sulphate deposit with the preservation of original sulphate structures and textures). Except the structural pattern, the palaeogeographic conditions (areas lacking sulphates or where the sulphate horizon is substantially thinner) appear to be one of the important factors responsible for sulphate transformation. Intensity of the transformation process decreased with distance from such sedimentary discontinuities.

INTRODUCTION

The Miocene (Badenian) sulphate (gypsum and anhydrite) deposits of the Carpathian Foredeep were epigenetically transformed in favourable structural and hydrochemical conditions under impermeable sedimentary cover. The transformation process, activated mainly by hydrocarbons and bacteria, could develop at different depths and in various parts of the sulphate horizon which is widespread in the Carpathian Foredeep. The main products of this complex biochemical process are postsulphate limestones and native sulphur. Epigenetic origin of sulphur-bearing and barren limestones is especially well illustrated (according to e.g. K. Pawłowska, 1962, 1965; S. Pawłowski, 1963, 1968, 1970; S. Pawłowski *et al.*, 1965, 1979, 1985; B. Kubica, 1992; B. Kubica, K. Pawłowska, 1984; M. Nieć, 1982, 1992; T. Osmólski, 1972; M. Pawlikowski, 1982) by the presence of postsulphate structures and textures typical of originally sulphate (mainly gypsum) facies (comp. also A. Gąsiewicz, 1994*a*, *b*). Particularly, such structures as, for instance, calcite and/or sulphur

pseudomorphs after gypsum breccia and sabre-like gypsum crystals are distinctive features of these deposits. According to the quoted authors, further evidence for epigenetic alteration is the presence of sulphate "buttes" or "islands" and sulphate relics found within secondarily (i.e. epigenetically) formed limestones.

Elevated tectonic structures (fault uplifted blocks) facilitated the accumulation of hydrocarbons and fluids, and are believed by some workers (e.g. S. Pawłowski, 1963, 1968, 1970; S. Pawłowski *et al.*, 1965, 1979, 1985, 1987; B. Kubica, 1992; T. Osmólski, 1963, 1972; M. Nieć, 1982, 1992; Z. Krysiak, 1985, 1987; A. S. Sokolov, 1959, 1965) to serve as a framework (and thus the main ore-forming factor) for the transformation processes. However, a regional analysis of the sulphate formation indicates two distinct features: firstly, the sulphate bodies (developed on a macroscale as lenses, covers, nests, intrastratal beds, and irregular aggregates) are found within the postsulphate limestone sequences, and secondly, the sulphur ores seem to be connected with areas lacking sulphates or with regions with a substantially thinner sulphate horizon.

All these observations suggest that (1) the process of sulphate transformation was characterized by varying intensity reflected by different stages of the sulphate alteration, and (2) except the conditions mentioned above, one of the important factors responsible for the sulphate alteration (and thus sulphur ore formation) appears to be the palaeogeographic conditions connected with the extent and the development of the sulphates series. These local discontinuities in the development of the sulphate horizon seem to govern the distribution of both the metasomatic processes and their products.

DIAGENETIC PROCESSES IN SULPHATES

As it has been commonly assumed (e.g. S. Pawłowski *et al.*, 1979, 1985; B. Kubica, 1992 with references therein), diagenesis of the Miocene sulphates (gypsum and anhydrite) of the Carpathian Foredeep developed in two different settings, which were responsible for the observed lithologic variety of the host rocks and the products of the diagenetic processes. They include (1) normal, surface- or subsurface-connected diagenetic environments linked mainly with the recrystallization and dehydratation of sulphates (for details see B. C. Schreiber, 1988; comp. also M. Pawlikowski, 1982), and (2) diagenetic setting connected with secondary epidiagenetic or epigenetic (i.e., metasomatic) transformation of sulphates into limestones and native sulphur. The distinction is made in order to differentiate normal versus massive diagenetic (epigenetic) alterations.

SULPHATE DIAGENESIS

During Badenian and Sarmatian times a differential rate of subsidence developed across the Carpathian Foredeep. It caused the sulphate horizon to be buried at progressively greater depths closer to the basin axis. Consequently, compaction and mechanical dewatering occurred only in deeper parts of the foredeep. It caused dehydrites (*sensu* B. Kubica, 1972) to form at around 300 m depth. This diagenetic facies, intermediate between gypsum and anhydrite, represents gypsum rocks depleted in crystallization water of gypsum. Therefore, it commonly consists of partly obliterated sedimentary structures (for instance selenitic, laminated, or breccia structures). It is interesting to note that the recrystallization and dehydratation of gypsum crystals may develop at shallower depths (around 200–300 m) if the host rocks occurred in zones of tectonic discontinuities. Additionally, field observations indicate that at around 500 m gypsum does not contain any water of crystallization and forms anhydrite. Anhydrite from deeper parts of the basin often preserves relics of the original gypsum structures. Conversion of crystalline gypsum to anhydrite has been explained by J.-M. Rouchy (1976).

These diagenetic phenomena in sulphate deposits have a distinct regional zonation in the Carpathian Foredeep. It is possible to distinguish progressive (from exposed or shallowburied to deep-buried) sulphate diagenetic facies or zones consisting of gypsum, dehydrite, and finally anhydrite (e.g. B. Kubica, 1972, 1992; S. Pawłowski *et al.*, 1985).

In addition, some nodular varieties of anhydrite seem to resemble the original gypsum lithofacies fabrics, and these strata could also have been formed by the dehydratation of gypsum (e.g. B. C. Schreiber *et al.*, 1976) in either synsedimentary or burial environments. Therefore, many anhydrite beds preserve obliquely oriented, elongated anhydrite nodules which originally were gypsum crystals.

In some places the sulphate series exhibits features of rehydratation which developed mainly along distinct fractures often linked with fault systems. The synsedimentary and tectonic deformation of sulphate beds in the basin is also associated with these features.

EPIGENETIC (METASOMATIC) ALTERATION

In contrast to the previously described regional diagenetic changes within the sulphate deposits of the Carpathian Foredeep, much more intensive diagenetic and epigenetic alterations of sulphate series developed on a relatively local scale. They were associated with particular areas of the basin described below. These processes were responsible for the transformation of the sulphate sequence and the development of epigenetic, postsulphate (i.e. postgypsum and postanhydrite) carbonates (mainly limestones) and other (uncommon) rocks accompanied by sulphur mineralization.

METASOMATISM

According to A. Bolewski and M. Turnau-Morawska (1963, p. 315), metasomatism is defined as the process of transforming rock in both mineral and chemical composition by the influence of external chemical factors. It leads to the enrichment of input components and to depletion of removed components (by-products of the process). The components involved in chemical reactions during the transformation process tend toward a state of chemical equilibrium of the system influenced by additional variables such as temperature and pressure.

The transformation process of the Carpathian Foredeep sulphates affected both hydrated sulphates (gypsum) and dehydrated sulphates (anhydrite). It caused the lithological alteration of sulphates through an external carbon and hydrogen supply and a relocation of sulphur (originally bound into sulphate ions), crystallization water of gypsum and water originating as a by-product of the reactions. Carbon and hydrogen derived from hydrocar-

bons are commonly believed to be the main driving factors of the alteration processes with respect to Polish sulphur ores (see also a review of J. Parafiniuk *et al.*, 1994).

Among the main host rock elements released during the alteration and taking part in the metasomatism of sulphates were chemically stable elements (calcium) and chemically mobile components (sulphate ions, carbon dioxide, crystallization water of gypsum, hydrogen sulphide, and hydrocarbons). Carbon dioxide and hydrogen sulphide were secondary compounds (i.e. compounds formed due the alteration processes) while hydrocarbons were the external components. The percentage of chemically stable components in the host rocks (gypsum and anhydrite) is low: Ca content ranges from 23.3 (in gypsum) to 29.4% (in anhydrite) and mobile sulphur — from 18.6 (in gypsum) to 23.5% (in anhydrite). These data indicate both a high mobility and intensive exchange of the components (particularly sulphur) engaged in the transformation process. For this reason, traceable amounts of native sulphur are commonly found around the ore bodies, in both horizontal and vertical directions. Thus, the sulphur mineralization formed an aureole developed in sulphates surrounding the ore accumulations, in the uppermost part of the underlying unit (sands, sandstones, and siltstones of the Baranów Beds), and in the lowermost part of the overlying unit (siltstones and marls of the Pecten-Spirialis Beds). The highly stable calcium ion was bound into the CO_3^{2-} ion and instead of sulphates formed a new (secondary in the sense of origin) rock: postsulphate limestones with or without pseudomorphs after original structures and textures, and unaltered relics of the host rock.

Generally, during the course of the metasomatic mobilization of sulphur there was a change of the sulphur species from S⁶⁺ (in sulphates) to S^o in native sulphur. Sulphur's high chemical affinity for metals and elements with a low valence may additionally argue for the presence of an intermediate stage (in the form of H₂S) during the formation of native sulphur. In this case, elemental sulphur precipitated from hydrogen sulphide and the valence of S changed from S⁶⁺ through S²⁻ to S^o. Generally, the ionic transition from an elemental state (gases, liquids) to a combined state (solids) releases energy. Ionic energy in the crystal lattice for a unit charge may be expressed in units defined by A. J. Fersman (*fide* K. Smulikowski, 1952) as W_{ek} . This energy is directly proportional to the valence (W) and inversely proportional to the ionic radius (R): $W_{ek} = W/2R$

A sulphate ion taking part in the alteration process has an ionic radius equal to 0.035 μ m which is five times lower than that of H₂S (0.176 μ m), three times lower than of S^o (0.106 μ m) and also lower than CO₃²⁻(0.039 μ m). Thus, W_{ek} SO₄²⁻=0.32 and is significantly lower than W_{ek} CaCO₃, which is equal to 1.26. As is made clear from these calculations, the metasomatic alterations of sulphates into carbonates tend to replace the ions of lower ionic energy with ions of higher ionic energy.

The course of metasomatic reaction was certainly complex and multiphase, with an as yet unresolved problem of which factor was responsible for the precipitation of native sulphur from hydrogen sulphide (comp. also J. Parafiniuk *et al.*, 1994). Elemental sulphur, as a by-product of the alteration process, was precipitated in the available vugs of a secondary (carbonate) framework. Considering the low solubility of sulphates at surface or relatively shallow-subsurface temperatures $(10-30^{\circ}C)$, and a lack of suitable substances able to dissolve sulphates, a biogenic mediation in this process appears as the most probable path of sulphate alteration and sulphur mobilization (D. W. Kirkland, R. Evans, 1976). Bacteriogenic origin of sulphur-bearing limestones is largely indicated by isotopic data (J.

Parafiniuk *et al.*, 1994) and seems to be supported by organic relics found in the limestones and interpreted as bacterial remains (J. Czermiński, 1960; W. Ryka, 1988).

At the present stage of knowledge on the formation of Polish sulphur deposits, it is difficult to say if all mobilized elemental sulphur (from original sulphates) went through the intermediate (hydrogen sulphide) stage of the alteration process. In some boreholes from zones lacking significant native sulphur concentration (usually surrounding the sulphur ores, like for example Świeżyca, Lipa, Horyniec, Solec and others) (Figs. 2, 5) a high concentration of H_2S was found dissolved in the groundwater. This groundwater occurs in the postsulphate barren limestones and in a sandy series of the Baranów Beds underlying the sulphate horizon. The presence of H_2S in these deposits may be explained by a more reducing environment which, in the case of oxygen deficiency, caused fixation of sulphur into hydrogen sulphide. This overall metasomatic reaction:

sulphates \rightarrow carbonates + native sulphur

could also go in the reverse direction. Some workers (e.g., I. I. Aleksenko, 1974; E. Heydari, C. H. Moore, 1989) however, question a biogenic origin of hydrogen sulphide. They present evidence that native sulphur found in association with hydrocarbons and H₂S at high temperature and pressure in deep boreholes (up to a few thousand metres) may be formed by a thermochemical reduction of sulphates. In the deeper part of the Carpathian Foredeep of Poland, for instance in the Kańczuga borehole (other boreholes are listed by P. Karnkowski, 1994) at 1530 m depth and about 100°C, there occur postanhydrite limestones and native sulphur which could be of the same origin. Additionaly, L. F. Hatch (1972) documented the precipitation of native sulphur by means of pure chemical reactions with the use of methane.

MASS-BALANCE

Theoretical calculations indicate that sulphate alteration was accompanied by a decrease of the host rock volume depending upon the degree of its hydratation, ranging from 21 to 42%, and averaging 31.5%. Moreover, these calculations assume stoichiometric proportions and chemically pure components. However, under natural conditions, gypsum and anhydrite occur with various mineral substances (such as clays, sands, calcium carbonates, and others) which do not actively participate in the metasomatic reactions. In addition, as has been documented several times (e.g. S. Pawłowski *et al.*, 1979, 1985; B. Kubica, 1992), in the postsulphate limestone sequences there occur various amounts of gypsum or anhydrite which are interpreted as unaltered relics of the host rock. Therefore, depending upon the content of the initial sedimentary mineral fractions (neutral in the reactions) and the degree of sulphate transformation, the rock volume decrease due to the alteration process differs from the theoretical value and ranges from 20 to 36%. Furthermore, the areas of intensive sulphate alteration are characterized by a smaller thickness of the postsulphate carbonate series in comparison to both the thickness of the surrounding sulphate series and the sulphate buttes within the altered sequences.

The process of metasomatism from sulphate-bearing rock to limestone leads to a decrease in rock volume and concurrent increase in bulk density of limestones, and results in release of water and sulphur. The latter occurred in the gaseous form of hydrogen

sulphide (during the first stage of the alteration). This may be best explained by the fact that the calcium ion increases its own percentage of the molecular weight of the compound from 23.3% in sulphates to 40.08% in limestones. Molecular weight of limestones (100.09) is 42% lower than that of gypsum (172.08) and 21% lower than that of anhydrite (136.10).

Most of the precipitated elemental sulphur came from an intermediate hydrogen sulphide stage. This suggestion seems to be supported by both horizontal and vertical irregularity in native sulphur distribution and by the results of isotope analyses (see J. Parafiniuk *et al.*, 1994). Both the sulphur distribution and content in the individual ore fields are highly inconsistent with the sulphur distribution and concentrations predicted by the metasomatic model and equations. In a given ore field the native sulphur concentrations are 2–3 times higher than the sulphur content bound in the host rock (B. Kubica, 1965) as sulphates. In addition, there are sometimes pure sulphur intergrowths as thick as 1 m occurring in the sulphur-bearing sequences. Despite a high mobility of sulphur (in the form of hydrogen sulphide), possibly other factors could favour such anomalous concentrations of this mineral. An important role was most probably played by a complex pattern of fluid circulation and a pulsative supply of hydrocarbons along locally privileged pathways of oxygen contribution.

In summary, the process of sulphate alteration activated by hydrocarbons in the presence of bacteria released stable calcium ions and mobile sulphate ions from the host rock. This multiphase process formed CO_2 , H_2S , and water which, due to complex interactions, led to the formation of unstable $Ca(HCO_3)_2$ and finally to postsulphate calcium carbonate. In favourable geological settings, hydrogen sulphide was oxidized to elemental sulphur which sometimes could be precipitated in economic concentrations. Because the main factors controlling the epigenetic process of sulphate transformation are biogenic, the term "biogenic metasomatosis" applied by M. Nieć (1982) to these rocks is justified.

METASOMATIC STAGES

The main product of the sulphate alteration are limestones with a variable content of clayey material and native sulphur depending on the original admixture in the host rock. At higher concentrations of clay, clayey limestones and marls or even pure clays could be formed. However, the percentage of these lithofacies in the altered sequence is quite low. The postsulphate limestones are mainly cryptocrystalline with locally preserved relics of original structures and textures. A local lack of relics of original structures and textures in the secondary limestones may be the result of later diagenetic obliteration processes, such as recrystallization (*sensu* M. Nieć, 1982, 1986).

Intensity of the metasomatic processes is variable in the areas of sulphur ore occurrence. Taking into account the relation of unaltered (sulphates) and altered (carbonates) deposits it is possible to distinguish various stages of metasomatic intensity: from initially through selectively to completely altered sequences.

Initial metasomatism is observed in the sulphate series mainly as etched (to a varying extent) sulphate crystals and as patchy, discontinuous, and streaky carbonates (the products of the host rock transformations). The altered fragments often preserve the original internal structures (for instance gypsum lamination or the shape of original gypsum crystals and

breccia fragments and others). At this stage of the process there are found void-filling aggregates of native sulphur irregular in both size and shape, and bounded by sulphate crystals. The initial metasomatism commonly appeared in tectonically fractured zones, along the discontinuity surfaces comprising the intergrowth crystal planes or developed at distinct lithological boundaries (e.g., at a massive gypsum/crystalline gypsum lithofacies boundary). It is here assumed the alteration developed along the contacts of selenitic crystals. It seems probable that the laminated gypsum facies, with the laminae enriched in the primary carbonate fraction, were most susceptible to alteration in comparison to other gypsum lithofacies, especially to coarse-crystalline selenitic facies.

Selective metasomatism is evidenced by the alteration of particular portions of the gypsum series. Consequently, there is the alternation of altered and non-altered beds and layers (for example, the following stratal alternation: limestones/sulphates/limestones/sulphates). Thusly formed metasomatic limestones commonly are accompanied by micro-faults, tectonic fractures, and especially by clay interlayers. In addition, this type of the metasomatism is documented by the presence of sulphate buttes or lenses, intrastratal sulphate layers, and sulphate beds preserved within the postsulphate series.

Complete metasomatism is characterized by a full alteration of the sulphate series into postsulphate limestones which may or may not preserve the original structures and textures. A carbonate matrix often contains clay and sometimes irregular pore spaces filled with liquid hydrocarbons. At this stage of the process the postsulphate carbonate/sulphate contacts are irregular and sharp, commonly without any gradual transition. This could have resulted, as is interpreted here, only due to a complete chemical transformation of the original rocks.

Generally, the metasomatic transformations started in fractured, porous, and permeable zones and were inhibited by either clay interlayers, streaks, or very coarse-crystalline selenitic gypsum crystals.

PALAEOGEOGRAPHIC AND STRUCTURAL CONDITIONS OF SULPHATE METASOMATISM

UPPER BADENIAN-SARMATIAN BASIN EVOLUTION

During the final stages of the sulphate deposition in the Carpathian Foredeep there was intensive erosional removal of the deposits from elevated areas (including so-called Rzeszów "island", where sulphates were completely removed). This is documented by a few horizons of sulphate breccia up to 30 m thick. These horizons are evidence of remobilization and redeposition of clastic gypsum deposits by slumps, debris flows, and turbidites (T. M. Peryt, A. Kasprzyk, 1992). Sulphate deposition was followed by clastic sedimentation siltstones and marls of the *Pecten-Spirialis* Beds which unconformably overlie variously eroded sulphate sequences. The clastic deposits represent open marine sedimentary conditions and are characterized by typical faunal assemblages (e.g. K. Pawłowska, 1965, 1994; S. Pawłowski *et al.*, 1985).

At the Badenian/Sarmatian boundary, Late Alpine tectonic block movements reactivated older fault systems (mainly along NW-SE longitudinal faults) thus forming elongated

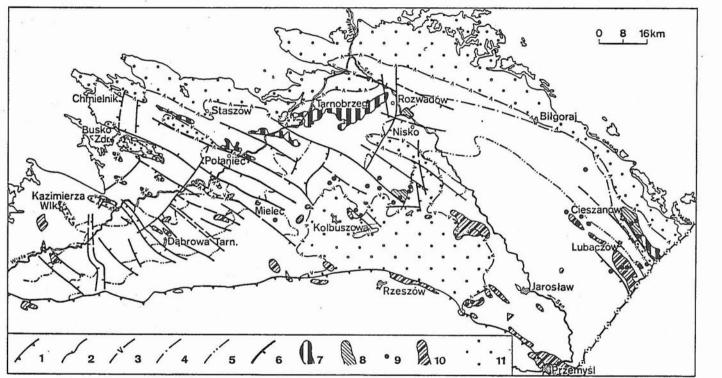


Fig. 1. Location of sulphur ores, sulphur perspective areas, gas and oil fields and a simplified tectonic pattern of the Carpathian Foredeep

1 — northern border of the Carpathian orogen, 2 — northern extent of the Miocene, 3 — extent of sulphates, 4 — isohypse of sulphate horizon at 750 m b.s.l., 5 — isohypse of sulphate horizon at 300 m b.s.l., 6 — faults, 7 — sulphur deposits, 8 — sulphur undiscovered areas, 9 — boreholes with sulphur-bearing limestones or with native sulphur aggregates in both postsulphate and sulphate deposits, 10 — gas and oil fields (after S. Depowski, 1990), 11 — sulphate-free areas

402

Bolesław Kubica

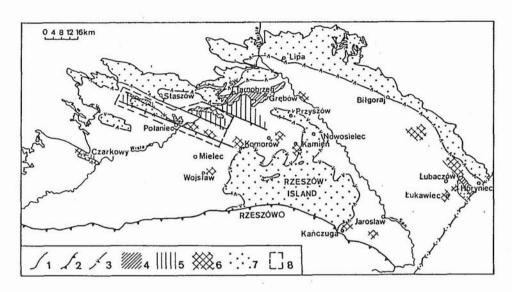


Fig. 2. Location of sulphate-free areas and metasomatically altered deposits in the Carpathian Foredeep of Poland 1 — extent of the Miocene, 2 — northern border of the Carpathian orogen, 3 — extent of sulphates (gypsum-anhydrite), 4 — sulphur ores, 5 — postsulphate barren limestones, 6 — zones of metasomatically altered sulphates, 7 — sulphate-free area, 8 — area presented in Figs. 4 and 5

Lokalizacja obszarów pozbawionych siarczanów oraz stref objętych procesami metasomatozy w zapadlisku przedkarpackim na terenie Polski

1 — zasięg osadów miocenu, 2 — północna granica Karpat, 3 — zasięg siarczanów (gipsów-anhydrytów), 4 — złoża siarki rodzimej, 5 — wapienie posiarczanówe płonne, 6 — strefy metasomatycznych przeobrażeń siarczanów, 7 — obszar pozbawiony siarczanów, 8 — obszar przedstawiony na fig. 4 i 5

horsts and grabens (comp. also M. Jarosiński, 1992 with references therein). Thus, a basic structural plan was established which has been only slightly modified during Sarmatian time (a period of fault movements and intensive subsidence, particularly developed along the basin axis) (see also K. Pawłowska, 1994). In the Sarmatian age, the sulphate horizon was covered by an impermeable clay cap. A combination of both tectonic and depositional conditions created suitable traps for hydrocarbons which migrated from the folded Carpathian orogenic belt. Essentially flat tectonic structures found in the northern periphery of the foredeep are devoid of a well developed seal, therefore this led to gradual removal (mainly by migration and oxidation) of accumulated hydrocarbons. The oxidation of hydrocarbons in the presence of sulphates and bacteria in a mineralized water environment was accompanied by the formation of significant amounts of hydrogen sulphide. The tectonic stabilization of both the Carpathian orogen and foreland (at the end of the Sarmatian

Lokalizacja złóż siarki, obszarów perspektywicznych dla wystąpień osiarkowania, złóż gazu ziemnego i ropy naftowej na tle uproszczonego obrazu tektonicznego zapadliska przedkarpackiego

^{1 —} północna granica Karpat; 2 — północny zasięg utworów miocenu; 3 — zasięg siarczanów; izohipsy spągu siarczanów: 4 — na głęb. 750 m p.p.m., 5 — na głęb. 300 m p.p.m.; 6 — uskoki; 7 — złoża siarki; 8 — obszary perspektywiczne dla wystąpień osiarkowania; 9 — otwory wiertnicze, w których stwierdzono wapienie osiarkowane lub skupienia siarki w wapieniach posiarczanowych lub w siarczanach; 10 — złoża gazu i ropy naftowej (według S. Depowskiego, 1990); 11 — obszary pozbawione siarczanów

Table 1

Mineral + formula	Formula Wt [g]	Stable components [%]	Mobile components [%]
CaSO4 2H2O (gypsum)	172.08	Ca (23.3)	SO ₄ ²⁻ + 2H ₂ O (76.7)
CaSO4 (anhydrite)	136.10	Ca (29.4)	SO ²⁻ (70.6)
CaCO ₃ (limestone)	100.09	Ca (40.1)	CO ₃ ²⁻ (59.9)
S^{2+} , S^{4+} , S^{6+} , S^{2-} (sulphur as element, sulphur bound to sulphate ion and in gaseous form H ₂ S)	32.06	-	S (18.6 in gypsum) (23.5 in anhydrite) (94.1 in H ₂ S)
Ca ²⁺	40.08		-
SO4	96.02	-	-
CO3 ²⁻	59.98	-	secondary component
CH4	16.01	-	supply component
H ₂ S	34.06	-	secondary component
H ₂ O	17.99	-	20.91 (two molecules o crystallization water of gypsum)

Chemical characteristics of the mineral phases involved metasomatic alteration of sulphates

and the beginning of Pliocene times) was probably a last requisite for the metasomatic alteration of sulphates into the postsulphate limestones and native sulphur.

RELATIONSHIP BETWEEN HYDROCARBON CONCENTRATIONS AND TECTONIC STRUCTURES

A regional analysis based upon the abundant gathered borehole data demonstrates a close relationship between the occurrence of metasomatic processes and the presence of hydrocarbons, native sulphur concentrations, and fault uplifted tectonic blocks (Fig. 1). In the deeper part of the Carpathian Foredeep area this relationship is two-fold:

1. Hydrocarbons and postanhydrite limestones occur in the same elevated tectonic structures (e.g. Lubaczów, Uszkowce, Kańczuga, and Wojsław, Fig. 2).

2. Generally, substantial hydrocarbon concentrations occur mainly in the elevated tectonic structures localized mainly in the deeper, more "internal" (i.e. adjacent to the Carpathian orogen boundary) part of the foreland (comp. also P. Karnkowski, 1994). In contrast, the tectonic structures with intensive metasomatic transformations (reflected by the sulphur ore concentrations) essentially occur in the distinctly shallow and marginal ("external") part of the foreland. Such a mineral zonation is best defined in Western Ukraine (I. I. Aleksenko, 1969) and a similar pattern seems to occur in the Polish part of the Carpathian Foredeep. In addition, bituminous sulphur (with up to several percentage of

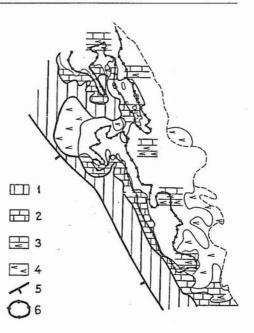


Fig. 3. Occurrence of the sulphate alteration in the proximity of sulphate-free areas observed in the Western Ukraine (after Z. A. Komleva, 1963)

1 — sulphate-free area, 2 — postsulphate barren limestones, 3 — limestones and sulphur-bearing gypsum, 4 — non-altered gypsum, 5 — faults, 6 — extent of sulphur mineralization

Przykład przeobrażeń siarczanów na terenie Zachodniej Ukrainy w sąsiedztwie wysp bezsiarczanowych (według Z. A. Komlevej, 1963)

1 — obszar pozbawiony siarczanów, 2 — wapienie posiarczanowe płonne, 3 — wapienie i gipsy osiarkowane, 4 — gipsy nieprzeobrażone, 5 — uskoki, 6 zasięg osiarkowania

bitumens) has been found in the Polish and Ukrainian parts of the Carpathian Foredeep, in the USA, and in Iraq. In the Carpathian Foredeep bituminous sulphur commonly occurs deeper than 300 m.

In the light of the geological research discussed above, the participation of hydrocarbons in sulphate metasomatism seems to be incontestable. This fact has also been established for sulphur ores found elsewhere in Poland, Ukraine, Russia, USA, and Iraq.

PALAEOGEOGRAPHIC CONDITIONS OF THE EPIGENETIC DEPOSITS

Except the tectonic structural conditions, the sulphate metasomatism was strongly dependent on the palaeogeographic extent of sulphates (Fig. 2). This is particularly relevant with regard to areas devoid of or with only a thin sulphate horizon. Such areas are common and sometimes cover a large extent of the basin area; they also commonly co-occur with sulphur deposits. They are known to occur in Western Ukraine (e.g. L. N. Kudrin, 1969; Z. A. Komleva, 1963) (Fig. 3), and extend west through southern and into western Poland. The most commonly occurring and largest sulphur deposits in the northern part of the Carpathian Foredeep are often connected with the relatively extensive area called the Rzeszów "island" (R. Ney *et al.*, 1974) — Fig. 2. The presence of such areas is connected with the primary and/or secondarily reduced (mainly erosionally removed) the sulphates extent. Additionally, narrow areas lacking sulphates are often associated with fault zones commonly accompanying elevated tectonic blocks. All these areas lacking in sulphates are associated with fault uplifted elevations and are believed to be, according to the author, the areas favourable for metasomatic sulphate alteration because of their highly favourable conditions for the accumulation of hydrocarbon and mineralized water.

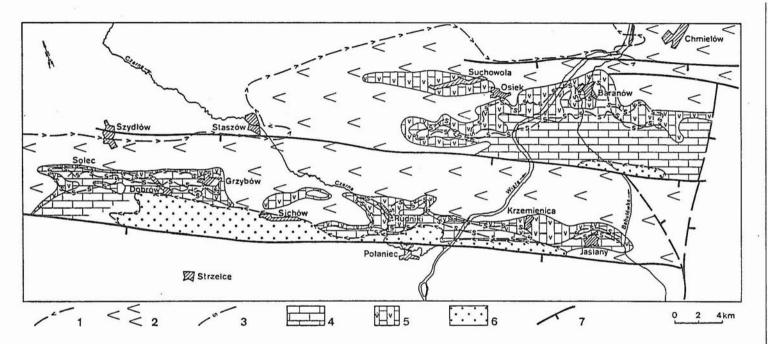


Fig. 4. Occurrence of metasomatic alterations associated with sulphate-free area between Grabki - Grzybów - Rudniki - Krzemienica and Osiek - Baranów Sandomierski (for location see Fig. 2)

1 — extent of gypsums, 2 — non-altered sulphates, 3 — extent of sulphur mineralization, 4 — postsulphate limestones, 5 — gypsums partly metasomatically altered into epigenetic limestones, 6 — sulphate-free area, 7 — faults

Procesy metasomatozy w otoczeniu bezsiarczanowej wyspy między Grabkami – Grzybowem – Rudnikami – Krzemienicą oraz Osiekiem – Baranowem Sandomierskim (lokalizacja na fig. 2)

1 — zasięg gipsów, 2 — siarczany niezmienione, 3 — zasięg osiarkowania, 4 — wapienie posiarczanowe, 5 — gipsy częściowo przeobrażone w wapienie, 6 — obszar pozbawiony siarczanów, 7 — uskoki

406

Bolesław Kubica

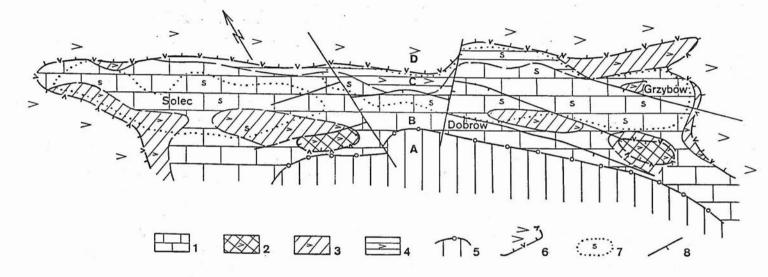


Fig. 5. Zonal lithologic differentiation (A-D zones) associated with Solec - Dobrów - Grzybów sulphur ore (for location see Fig. 2)

1 - postsulphate limestones; 2 - gypsum buttes preserved in postsulphate limestones; 3 - intrastratal non-altered gypsums in postsulphate limestones; 4 - gypsum covers overlying postsulphate limestones; 5 - sulphate-free area; 6 - non-altered gypsum deposits; 7 - extent of sulphur mineralization; 8 - faults; lithological zonation resulted of metasomatic alteration of sulphates: A - sulphate-free zone, B - postsulphate barren limestones zone, C - sulphur-bearing limestone zone, D - non-altered sulphate zone

Przykład strefowego zróżnicowania litologicznego w otoczeniu złoża siarki Solec - Dobrów - Grzybów (strefy A-D) (lokalizacja na fig. 2)

1 — wapienie posiarczanowe; 2 — ostańce wyspowe gipsów wśród wapieni posiarczanowych; 3 — śródpokładowe niezmienione gipsy w obrębie wapieni posiarczanowych; 4 — pokrywy gipsów na wapieniach posiarczanowych; 5 — obszar pozbawiony siarczanów; 6 — gipsy nie objęte procesami transformacji; 7 — zasięg osiarkowania; 8 — uskoki; strefy zróżnicowania metasomatycznego siarczanów: A — strefa pozbawiona siarczanów, B — strefa wapieni posiarczanowych płonnych, C — strefa wapieni osiarkowanych, D — strefa siarczanów nieprzeobrażonych

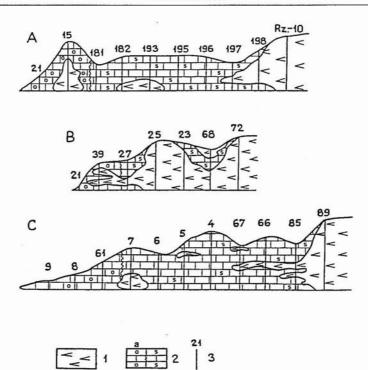


Fig. 6. Cross-section through metasomatically altered deposits: A — Grzybów sulphur ore, B — Rudniki sulphur ore, C — Osiek – Baranów Sandomierski sulphur ore

1 — gypsum; 2 — postsulphate limestones: a — barren, b — sulphur-bearing; 3 — borehole

Przekroje obrazujące strefowe zróżnicowanie litologiczne złóż: A — Grzybów, B — Rudniki, C — Osiek - Baranów Sandomierski

1 - gipsy; 2 - wapienie posiarczanowe: a - płonne, b - osiarkowane; 3 - otwór wiertniczy

The largest areas of the altered sequences are confined to the shallow (northern) and marginal part of the basin, where the main sulphur ores of Poland occur (Figs. 4, 5). Figure 4 illustrates the occurrence of metasomatic alteration and the extent of the postsulphate limestone series in the Baranów Sandomierski region; the cross-sections (Fig. 6) show relationship between sulphur-bearing and barren limestones and non-altered sulphates. A very extensive (over 50 km long) belt of the epigenetic deposits occurs from Grabki (to the west of Szydłów) through Solec, Grzybów, Rudniki, and Gawłuszowice to Jaślany (to the north of Mielec). This zone is localized on a horst structure which in the southwestern part contain an elongated zone devoid of sulphates. The second large belt (over 20 km long) of these rocks occurs between Suchowola and Wola Baranowska.

The most extensive area of transformed rocks occurs in the Tarnobrzeg – Grębów area (Fig. 2), especially in its southern part. This area is characterized by remarkable thinning of the sulphate series (Nagnajów, Dąbrowica, Kierz, Jadachy, and Zapolednik, all to the

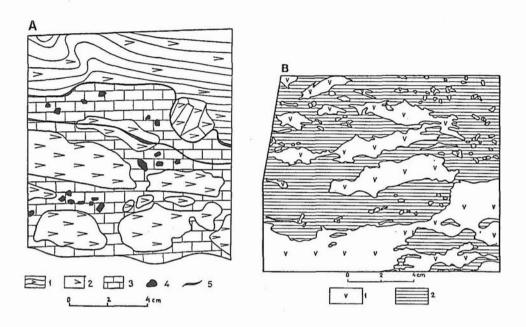


Fig. 7. Postgypsum limestones with relics of non-altered gypsum crystals

A: 1 — laminated gypsum, 2 — crystalline gypsum, 3 — postgypsum limestones, 4 — sulphur aggregates, 5 — clay streaks; core slab., borehole Rudniki 68, depth of 216.9 m; B: 1 — gypsum deposits, 2 — postgypsum limestones; core slab., borehole Jamnica K-24, depth of 263 m

Wapienie pogipsowe z zachowanymi reliktami niezmienionych gipsów

A — fragment rdzenia wiertniczego z otworu Rudniki 68, głęb. 216,9 m: 1 — gipsy laminowane, 2 — gipsy krystaliczne, 3 — wapienie pogipsowe, 4 — skupienia siarki, 5 — zailenia (ekrany ilaste); B — fragment rdzenia wiertniczego z otworu Jamnica K-24, głęb. 263 m: 1 — gipsy, 2 — wapienie pogipsowe

south of Tarnobrzeg ore) and by a zone devoid of these deposits located to the west of Tarnobrzeg ore (Suchorzów – Świniary).

In addition, the metasomatic products are associated with an elongated (from Jeżowe through Nowosielec towards Przyszów, Jadachy, and Suchorzów) and arched sulphate-free (probably due to erosion) branch of Rzeszów "island" (Fig. 2).

In the western part of the Carpathian Foredeep the epigenetic series are known firstly from the oldest Polish mine area (comp. B. Kubica, 1994) in the Czarkowy – Posądza region (Fig. 2), where they are associated with the sulphate-free Nida and Słomniki Horsts (T. Osmólski, 1972; Z. Krysiak, 1987). In the Lower Silesia (Rybnik region), the metasomatic alteration of sulphates is found close to the southern sulphate extent and also in a narrow fault system zone developed in the vicinity of Pszów and Rogów (S. W. Alexandrowicz, 1965).

As is evidenced by the above, the largest altered sequences are concentrated in the well explored marginal parts of the basin. They also were found (on a limited scale) in the deeper part of the Carpathian Foredeep to which little attention has been paid so far. Therefore, they are listed below.

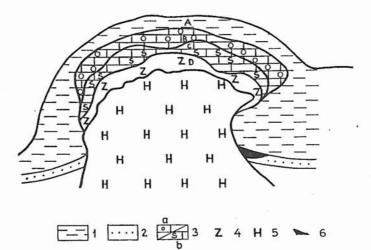


Fig. 8. Schematic cross-section of the cap rocks of a U.S. Gulf Coast salt diapir with ideal sequence of lithotypes (after H. Blatt *et al.*, 1980)

1 — clay cover; 2 — sandstones; 3 — postsulphate limestone: a — barren, b — sulphur-bearing; 4 — anhydrite cap; 5 — salt stock; 6 — oil deposits; A-D — as in Fig. 5

Schematyczny przekrój przez czapę siarczanową siarkonośnego wysadu solnego basenu Zatoki Meksykańskiej (według H. Blatta i in., 1980)

1 — pokrywa ilasta; 2 — piaskowce; 3 — wapienie posiarczanowe: a — płonne, b — osiarkowane; 4 — czapa anhydrytowa; 5 — wysad solny; 6 — złoża węglowodorów; A-D — jak na fig. 5

Metasomatic alterations occur in the vicinity of Horyniec (Fig. 2) and in the horst structure of the Basznia orebody. The intensity of the process was greater where there was less or no sulphate deposits.

Metasomatic alterations (of various intensity) at depths greater than 1000 m are observed in the vicinity of Wola Obszańska and Uszkowce (at depth of 1309–1347 m) (still around sulphate-free area in Lubaczów region) where reservoirs of gaseous hydrocarbons also occur (comp. P. Karnkowski, 1994).

In the vicinity of Cetynia (at depth of 941–947 m), Lubaczów (at depth of 1013–1020 m), and Łukawiec (at depth of 1477.5 m) (Fig. 2) the alterations are associated with areas of both gas concentration and thinning of the sulphate unit localized close to the fault systems.

The initial to complete metasomatic stages are observed in the vicinity (Fig. 2) of Mirocin (near Jarosław), Rokitnica, and Kańczuga (at depth of 1488 and 1529 m). They occur from 1496 to 1536 m depth; nearby, gas fields and the limit of anhydrite extent are both associated with elevated, domal tectonic structures.

In the central part of the foredeep, in the vicinity of Kamień, Wola Ranizowska, and Komorów (Fig. 2), sulphur mineralization occur from 727 to 760 m depth and is connected with anhydrite bodies isolated from the main deposit. In the vicinity of Lipnica and Zielonka (from 751 to 818 m depth), and Wojsław (at depth of 698 m) barren postsulphate limestones (from a few up to 20 m thick) occur as well.

Generally, as is clear from the above, most of the mentioned occurrences of epigenetic deposits in the Carpathian Foredeep are found in proximity to the sulphate-free areas or at

the limit of sulphate extent. In addition, these areas are often associated with or are bounded by fault systems forming uplifted blocks. This relation has previously been suggested by S. Kwiatkowski (1962) for the Grzybów ore body. These structures in turn are commonly associated with hydrocarbon accumulations. Thus, the palaeogeographic factor played the most important role in the formation of sulphur mineralization and should be used (as a criterion) in searching for sulphur in the foredeep.

LITHOLOGIC ZONATION

As documented above, metasomatic processes in the Carpathian Foredeep were activated at distinct sedimentary or tectonic discontinuities of the sulphate horizon. The characteristics of all investigated areas (with sulphur mineralization or barren limestones) allow development an idealized model of the distribution of metasomatic products. This distribution shows a general lateral lithologic zonation of sulphur-bearing and barren limestones, and sulphate deposits. Generally, it is possible to distinguish (Fig. 3, 5, 8) four main zones. The sulphate-free area (zone A) adjoins the postsulphate barren limestones (zone B), which in turn pass into the sulphur-bearing limestones (zone C). This zone borders the most external zone (D) represented by the sulphate deposits (the main lithology in the Carpathian Foredeep). However, zone D is heterogeneous, especially where it is in direct contact with the sulphur-bearing limestones and sulphate deposits occurs. Therefore, it is common to find sulphate buttes, intrastratal layers, and beds of irregular sulphate intergrowths (all indicating the presence of selective metasomatism — Fig. 7).

Externally adjacent to the subzone of selective metasomatism, is a very discontinuous and narrow subzone with the features of initial metasomatism. Outside of these subzones, uniform (in the sense of traceable epigenetic evidences of metasomatic alteration) and extensive sulphate lithofacies occur in the basin. This pattern of metasomatic lithological zonation typical of the Carpathian Foredeep is presented in Figs. 3–6.

A pattern of lithologic zonation associated with stratiform sulphur ores similar to that of the Carpathian Foredeep can also be seen in the cap rock ore deposits of the U.S. Gulf Coast Basin (Fig. 8). Generally, the lateral zonation of the cap rocks is also confined to the discontinuity (diapiric intrusion in this case) and is associated with hydrocarbon reservoirs (gas and oil fields).

CONCLUSIONS

1. The metasomatic alteration of the Carpathian Foredeep sulphate deposits is characterized by various stages of transformation: from initial through selective to complete metasomatism.

2. A detailed analysis of the lithological differentiation of the sulphate horizon in the Carpathian Foredeep indicates that structural factors as well as palaeogeography (sulphate-free areas confined to erosional events or narrow zones associated with tectonic fault systems and zones of substantial thinning of the sulphate horizon) played an important role in sulphur ore formation.

3. As the result of metasomatic alterations, the following general lithological zonation in the lateral distribution (from the lithofacies discontinuity to widespread and uniform sulphate deposits) of the postsulphate and host rocks is observed: lithologic discontinuity (represented by sulphate-free deposits or a substantially thinned sulphate-horizon) as zone A, postsulphate barren limestones (zone B), postsulphate sulphur-bearing limestones (zone C), and sulphate deposits (zone D). The last may be subdivided further into the selective metasomatic subzone followed by the initial metasomatic and the unaffected sulphate deposit subzones.

Translated by Andrzej Gąsiewicz

Zakład Geologii Surowców Mineralnych Państwowego Instytutu Geologicznego Warszawa, ul. Rakowiecka 4 Received: 23.11.1993

REFERENCES

- ALEKSENKO I. I. (1969) Geologiczeskoje strojenie Predkarpatskogo bassejna i genesis mestorożdienij siery. In: Geologia miestorożdienij samorodnoj siery. Izd. Niedra. Moskwa.
- ALEKSENKO I. I. (1974) Genesis miestorożdienij siery Predkarpatskogo bassejna. Bull du VI Congr. de l'Assoc. Geol. Carpatho-Balkan., 3.
- ALEXANDROWICZ S. W. (1965) Geological conditions of sulfur occurrence in the Miocene deposits, vicinities of Rybnik (in Polish with English summary). Prz. Geol., 13, p. 270–272, no. 6.
- BLATT H., MIDDLETON G. V., MURRAY S. P. (1980) Origin of sedimentary rocks. 2nd. ed., Prentice Hall, Inc. Englewood Cliffs. New York.
- BOLEWSKI A., TURNAU-MORAWSKA M. (1963) Petrografia. Wyd. Geol. Warszawa.
- CZERMIŃSKI J. (1960) Microorganic structures of native sulphur in Tortonian (in Polish with English summary). Kwart. Geol., 4, p. 531-537, no. 3.
- DEPOWSKI S. (1990) Deposits of energy raw materials. In: Geology of Poland, 6, p. 54-77.
- GASIEWICZ A. (1994a) Gypsum-host limestones facies of the Polish sulphur deposits: an analog of selenitic gypsum facies? Geol. Quart., 38, p. 415–448, no. 3.
- GASIEWICZ A. (1994b) Gypsum-ghost limestones and selenitic gypsum relation of the Osiek Baranów Sandomierski sulphur deposit. Geol. Quart., 38, p. 449–472, no. 3.
- HATCH L. F. (1972) What make sulphur unique. Hydrocarbon Proc., 7, p. 75-78.
- HEYDARI E., MOORE C. H. (1989) Burial diagenesis and thermochemical sulfate reduction, Smackover formation, southeastern Mississippi salt basin. Geology, 17, p. 1080-1084.
- JAROSIŃSKI M. (1992) The tectonics of the argillaceous rocks of the cover of the sulphur deposit in Machów near Tarnobrzeg in the light of the mesostructural analysis (in Polish with English summary). Geol. Quart., 36, p. 121–150, no. 1.
- KARNKOWSKI P. (1994) The Miocene deposits of the Carpathian Foredeep (according to the results of oil and gas prospecting). Geol. Quart., 38, p. 377–394, no. 3.
- KIRKLAND D. W., EVANS R. (1976) Origin of limestone buttes gypsum plain, Culberson county, Texas. Ass. Petrol. Geol. Bull., 60, p. 2005–2018, no. 1.
- KOMLEVA Z. A. (1963) Gidrogeołogija i gidrochimija Predkarpatskogo sieronosnogo bassiejna. Matier. Symp. Gostgorchimprojekt..
- KRYSIAK Z. (1985) The role of tectonic factors in processes of formation of the Machów sulfur deposit (in Polish with English summary). Prz. Geol., 33, p. 28–33, no. 1.

KRYSIAK Z. (1987) — Tectonic conditions for location and formation of sulphur deposits at Czarkowy and Posądza (in Polish with English summary). Prz. Geol., 35, p. 503–506, no. 10.

KUBICA B. (1965) — Lithological characteristic of the Miocene chemical deposits within the fork of the Vistula and San rivers (in Polish with English summary). Prz. Geol., 13, p. 247–252, no. 6.

KUBICA B. (1972) — On the dehydratation process of gypsums in the Carpathian foredeep (in Polish with English summary). Prz. Geol., 20, p. 184–189, no. 4.

KUBICA B. (1992) — Lithofacial development of the Badenian chemical sediments in the northern part of the Carpathian Foredeep (in Polish with English summary). Pr. Państw. Inst. Geol., 133.

KUBICA B. (1994) — The discovery of the new sulphur deposits between the Vistula and San rivers (the Carpathian Foredeep, southern Poland) — a historical review. Geol. Quart., 38, p. 341–352, no. 3.

KUBICA B., PAWŁOWSKA K. (1984) — Native sulphur deposits and perspectives of their prospecting in Miocene formation of the Carpathian Foredeep (in Polish with English summary). Proc., Symp. Górnictwo Sur. Chem. Kraków, p. 582–596.

KUDRIN L. N. (1969) — Facii i paleogeografija wierchnietortonskogo wremieni Predkarpatskogo sieronosnogo bassiejna. In: Geologia mestorożdienij samorodnoj siery, p. 95–112. Izd. Niedra. Moskva.

KWIATKOWSKI S. (1962) — Quelques observations sur la genése des calcaires sulfuriféres de la région de Grzybów (in Polish with French summary). Rocz. Pol. Tow. Geol., 32, p. 339–358, no. 3.

NEY R., BURZEWSKI W., BACHLEDA T., GÓRECKI W., JAKÓBCZAK K., SŁUPCZYŃSKI K. (1974) — Outline of paleogeography and evolution of lithology and facies of Miocene layers on the Carpatian Foredeep (in Polish with English summary). Pr. Geol. Komis. Nauk Geol. PAN, Kraków, 82.

NIEC M. (1982) — Genetic problems of biochemogenic native sulphur deposits on example of Mishraq deposit, Iraq (in Polish with English summary). Zesz. Nauk. AGH, 858, Geologia, no. 28.

NIEĆ M. (1986) — Sulphur deposits transforming processes (in Polish with English summary). Prz. Geol., 34, p. 366–374, no. 7.

NIEĆ M. (1992) — Native sulfur deposits in Poland. In: Native sulfur developments in geology and exploration (eds. G. R. Wessel, B. H. Wimberly), p. 23–50. Littleton, Colorado.

OSMÓLSKIT. (1963) — Miocene deposits within the fork of the Nida and Vistula rivers and their sulphur contents (in Polish with English summary). Kwart. Geol., 7, p. 337–352, no. 2.

OSMÓLSKIT. (1972) — The influence of the geological structure of the marginal parts of the Działoszyce Trough on the metasomatosis of gypsum (in Polish with English summary). Biul. Inst. Geol., **260**, p. 65–188.

PARAFINIUK J., KOWALSKI W., HAŁAS S. (1994) — Stable isotope geochemistry and the genesis of the Polish native sulphur deposits — a review. Geol. Quart., 38, p. 473–496, no. 3.

PAWLIKOWSKI M. (1982) — Mineralogical and petrographical study of alteration products of the Miocene gypsum rocks in the Wydrza sulphur deposit (in Polish with English summary). Pr. Miner. Komis. Nauk Miner. PAN, Kraków, 72.

PAWŁOWSKA K. (1962) — On gypsum, native sulphur and post-gypsum rocks from the Miocene of the Holy Cross Mts. (Poland) (in Polish with English summary). In: Księga Pamiątkowa ku czci Profesora Jana Samsonowicza, p. 69–82. Wyd. Geol.- PAN. Kom. Geol. Warszawa.

PAWŁOWSKA K. (1965) — Miocene sulphur deposit (in Polish with English summary). Prz. Geol., 13, p. 246–247, no. 6.

PAWŁOWSKA K. (1994) — Miocene and its basement in sulphur-bearing areas of marginal part of the Carpathian Foredeep — summary. Geol. Quart., 38, p. 365–376, no. 3.

PAWŁOWSKI S. (1963) — Tertiary and raw material problems in the Carpathian foredeep (in Polish with English summary). Pr. Inst. Geol., 30, cz. 4, p. 301–320.

PAWŁOWSKI S. (1968) — Geology of sulphur deposits in Poland. 23rd Intern. Geol. Congress, Czechoslovakia, Proc. Sect., 8, p. 249–267. Praha.

PAWŁOWSKI S. (1970) — Geologia złóż siarki w Polsce. Biul. Inst. Geol., 251, p. 614-635.

PAWŁOWSKI S., PAWŁOWSKA K., KUBICA B. (1965) — Sulphur mine at Piaseczno (in Polish with English summary). Prz. Geol., 13, p. 252–257, no. 6.

PAWŁOWSKI S., PAWŁOWSKA K., KUBICA B. (1979) — Geology and genesis of the Polish sulphur deposits. Econ. Geol., 74, p. 475–483, no. 2.

PAWŁOWSKI S., PAWŁOWSKA K., KUBICA B. (1985) — Geology of the Tarnobrzeg native sulphur deposit (in Polish with English summary). Pr. Inst. Geol., 114.

PAWŁOWSKI S., PAWŁOWSKA K., KUBICA B. (1987) — Deposits of native sulphur. In: Geology of Poland, 6, p. 372–412.

PERYTT. M., KASPRZYK A. (1992) — Earthquake-induced resedimentation in the Badenian (Middle Miocene) gypsum of southern Poland. Sedimentology, 39, p. 235–249, no. 2. ROUCHY J. -M. (1976) — Sur la genese de deux principaux types de gypse (finement lite et en chevrons) du Miocene terminal de Sicile et d'Espagne meridionale. Rev. Geogr. Phys. Geol. Dyn., 18, p. 347–364, no. 4.

RYKA W. (1988) — The origin of the Tarnobrzeg native sulphur deposit in the light of petrographical studies. Biul. Państw. Inst. Geol., 359, p. 7–20.

SCHREIBER B. C. (1988) — Subaqueous evaporite deposition. In: Evaporites and hydrocarbons (B. C. Schreiber ed.), p. 182–255. Columbia University Press. New York.

SCHREIBER B. C., FRIEDMAN G. M., DECIMA A., SCHREIBER E. (1976) — Depositional environments of Upper Miocene (Messinian) evaporite deposits of the Sicilian Basin. Sedimentology, 23, p. 729–760, no. 6. SMULIKOWSKI K. (1952) — Geochemia. Pr. Spec. Państw. Inst. Geol., 1.

SOKOLOV A. S. (1959) — Geologiczeskije zakonomiernosti strojenia i rozmieszczenija miestorożdienij samorodnoj siery. Trudy Gos. Inst. Gornochim. Syrja, 5, p. 237–267.

SOKOLOV A. S. (1965) — O genesisie samorodnoj siery. Litologia i poleznyje iskopajemyje, no. 2.

Bolesław KUBICA

PALEOGEOGRAFICZNE UWARUNKOWANIA METASOMATYCZNYCH PRZEMIAN BADEŃSKICH SIARCZANÓW W ZAPADLISKU PRZEDKARPACKIM

Streszczenie

W mioceńskich (badeńskich) osadach siarczanowych w sprzyjających warunkach strukturalnych i hydrochemicznych, pod przykryciem utworami nieprzepuszczalnymi, obserwujemy przeobrażenia typu metasomatycznego. Produktami przemian chemiczno-biogenicznych są wapienie posiarczanowe (pogipsowe) z siarką rodzimą. Procesy metasomatozy gipsów i anhydrytów charakteryzują się zmiennym natężeniem, od stadiów wstępnych, poprzez selektywne, do całkowitego ich przeobrażenia w utwory węglanowe (wapienie, wapienie margliste i margle) z zachowaniem np. pseudomorfoz po kryształach gipsów, struktur po brekcjach gipsowych i anhydrytowych, a zwłaszcza tekstur laminacyjnych, szeroko manifestujących się w odmianach zbitych skał siarczanowych.

Procesy metasomatozy aktywizowane były głównie przy udziale węglowodorów i bakterii w obrębie struktur podniesionych. To szeroko manifestujące się zjawisko w mioceńskich siarczanach obserwujemy w zapadlisku przedkarpackim na różnych głębokościach, zarówno w Polsce (do 1540 m), jak i na terenie Zachodniej Ukrainy.

Analiza obszarów i struktur, w obrębie których miały miejsce przeobrażenia siarczanów, potwierdza tezę, że jednym z istotnych czynników przemian w tych strefach, m.in. w zapadlisku przedkarpackim, były warunki paleogeograficzne, a zwłaszcza obserwowane tu wyspy pozbawione gipsów i anhydrytów. Przeobrażenia siarczanów najczęściej notowane są w sąsiedztwie takich wysp i wąskich, wydłużonych, przyuskokowych stref nieciągłości.

Istnieje wyraźna lateralna strefowość w rozkładzie litofacji węglanowej, siarczanowej i mineralizacji siarkowej. Poczynając od nieciągłości A występuje pas wapieni posiarczanowych płonnych B, a następnie strefa wapieni osiarkowanych C przyparta do siarczanów D wstępnie przeobrażonych z gniazdami lub wpryskami siarki na przejściu ze strefy C. Podobne zjawiska obserwujemy w czapach siarczanowych wysadów solnych w Zatoce Meksykańskiej w USA i Meksyku. W tym przypadku przeobrażenia tych utworów aktywizowały się przeważnie w strefie kontaktu siarczanów z utworami ilasto-piaszczystymi osłony wysadu (rodzaj nieciągłości). We wszystkich przypadkach intensywność przeobrażeń maleje w miarę oddalania się od nieciągłości.