Speleogenesis and Evolution of Karst Aquifers
The Virtual Scientific Journal
ISSN 1814-294X
www.speleogenesis.info

The role of karst in the genesis of sulphur deposits, Pre-Carpathian region, Ukraine

Alexander B. Klimchouk

Institute of Geological Sciences, Ukrainian Academy of Sciences
Email: klim@speleogenesis.info

Re-published from: Environmental Geology 1997, 31 (1/2), 1-20

Abstract

Most of exogenous epigenetic sulphur deposits are clearly associated with intensely karstified carbonate and sulphate rocks. This paper demonstrates, using the Pre-Carpathian region as an example, that karstification is one of the most important processes guiding the formation of sulphur deposits. This is determined by a coincidence of some major prerequisites of these two processes.

In the Podol'sky and Bukovinsky regions the Miocene aquifer system is well drained by erosion valleys; the giant network caves known here in gypsum formed under past artesian conditions. In the region of sulphur deposits, associated with the same karstified gypsum strata, true artesian conditions still prevail. Hydrogeologic data show that abundant cavities detected in the vicinity of sulphur deposits can be interpreted as having the same origin as the relict caves of the Podol'sky and Bukovinsky regions. The widespread belief that the gypsum/anhydrite bed in the region is an aquifuge separating the Miocene aquifers is inadequate. This belief caused much controversy with regard to the genetic interpretations of sulphur deposits in the region. Cave systems formed by the upward water flow through the gypsum/anhydrite bed govern the water exchange between the aquifers within the aquifer system.

A new karst model for the formation of sulphur deposits is suggested. It agrees well with the hydrogeological features of the Miocene sequence and with biogeochemical mechanisms of sulphur origin in low-temperature diagenetic environments.

Keywords: sulphur deposits, bioepigenetic sulphur, sulphate karst, speleogenesis, Pre-Carpatians, Western Ukraine.

Introduction

The Pre-Carpathian sulphur-bearing basin is one of the largest in Eurasia. In this basin all economic sulphur deposits are spatially and genetically related to the Miocene gypsum and anhydrite bed. This is one of the classic regions of exogenous epigenetic sulphur deposits in sulphate/carbonate rocks (Sokolov, 1972; Kityk, 1979). Despite more than 40 years of geologic and hydrogeologic investigations the formation of the sulphur deposits was not clearly understood. Previous models are contradictory in their interpretations of host-rock geology, ore localization, biological and geochemical sulphur-related processes, particularly in relation to the regional settings.

The widespread karst in the Pre-Carpathian region is related to the same gypsum-anhydrite bed as the sulphur deposits. The Podol'sky and Bukovinsky areas contain vast maze caves, including the five longest gypsum caves in the world, which are now decoupled from their formational, truly confined, environment. The gypsum-bearing Miocene sequence is now largely drained through these areas. There are a lot of data on karst at sulphur deposits, in the artesian flow area, but the structure of karst systems and their role in water exchange remained little understood. Because of the studied relict caves and sulphur deposits are in different contemporary geomorphic and hydrogeologic settings, and because karst scientists have little exchange of ideas with local ore geologists and hydrogeologists, the sulphate karst in the whole region has never before been considered in a unified theory.

Many investigators of exogenous epigenetic sulphur deposits, not only in the Pre-Carpathians but throughout the world, have noticed their relation to intense karstification of sulphates and carbonates, and some have mentioned a possible relationship between karst processes and the origin of sulphur. However, the causes for this relationship remained unclear.

This paper considers the role of karst in the formation of sulphur deposits, with special reference to the Pre-Carpathian region. It integrates the karst hydrogeology in the vicinity of sulphur deposits, the structure of karst systems and groundwater flow pattern, mechanisms of karst development, and biogeochemical sulphur processes. To focus on this goal, only the karst older than, and contemporaneous with, the sulphur ore is considered here.

Karst and the genesis of sulphur deposits: the state of the art

Having noted the increase of the thickness of sulphur ore and of the number of sulphur-bearing horizons within highly karstified areas of the Vodinsky deposit in the Volga region, Russia, Borodaev (1936) and Markov (1954) suggested that karst processes not only destroy but also form ore bodies (as cited by Otreshko, 1966b). Peresun'ko (1960) noted the spatial coincidence of ore bodies and karst in sulphur deposits in Central Asia and the Pre-Carpathians. In his opinion (p.135) karst phenomena are inextricably related to the sulphur-forming processes. In other work he noted that interpretation of karst in sulphur deposits was limited by a poor understanding of their hydrogeological settings, but that a study of the genesis, character and intensity of karst around sulphur deposits is of a great practical value (Peresun'ko, 1961). Babinets and Tsapenko (1960) indicated that the belt of deposits of mineral water bearing H_2S in the Pre-Carpathians is associated with karst processes in Miocene gypsum rocks, but they did not discuss the nature of this relationship.

The association between the sulphur formation and karst in sulphate/carbonate strata of the Volga-Kama region had been noticed by Stankevich (1968). Tkachouk and Koltun (1963) stated that a detailed investigation of subsurface karst in the gypsum/anhydrite of the Pre-Carpathians was needed for prospecting and exploitation of the sulphur. Pertzovich (1969) stressed that the determination of the age of karst in gypsum/anhydrite and carbonate rocks in the Pre-Carpathians was important to solving the problem of the genesis of native sulphur. Polkunov et al. (1979) studied the details of karst in the vicinity of sulphur deposits of the Pre-Carpathians (see below), and pointed out that karst features are important aspects of ore fields and deposits.

The pronounced role of karst in the formation and localization of bioepigenetic calcite and sulphur mineralization has been shown for deposits in the Delaware basin of west Texas (Wallace and Crawford, 1992; Miller, 1992). These minerals are formed within the thick late Permian evaporites of the Castile and Salado Formations and are associated with large caves filled with late Cretaceous conglomerates and karst breccias. Paleosystems of cave channels provided permeability within the gypsum/anhydrite and served as migration paths for hydrocarbon-bearing water into the zone of sulphate reduction from the underlying aquifer, the Bell Canyon Formation.

A clear statement of the role of karst in the formation of sulphur deposits was given by Otreshko (1966b): "*Karst, most likely, must be included among the major factors determining the genesis, transformation, and destruction of deposits*". In another work he suggested that the presence of karst is one of the basic guidelines for prospecting for sulphur deposits (Otreshko, 1966a).

Otreshko (1966a, 1966b, 1974) discussed a paleogeographic regularity which had been outlined for the first time by Teodorovich (1943) and Sokolov (1956): *sulphur deposits are associated with areas where the clay caprock overlaying sulphate/carbonate sequences is considerably scoured by erosional action*. Numerous examples of sulphur deposits in the Pre-Carpathians, Volga region and Central Asia, show that ores are localized beneath, or adjacent to, late Neogenic buried valleys. In the Pre-Carpathians in particular, there is a distinct inverse relationship between the thickness of sulphur-bearing and barren limestones overlying the gypsum and the thickness of the overlying clay caprock (Otreshko, 1974). The reasons why epigenetic limestones and native sulphur are associated with erosionally scoured structures remained unclear. Otreshko (1966a) also suggested that the association between karst and sulphur ores is determined by that ores occur beneath erosionally scoured areas exposed to descending percolation and, hence, they are more susceptible to destruction by karst processes. In this case the post-ore karst is meant that apparently contrasts with the above cited statement by Otreshko on the ore-forming role of karst.

Pisarchik and Rusetskaja (1972) considered the sulphur deposits of the Pre-Carpathians to have formed during the hypergene transformation of sulphate rocks. They concluded that the history of drainage and karst development, as well as the neotectonics that controls them, are of great significance to hypergenic processes, and particularly to the origin of sulphur.

Osmolski (1976) examined the role of karst in the gypsum/anhydrite stratum in the formation of sulphur deposits in Poland. The drawn an important conclusion that karstification of gypsum/anhydrite had facilitated water circulation, leading to the formation of an aquifer and, in the process, opening migration paths for hydrocarbons. He believed that the processes, leading to replacement of sulphates by calcite and sulphur could have been limited to the gypsum strata exposed to two phases of karstification in pre-Sarmatian time. He invoked the traditional concept of karst development by descending water, an idea that is not supported by data from the Ukrainian Pre-Carpathians.

One of the major phases in the formation of sulphur deposits is considered by Gajdin (1983) to be the development of sulphate karst which result in the opening of migration paths for hydrocarbons from the sub-gypsum aquifer into the sulphates. He also pointed out that sulphur ores form zonally, extending from the underlying aquiferous rocks and karst cavities in the sulphates.

Most studies of karst in the vicinity of sulphur deposits have been merely descriptive and have not clarified the genesis of karst, its hydrogeological and ore-forming role. Only in the above-cited works of Gajdin, Osmolsky, Wallace and Crawford and Miller, has the role of karst been outlined in the context of development of water-exchanging paths and bringing sulphates in contact with hydrocarbons.

A general interpretation of the conjunction of karst development and native sulphur formation can be derived from the fact that both processes share many basic prerequisites. Formation of bioepigenetic sulphur requires the presence of: (1) sulphate rocks, (2) hydrocarbons, (3) oxidizing agents, and (4) conditions favourable to the interaction of reactants, namely: (4a) transporting solutions, (4b) permeability of the host rocks, and (4c) hydrodynamic conditions necessary to cause the movement of solutions. The above conditions are sufficient only if certain favourable physical and chemical environments are brought in interaction over sufficient time. It is important to note that conditions 1, 4a, 4b and 4c are the basic requirements for karst development as outlined by Sokolov (1962). *Thus, as a rule, karstification must occur for sulphur deposits to form*. Moreover, formation of an extensive sulphur deposit requires large-scale sulphate reduction, which can be maintained only in the presence of sufficient dissolution surface of sulphate. Secondary permeability and subsurface dissolution surfaces are created by speleogenesis.

Geological settings of the Pre-Carpathian sulphur-bearing basin

The Pre-Carpathian sulphur-bearing basin lies within Miocene gypsum/anhydrite, and all economic sulphur deposits are related to these rock both spatially and genetically. The sulphur is located in the transitional zone between the Eastern-European and Western-European platforms and the Carpathian foredeep (Fig. 1; Kityk, 1979). Upper Badenian sulphate rocks stretch sub-parallel to the Carpathian folded region through southern Poland, western Ukraine, and north of Romania. Further discussion in this paper is limited to the Ukrainian part of the basin (Fig. 2). Economically viable sulphur deposits adjoin the foredeep edge of the platform. The gypsum/anhydrite "belt" is narrowest in the northwest section and extends southeast for more than 300 km through Ukraine. In it's southeast part, this belt widens up to 100 km encompassing some interiors areas of the platform (Podol'sky area).

Miocene sedimentary rocks within the platform fringe overlie the eroded strata of Cretaceous or, less commonly, earlier age. The Cretaceous succession is represented by terrigenous and carbonate sediments, mostly by marls, sandstones, detrital, and argillaceous limestones. The Miocene succession consists of Badenian and Sarmatian deposits. The Lower Badenian, beneath the gypsum, includes mainly carbonaceous, argillaceous, and sandy deposits near the foredeep (70-90 m thick), that grade into calcareous bioherm and sandy facies toward the interior of the platform (10-30 m thick). In the vicinity of most sulphur deposits, the Lower Badenian is composed mainly of lithothamnion limestones.

The gypsum/anhydrite stratum (GAS) and overlying pelitic and crystalline limestones comprise the Tyrassky Formation of Upper Badenian age. The sulphate stratum, 35-50 m thick, consist of gypsum in the interior of the platform (Podol'sky area); but toward the foredeep the anhydrite content increases. The present extent of sulphates on the platform is as much as 20,000 km2. The GAS is rather variable in structure and texture. In the Podol'sky area, it consists of three-units, which, in ascending order, include crypto- and microcrystalline massive gypsum, bedded microcrystalline and megacrystalline gypsum. In the upper unit, the gypsum displays large spherules (Klimchouk et al., 1995). Toward the foredeep, the GAS becomes more homogeneous and aphanitic. Interbeds of carbonate and clay are rare and thin.

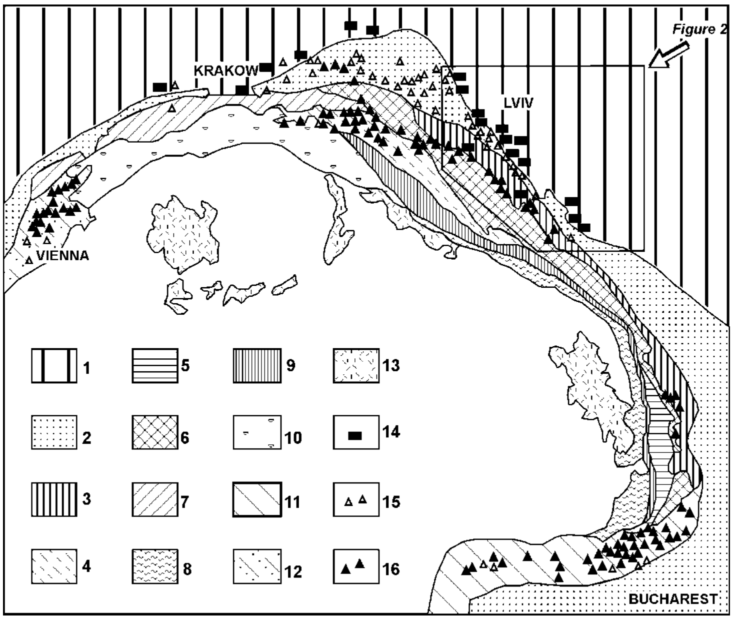

Fig. 1. Distribution of sulphur, gas and oil deposits in relation to major tectonic structures of the Pre-Carpathians and Carpathians (from Kityk, 1979). 1 = platforms. *Carpathian foredeep*: 2 = outer zone, 3 = inner zone. *Carpathian folded region*: 4-10 = tectonic zones, 11 = periclinal depression of eastern Carpathians, 12 = Vienna Trough; 13 = effusive formations, 14 = sulphur ore deposits, 16 = gas reservoirs, 17 = oil reservoirs.

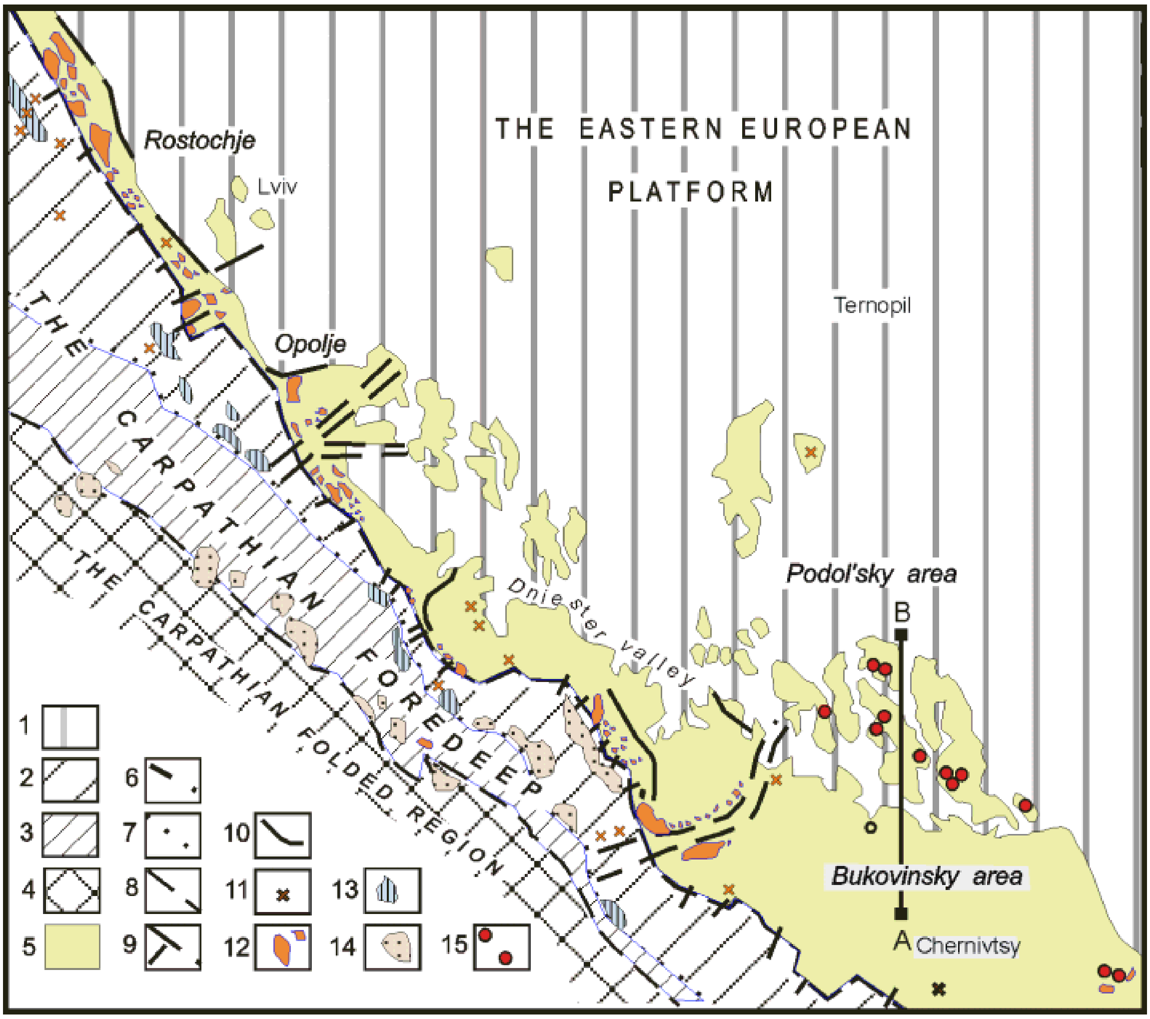

Fig. 2. Location of gypsum stratum, sulphur and hydrocarbon deposits, and large caves of the western Ukraine (modified from Polkunov et.al., 1990). 1 = Eastern-European platform fringe. *Carpathian foredeep*: 2 = outer zone, 3 = inner zone. 4 = Carpathian folded region. 5 = sulphate rocks in the platform. *Tectonic boundaries*: 6 = platform/foredeep, 7 = outer/inner zone of the foredeep, 8 = foredeep/folded region. 9 = other major faults. 10 = flexures. 11 = zones of sulphur mineralization. 12 = sulphur ore deposits. 13 = gas reservoirs. 14 = oil reservoirs. 15 = large maze caves in the gypsum.

The layer of pelitic and crypto-crystalline limestones, ranging from several dozens cm to more than 25 m in thickness, normally overlies the GAS. Its origin, which is closely related with that of sulphur, is still controversial (Grinenko et al., 1966; Mamchur, 1972; Sakseev, 1972; Lein et al., 1977). The upper limestones contain two genetic varieties. The pelitic limestones (locally called "Ratynsky") are evaporitic in origin. They are 0.2-10 m thick and occur over almost the entire GAS area. In places they contain minor veins or pockets of sulphur within fissures and caverns. The other variety of limestone, which is crypto- and microcrystalline, formed epigenetically by metasomatic or hydrogenic replacement of the GAS during sulphate reduction. This limestone varies in thickness up to 25 m and is prevalent in the areas of sulphur deposits. In places it has completely replaced the GAS and is either sulphur-bearing or barren. There is a prominent inverse relationship between the thickness of the crystalline limestones and overlying clay cover (Fig. 3; Otreshko, 1974): the epigenetic limestone is thickest where the clay cover has been partially eroded. In places, epigenetic limestones are found also beneath the GAS (Sakseev, 1966; Composition, 1979).

The Ratynsky and epigenetic limestones differ greatly in carbon isotope composition. Values of σC13 vary in the Ratynsky limestone from -8 to -3 ‰, whereas the epigenetic limestone gives values ranging from -32 to -65 ‰ (Fig. 4; Mamchur, 1972; Lein et al., 1977). The isotopically light carbon comes from CO_2 generated by oxidation of methane during sulphate reduction, which then contributes to epigenetic calcite deposition. The sedimentary Ratynsky limestones were recrystallised in places and enriched with epigenetic calcite. In these situations they range in σC13 from -11 to -57 ‰. Considering that it is difficult to distinguish between the two varieties of limestone in the field, they will be collectively referred to as "supra-gypsum limestones" where their genesis is unknown or not relevant. The contact of these limestones with the underlying GAS varies from gradual to sharp, depending on the genesis of the limestone and the extent of hypergene alterations.

The Tyrassky Formation is overlain by argillaceous strata of the Kosovsky Formation, which is also of late Badenian age. Near the foredeep boundary these strata are mainly clays, with sandstone and carbonates in the lower part. In the interior of the platform, red algal argillaceous limestones with minor beds of sandstones prevail. The Upper Badenian strata grade upward into the Sarmatian marls and clays, whose thickness increases to 30-50 m toward the foredeep. Adjacent to the foredeep, Sarmatian strata are lithologically similar to the Kosovsky Formation. Together they constitute a clay overburden over sulphur deposits with a total thickness up to 80-100 m.

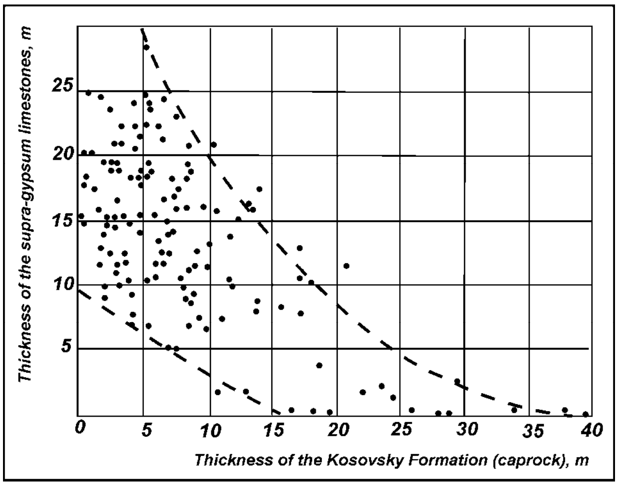

Fig 3. Relationship between the thickness of the supra-gypsum limestones and the Kosovsky Formation (caprock) at the Rozdol'sky sulphur deposit (from Otreshko, 1974).

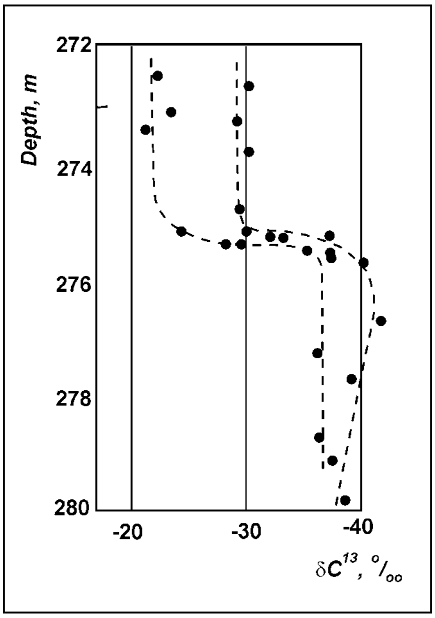

Fig. 4. Variation in isotopic composition of carbon from the Ratynsky pelitic limestone (at top) to the crystalline epigenetic limestone (at bottom) within the supra-gypsum aquifer of the Tyrassky Formation in the Pre-Carpathian (from Mamchur, 1972).

The Miocene formations are overlain by late Pliocene and Quaternary glacio-fluvial sands and loams (the north-west section of the gypsum/ anhydrite belt was exposed to the Mindel glaciation; Gerenchuk et al., 1972), and by high alluvial terraces of sand and gravel deposited in the Podol'sky area by Dniester River during the late Pliocene and early Pleistocene. There are many buried valleys entrenched 30-50 m into the Kosovsky and Sarmatian clays and, in places, into the upper part of the Tyrassky Formation (Figs 5-7). Some of these valleys are considered to be of Mindel-Riss age, others to be Middle Pleistocene (Kutepov and Tsjurupa, 1969; Kutepov and Kozhevnikova, 1989; Sokolov et al., 1969).

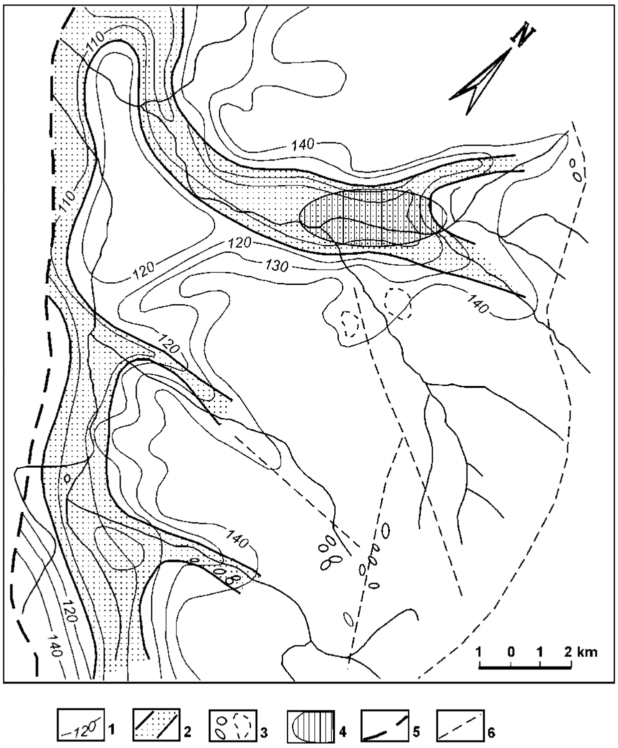

Fig. 5. Location of buried valleys at the Jazovsky sulphur deposit (modified from Kutepov and Kozhevnikova, 1989). 1 = elevation contours at top of Miocene strata; 2 = buried valleys; 3 = surface karst features; 4 = zone of high hydraulic conductivity in the Miocene aquifers, from due tracing tests; 5 = regional fault zone; 6 = other faults.

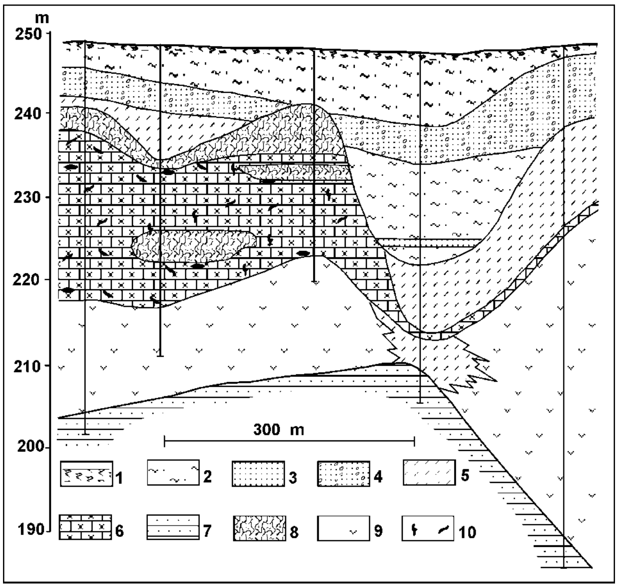

Fig. 6. Cross section of a buried valley at the Rozdol'sky sulphur deposit (from Sokolov et al., 1969). *Quaternary sediments*: 1 = soil; 2 = loam; 3 = sand; 4 = sand and gravel. *Miocene sediments*: 5 = clay; 6 = limestone; 7 = sandstone; 8 = brecciated limestone; 9 = gypsum and anhydrite. 10 = fissures.

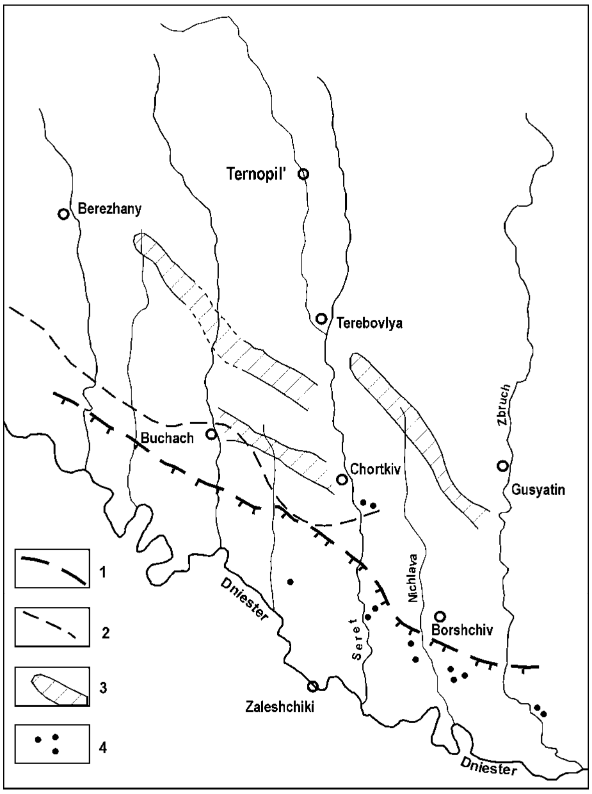

Fig. 7. Location of the ancient terraces of the Dniester River and other relict valleys and large caves in the Podol'sky area. Northern boundary of alluvium of the 7th terrace: 1 = according to Svynko (1979); 2 = according to Gofshtain (1962); 3 = relict valleys (Svynko, 1979); 4 = large caves in gypsum.

The present distribution of Miocene formations and levels of their denudation vary regularly from the interior of the platform toward the foredeep (Andrejchouk, 1988; Klimchouk, Andrejchouk, 1988). The Tyrassky Formation dips 1-3^{o} toward the foredeep and in the transitional zone is disrupted by block faults. Concurrently, the thickness of the Kosovsky and Sarmatian clay overburden increases, and the depth of erosional entrenchment decreases (Figs 8 and 9). These differences, the result of differential neotectonic movement, played the most important role in the hydrogeologic evolution of the Miocene aquifer system, as they determined the recharge-discharge and flow conditions, particularly the development of karst in the GAS and the formation of sulphur deposits.

Hydrogeology of the Miocene sequence

The Pre-Carpathian sulphur-bearing basin occupies the southwestern part of the Volyno-Podol'sky artesian basin (Babinets, 1961; Kityk, 1989; Shestopalov, 1981), and the second order Podol'sky and Bukovinsky drainage basins. The GAS spreads on an artesian monocline slope in which the regional flow is toward the southwest and south, from the interior of the platform toward the large Dniester valley and the Carpathian foredeep. On the south-west, along the fault boundary with the Carpathian foredeep, the Miocene and Cretaceous aquifers are brought into lateral contact with thick low-permeable clays of the Kosovsky formation. This causes an upward discharge of the aquifer system through the capping clays. The same situation takes place also along every major block fault of the platform fringe.

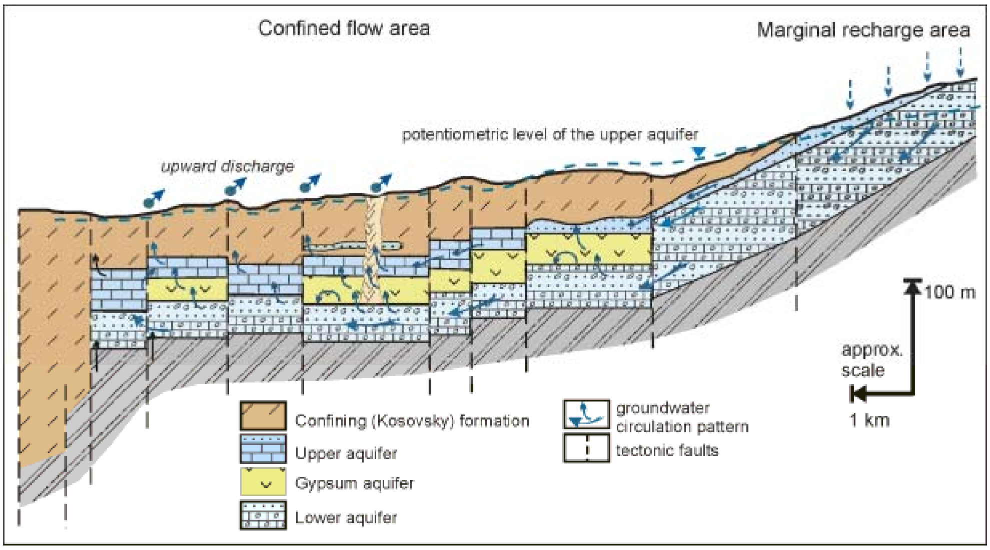

Fig. 8. Hydrogeologic profile across the gypsum/anhydrite belt near the Jazovsky sulphur deposit (line I-I' on Fig. 2) depicting natural (pre-quarrying) conditions. Geology based on the profile from Aleksenko (1967).

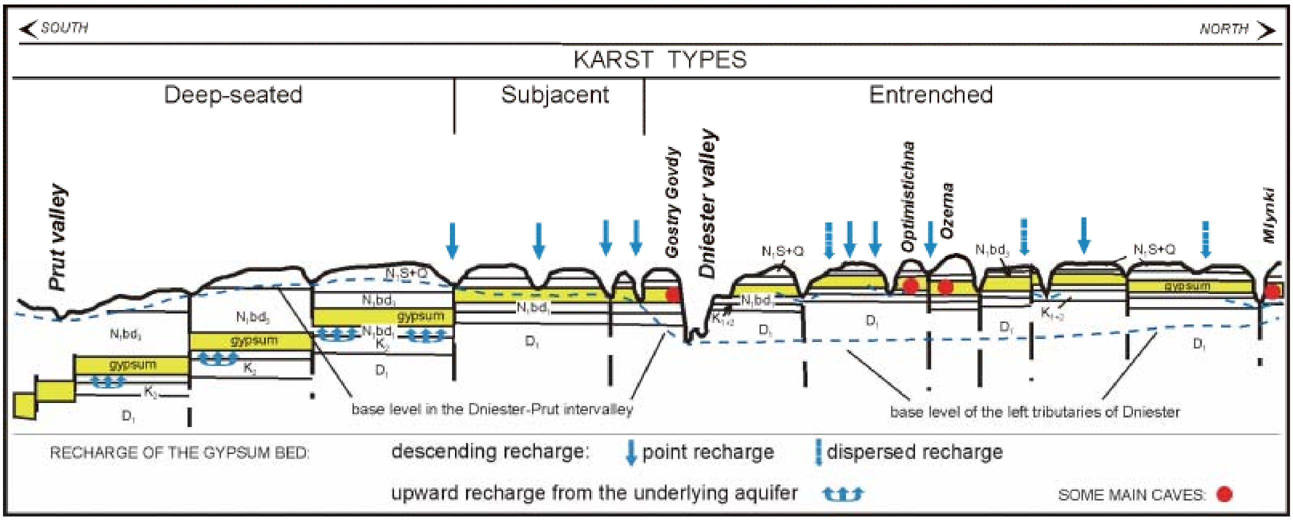

Fig. 9. Geologic/hydrogeologic settings of gypsum karst development in the Podol'sky and Bukovinsky areas in the southeastern section of the gypsum belt (line II-II' on the Fig. 2).

Present groundwater flow in the Miocene sequence is controlled by the geologic and geomorphic position of the individual strata. As noted above, these conditions alter regularly in the direction from interior of the platform toward the foredeep (Figs 8 and 9). North-northeast of the gypsum belt the sub-gypsum aquifer is exposed to the surface or lies beneath permeable Quaternary sediments. This is the main area of infiltration recharge (Rostochje, Lvov Plateau, Opolje, the northern part of the Podol'sky area). To the south-southwest (particularly in the Podol'sky area) the gypsum and capping clays remain not eroded, subdivided into isolated uplands by deeply entrenched left tributary valleys of the Dniester. The water table lies within the sub-gypsum formation, or, in places, within the lower part of the gypsum. The aquifer receives point recharge through karst sinkholes, and discharges in valleys via springs.

Further to the south-south-west, along the foredeep boundary, the gypsum stratum is almost intact. The aquifer system in the Miocene sequence is confined by the thick clays. Groundwater discharges upward along buried valleys and faults that breach the clay. The major regional fault that brings Miocene aquifers into lateral contact with the thick clay prevents further flow toward the Carpathian foredeep.

Paleohydrogeologic evolution and the formation of the above variations in the hydrogeologic conditions have been caused by differential neotectonic movements during late Neogene - Pleistocene, resulted in plunge of the platform fringe and compensating accumulation of the clay series, uplift of the interior part of the platform with accompanying denudation of clays and the gypsum, deep entrenchment of the Dniester valley and it's left tributaries. Present hydrogeologic settings of the Miocene sequence also differ considerably between the northwest (narrow) and southeast (wide) sections of the gypsum belt.

The northwest section of the GAS belt

In this region, the monoclinal slope is most clearly developed (Fig. 8), although it is complicated by block faulting. Most of the sulphur deposits are located there.

Within the uplands of Rostochje and Opolje, beyond the GAS limit, Lower Badenian strata lie just beneath the Quaternary cover on Cretaceous rocks of low permeability. In places, the Ratynsky limestones are also present. This is the main area of infiltration into the regional aquifer. In this area the aquifer is unconfined and contains HCO_3-Ca waters with TDS as much as 0.5 g/L. Beneath the Upper Miocene clays, the heads are high enough that some water flow upward into sandstone beds of the lower Kosovsky Formation. The Kosovsky and Sarmatian formations consist mainly of clays that constitute the cover of low permeability separating the Miocene and Quaternary aquifers. The hydraulic conductivity of clays does not exceed 10^{-6} cm/s, although it increases to as much as 10^{-3} cm/s in minor sandstone and siltstone beds in the lower part of the sequence. The permeability of the Kosovsky formation is greatest along faults, and buried valleys.

In the confined flow area, the GAS is absent only in places. Local upward discharge is concentrated along the Dniester valley (which is rather shallow in this section), as well as along buried valleys, where the thickness of the clay overburden diminishes. Along the foredeep, where regional faulting has brought the Miocene sequence into lateral contact with the thick Kosovsky clays, further flow in this direction is prevented.

In the confined flow area two aquifers are commonly distinguished in the Miocene sequence: (1) the "sub-gypsum" aquifer in the Lower Badenian lithothamnion limestones, sands and sandstones, and (2) the "supra-gypsum" aquifer in the Ratynsky and epigenetic limestones and lower part of the Kosovsky Formation.

The sub-gypsum aquifer is the major aquifer in the system. In the few areas where the gypsum is absent, the aquifer lies directly beneath the Upper Badenian strata. The aquifer contains rather homogeneous granular and fracture porosity and has hydraulic conductivity of 1.0×10^{-4} to 1.6×10^{-3} cm/s, but in the lithothamnion limestones there are karstified zones with hydraulic conductivity as high as 6×10^{-3} to 7×10^{-1} cm/s (Fedorova, 1985). Waters in the aquifer have calcium bicarbonate composition with TDS as high as 1.0 g/L. In places there are calcium sulphate waters with TDS up to 1.1 - 2.9 g/L and $SO_4^{=}$ content up to 0.8 - 1.7 g/L. Some waters contain H_2S at concentrations as high as 20-30 mg/L (Fedorova, 1985) with rare values up to 115 mg/L (Tsjurupa, 1960). In local areas Cl-Na methane-bearing waters flow upward along faults from the underlying Cretaceous rocks and adjacent foredeep with TDS up to 7.5 g/L (Babinets and Tsapenko, 1960). These waters are concentrated in a narrow zone adjacent to the foredeep boundary where the gypsum is absent and the sub-gypsum and supra-gypsum aquifers constitute a single hydrologic unit (Fedorova, 1985). The methane content in released gases reaches 92%; hydrocarbon gas shows have been observed at many sulphur deposits (Aleksenko, 1967; Srebrodol'sky and Kachkovsky, 1973). Methane is believed to be the main source of organic carbon for sulphate reduction in the Miocene sequence.

The supra-gypsum aquifer is 1 to 25 m thick with a highly varied but generally high porosity consisting of fractures, solution voids and conduits. Hydraulic conductivity normally ranges from 0.02 to 0.1 cm/s, with a maximum of 0.5 in karstified zones (Polkunov et al., 1979), which are mostly developed in the lower part of the aquifer, near the contact with the underlying gypsum. It is important to note that areas of the high hydraulic conductivity of the sub-gypsum lithothamnion limestones coincide with those in the supra-gypsum limestones (Babinets and Tsapenko, 1960). Waters are rich in calcium sulphate, or locally a calcium-sodium sulphate, with TDS of 1.0 - 3.6 g/L and $SO_4^{=}$ content of 1.5 - 2.0 g/L. High H_2S (34 - 200 mg/L; up to 370 mg/L in places) and CO_2 (120 to 167 mg/L) indicate sulphate reduction processes intensely operating within the aquifer (Babinets and Tsapenko, 1960; Tsjurupa, 1960).

It is a widely believed that the GAS is an aquifuge that separates the sub-gypsum and supra-gypsum aquifers (Peresun'ko, 1960; Tsjurupa, 1960; Goleva, 1962; Aleksenko, 1967; Koltun et al., 1972; Polkunov et al., 1979; Fedorova, 1985,1986; Kushnir, 1988; Kutepov and Kozhevnikova, 1989 and others). Most of these works recognise that hydraulic connection between the two aquifers takes place only in "windows" where the GAS is absent. Only a few authors (Babinets and Tsapenko, 1960; But, 1962; Gajdin, 1983, Fedorova, 1985) referred to the GAS as a water-bearing stratum. Babinets and Tsapenko (1960) emphasise that the Miocene sequence consist of a single aquifer, but But and Fedorova describe zones of enhanced hydraulic conductivity ($7.3x10^{-2}$ cm/s) in the gypsum/anhydrite that connect the aquifers above and below. According to Kutepov and Kozhevnikova (1989), the GAS can contain water in tectonically disrupted zones, where hydraulic conductivity can reach $3.8x10^{-2}$ cm/s. Only Gajdin (1983) clearly stated that the GAS is an aquifer in the vicinity of Pre-Carpathian sulphur deposits.

The thorough analysis of available field data allows to argue that it is a misconception to threat the GAS as an aquifuge and a separating bed. This has led to misinterpretation of the water circulation pattern in the Miocene sequence, considerable inaccuracy of predictions of water inflow to open-cut mines (Rozdol'sky and Jazovsky deposits), realisation of ineffective projects to prevent water inflow to quarries, but also to misinterpretation of the genesis of deposits. The latter will be discussed in the following chapters. The GAS prevents hydraulic connection between the two aquifers only in limited areas of some poorly fractured non-karstified blocks. In karstified areas, often rather extensive, the GAS is highly permeable and allows both vertical and lateral groundwater circulation.

Most authors considered the GAS to be an aquifuge *a priori*. Evidence, if given at all, included references to monolithic cores from boreholes, contrasting water chemistry between the aquifers, and discontinuities in potentiometric levels. However, monolithic cores are commonly obtained in strata with high conduit permeability. Different chemical composition of water above and below the gypsum simply reflects differences in lithologies, recharge pattern, and flow conditions. Finally, field data show insignificant head differences between the sub-gypsum and supra-gypsum aquifers. For example, at the Jazovsky deposit, under modern disturbed conditions, this difference is only 0.2-0.5 m; it is locally 1.5-2.0 m, but these data are from boreholes located several hundreds meters apart. Numerical modelling of area of the Jazovsky deposit has shown that a head difference of 10 m between the aquifers would require a zero hydraulic conductivity for the dividing GAS bed over an area of 35-40 km^2 (A. Ishchouk, personal communication), which is not feasible. Additionally, data obtained from the Jazovsky deposit during the pre-quarrying stage showed that considerable variations of a head (up to 10-20 m) in the supra-gypsum aquifer simply reflected the highly heterogeneous nature of karst permeability in the aquifer system (Fedorova, 1985).

The present author, along with A.Aksem, has conducted groundwater tracing in the Miocene sequence at the Jazovsky deposit for many years (30 injections, with tracers interception via boreholes). These experiments have shown well-developed fissure and conduit permeability in the GAS and a close hydraulic connection between karst waters in the GAS and those in the underlying aquifer. Tracers injected into the lower aquifer were frequently detected in the GAS, and vice versa. Regrettably, no active wells in the supra-gypsum aquifer were available during our tests. However, Fedorova (1985) reported that heads in two wells at the Jazovsky deposit, one completed in the GAS and the other in the sub-gypsum aquifer, immediately reacted to pumping of a third well completed in the supra-gypsum aquifer.

A close connection between waters of the sub- and supra-gypsum aquifers is also shown by the water flow and chemistry measured during open-pit mining of the sulphur deposits. For example, it had been assumed for most deposits that major inflow to quarries would be a function of only the specific storage in the supra-gypsum aquifer (Tsjurupa, 1960). But during exploitation of the Rozdol'sky and Jazovsky deposits, considerable and gradually increasing inflow occurred from the sub-gypsum aquifer and necessitated considerably greater pumping of water than predicted, which made it difficult to achieve the projected level of lowering. During the first years of water withdrawal, the sulphate content of the water in the supra-gypsum aquifer decreased, while the bicarbonate content increased. TDS decreased to 1.6 g/L, and H_2S content rose to 2-70 mg/L (Peresun'ko, 1960). This demonstrates considerable increase of inflow from the sub-gypsum aquifer. Later on these changes have become even more pronounced because of induced recharge from the Quaternary aquifer, piracy of surface runoff, and activation of karst collapse (Gajdin et.al., 1991; Andrejchouk and Klimchouk, 1993).

Many researchers explain the local variations of water chemistry in the supra-gypsum aquifer as the result of inflow from the sub-gypsum aquifer through "windows" in the GAS. Kushnir (1988) analyzed the water chemistry of wells in the vicinity of the Jazovsky sulphur deposit, comparing those where the GAS is present with those where it is absent. Where the "gypsum-anhydrite aquifuge" (Kushnir's term) is present, mean Ca^{++}, Cl^{-}, $SO_4^{=}$, pH, and TDS are lower than those in "windows" areas, and the minimum values are considerably lower. Paradoxically, he considers this to be the result of greater inflow of fresh water from the sub-gypsum aquifer along faults that conduct water through the sulphates. In fact, such inflow occurs through cave systems in the GAS, as shown in the following section.

All these interpretive problems about the GAS are remarkable examples of misconceptions resulted from overlooking of karst systems and poor understanding of their hydrogeological function, by geologists and hydrogeologists.

The southeastern section of the GAS belt

In this region the belt widens up to 80-100 km and extends far into the platform interior along the northern side of the Dniester valley (Fig. 9). A monoclinal artesian setting and slow water circulation within the Miocene strata have prevailed there since the early Pleistocene. Artesian flow to the southwest of the recharge area has been negligible due to the continuous spread of the Upper Miocene clay cover, which limits the discharge of water. Entrenchment of the proto-Dniester valley and its left tributaries during late Pliocene - early Pleistocene allowed upward discharge into the valley bottoms, which activated artesian flow. Later deepening of the valleys breached the artesian confinement and allowed drainage of the Miocene stata (entrenched karst zone on Fig. 9). In the Podol'sky area the water table presently lies within the sub-gypsum strata in interfluve massifs. This aquifer receives point recharge through karst systems where the gypsum and clay coverbeds are present, and diffuse recharge where the clay has been removed (Klimchouk et al., 1985). Draining of the gypsum made accessible vast relict maze caves within it (Klimchouk, Andrejchouk, 1988; Klimchouk, 1992). The setting is similar also immediately south of the Dniester valley.

In the Dniester-Prut interfluve area (Bukovinsky area) the GAS plunge conspicuously toward the foredeep along fault blocks. The Upper Miocene clays thicken in that direction, and the depth of erosional entrenchment diminishes. As a result, the water table is located within the GAS in the 3-15 km-wide belt that extends sub-parallel to the Dniester and Pre-Carpathian foredeep (subjacent karst zone, Fig. 9). Point recharge is favoured in this zone because of intense solution of the gypsum stratum and the presence of the clay cap. Groundwater flows north to the Dniester valley and south-southwest to the Prut valley. Flow becomes confined in the latter direction, near the foredeep, where the Tyrassky Formation lies at even greater depth (deep-seated karst zone, Fig. 9). Water from the confined aquifer discharges upward to the Prut valley. In some of the most uplifted blocks this valley has intersected the top of the Tyrassky Formation and has breached the artesian confinement. In the Kryvsky block this breaching took place during the final stage of the natural flow regime, when the water table established near the top of the GAS in the vicinity of the valley. Dewatering of the gypsum quarry since 1950s has lowered the water table, exposing the extensive Zolushka Cave, in which 92 km of passages have been mapped (Fig 10-E; Andrejchouk, 1988). This cave is representative of solution cavities within the present-day areas of confined flow.

Karst in the Tyrassky Formation

Karst in the sulphate/carbonate rocks of the Tyrassky Formation around sulphur deposits (in the artesian flow area) has been noticed by many investigators, although mainly in the Ratynsky (supra-gypsum) limestones. This is because close attention has been paid to this productive horizon and because its better availability for study in quarries, outcrops, and borehole cores. It is more difficult to study karst in the sulphates in the modern deep-seated (confined) karst zone. On the other hand, the well studied gypsum karst of the Podol'sky and Bukovinsky areas had long been considered the result of descending water circulation in unconfined hydrogeologic conditions similar to those of today; the concept which was clearly impossible to apply to the karst in the zone of artesian flow in the vicinity of the sulphur deposits.

Podol'sky and Bukovinsky areas

These areas contain the five longest gypsum caves in the world (Optimistichna - 214 km, Ozernaya - 117 km, Zolushka - 92 km, Mlynki - 28 km, Kristal'naya - 24 km), as well as many smaller caves. They display rather uniform maze-like patterns (reticulate or polygonal network of passages) with a passage density up to 320 km km^2 (see examples in Fig. 10). They are 2-4 storied systems that occupy areas of up to 2 km^2 each. It was believed until recently that these caves were formed by water from sinking streams flowing laterally through the gypsum to nearby valleys, or by flow between entrenched valleys (Dubljansky and Smol'nikov, 1969; Dubljansky and Lomaev, 1980). This idea implied unconfined hydrogeological conditions and did not shed light on the origin of cavities encountered in drill holes in the artesian parts of the GAS, such as at the sulphur deposits.

Recently a hypothesis of cave origin in artesian conditions has been developed, with special reference to the gypsum caves of the Podol'sky and Bukovinsky areas (Klimchouk, 1990; 1992; 1994). It was suggested that maze caves in the gypsum originated in a shallow, multi-storey artesian system as the result of upward water flow between aquifers, especially where discharge through the confining caprock was most concentrated, such as beneath large valleys. Solution by dispersed recharge from the underlying aquifer formed network mazes in the gypsum because enlargement of available fissures was rather uniform. Cave development was most active at areas of potentiometric low, where the confining caprock was thin due to erosional entrenchment, or (and) its permeability was enhanced by the presence of fault zones (Fig. 11). The multi-storey structure of caves was determined by a multi-storey occurrence of fissure networks, which occupy certain lithologic and structural intervals of the gypsum bed (Klimchouk et al., 1995). The pattern of fissures in networks does not coincide between adjacent horizons, allowing rather independent development of maze storeys at various levels.

It is interesting to note that before speleogenesis evolved, the gypsum actually served as an aquifuge separating strata of higher permeability. As conduits enlarged, the gypsum gradually became a karst aquifer with inhomogeneous hydraulic conductivity that is very high in areas where maze caves developed.

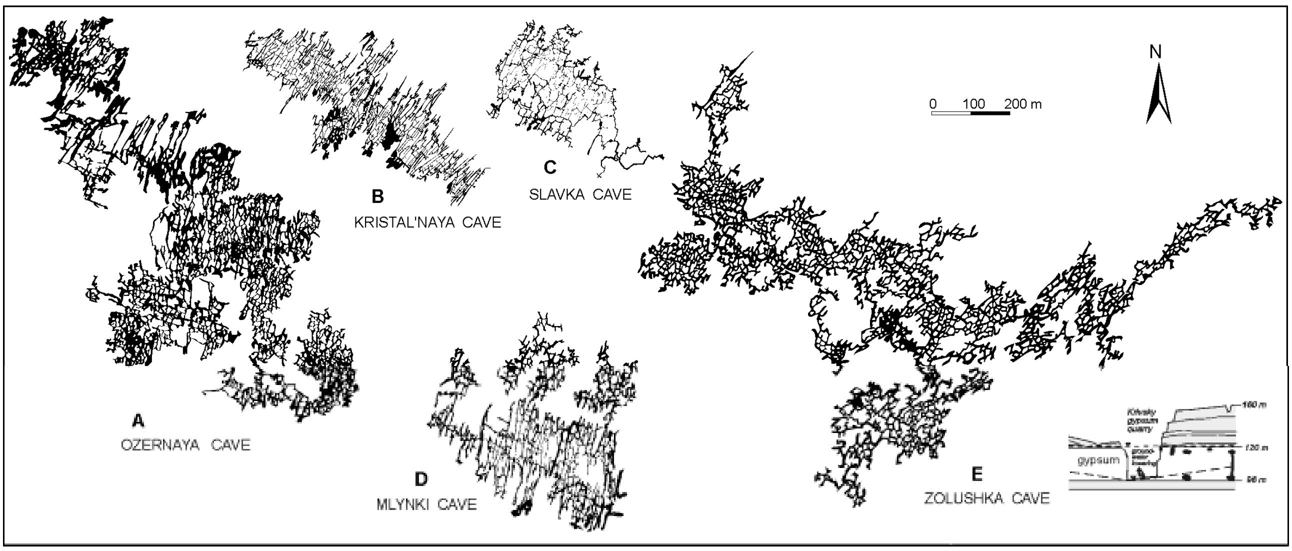

Fig. 10. Maps of some of the major gypsum maze caves in the Western Ukraine.

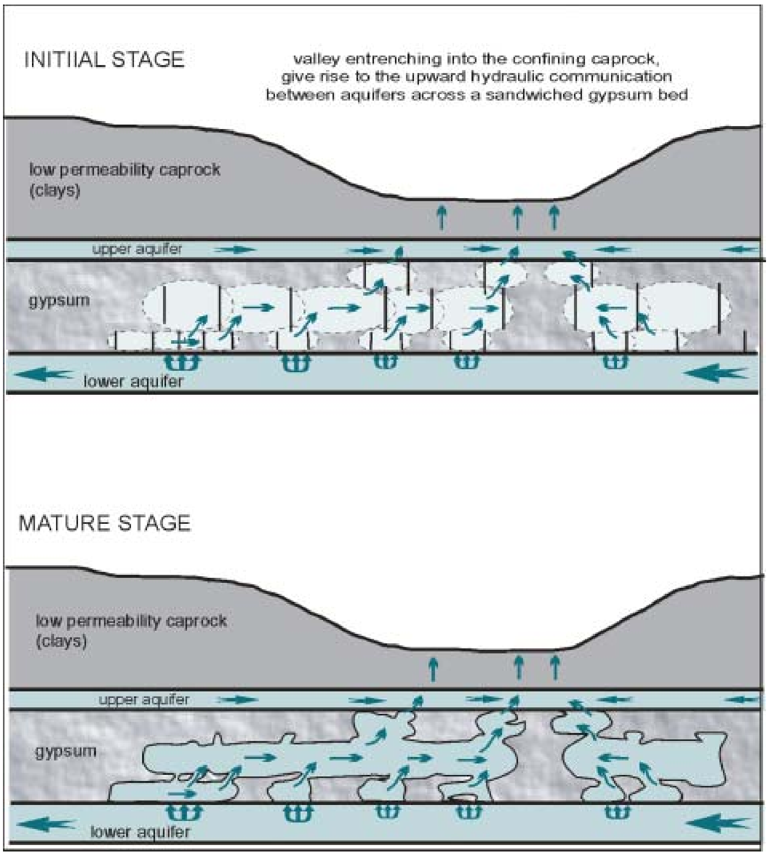

Fig. 11. Conceptual model of artesian speleogenesis in the Western Ukraine.

Deep river entrenchment in the Podol'sky area during the middle and late Pleistocene left the caves in a relict state above the piezometric surface. Only minor modification of cave morphology takes place today in areas of local sinking surface streams, and in the lower part of the gypsum where the water table is still above its bottom in some interfluve massifs. Within the slowly submerged part of the platform fringe (Bukovinsky area) the gypsum is still largely or entirely inundated, except in areas of artificial dewatering. Discovery of 92 km-long Zolushka cave by dewatering (Fig. 10-E) illustrates that cave origin under artesian conditions has proceeded until recently.

Thus, the caves in the Podol'sky area have developed in largely the same conditions as those present today in the belt adjoining the foredeep, where the sulphur deposits are located. The data on known relict caves and the concept of artesian speleogenesis, described above, can be applied to the interpretation of artesian karst in the vicinity of the sulphur deposits.

Northeast section of the GAS belt- the area of sulphur deposits

Fedorova (1985, 1986) suggested that karstified and permeable areas in the GAS at the Jazovsky deposit are located where the gypsum is thinnest, especially below buried valleys.

Kutepov and Kozhevnikova (1989) state that clay-filled and water-filled solutional cavities in the GAS at the Jazovsky deposit are most abundant where the GAS is thinnest, but that intense karstification is also present in places where the unit is rather thick. Drill holes in one area where the gypsum is 48 m thick, encountered 4-6 m high cavities about half filled with clay. Kutepov and Kozhevnikova (1989) suggest that dissolution is performed by ascending waters. Intense karstification of both the GAS and sulphur-bearing limestones was also mentioned by Bobrovnik and Golovchenko (1969), Merlich and Dacenko (1976), Pertzovich (1969).

Polkunov et al. (1979) characterize the GAS as an aquiclude, but they nevertheless present data about karst features within it and state that, although cavities occur throughout, they are most concentrated at the top and bottom of the GAS. Cavities encountered in drill holes have a maximum vertical range as much as 7.1 m at the Jazovsky deposit and 9.7 m at the Nemirovsky deposit.

The author has analysed data from nearly 100 wells in the GAS at the Jazovsky sulphur deposit and at the Nikolaevsky clay quarry. Solution cavities were encountered in 23% of the wells (in places as high as 35%), most of them open (water filled). Cavities had the greatest vertical dimensions at the Jazovsky deposit (up to 12 m).

Our survey supports the observation of Polkunov et al. that cavities occur mainly in the lower and upper parts of the GAS. This corresponds well with the multi-storey structure of relict maze caves known in the Podol'sky and Bukovinsky areas. At the Jazovsky deposit, tracers injected into the sub-gypsum aquifer were frequently detected at wells in the GAS, whether or not they intersect cavities. This indicates the upward pattern of groundwater flow through the gypsum/anhydrite.

The characteristics of karst in the GAS in the vicinity of the Pre-Carpathian sulphur deposits are compatible with the pattern and secondary filling of known cave systems in the Podol'sky and Bukovinsky areas and with the artesian model of speleogenesis mentioned above. This model readily explains the geologic, hydrologic and hydrochemical peculiarities of the supra-gypsum and sub-gypsum aquifers and their relationships. Thus it is appropriate to use this speleogenetic model to explain karst development in the GAS in the vicinity of sulphur deposits.

There is much more data published about karst features in the supra-gypsum limestones, the production horizon of sulphur. All researchers note the intense heterogeneous karstification of the limestone in the form of vugs and caverns up to 20-30 mm in diameter. The presence of larger cavities is also frequently noted. Tkachouk and Koltun (1963) refer to extensive development of large cavities, similar to those in the GAS, at sulphur deposits and other areas where the supra-gypsum limestones are thickest. A large cave in sulphur ore at the Tcharkowy deposit (Poland) was described by Push (cited in Polkunov et al., 1979). The large Medovaya Cave, of clearly phreatic morphology, is known in the presently drained part of the Ratynsky limestones at Lvov.

Polkunov et al. (1979) report intersection of cavities 3-5 m high in drill holes in certain areas of the Jazovsky deposit, where the GAS is absent and the sulphur-bearing limestones rest directly on lithothamnion limestones. This is explained as a "special case" of karst development below local base level due to action of water discharging under pressure from the lithothamnion limestones where these limestones are directly overlain by sulphur ores. These authors point out that at the Rozdol'sky deposit there is intense karstification of sulphur-bearing and barren limestones throughout all areas where they directly overlie the lithothamnion bed, with karst commonly developed at two distinct levels (at both the bottom and top of the limestones).

Collapse cavities are characteristic for the supra-gypsum limestones at all sulphur deposits. For example, during the geological mapping of mines, 247 collapse spots were noted within an area of 1.5 km2 of exposed limestones at the Rozdol'sky deposit. Karst collapses form continuous zones several hundreds meters wide extending 2-3 km (Polkunov et al., 1979). Similar features are also mentioned in the Jazovsky, Nemirovsky, Ljubensky, Zhydachevsky deposits, as well as for the Tarnobzeg deposit in Poland.

When interpreting karst in the Tyrassky Formation, either in the GAS or in the supra-gypsum limestones, almost all researchers have invoked the traditional concept of a "descending" karst, which (as described by Polkunov et al., 1979) develops in the vadose zone, and also in phreatic zone where drainage to local rivers is possible. Such conditions are absent in the area of the sulphur deposits. Tkachouk and Koltun (1963) noted the difficulty of using such an interpretation where there has been widespread development of karst beneath a thick clay cover and fluvial base level. Most authors assumed that karst formed during breaks in sedimentation in the pre-Ratynsky (Pertzovych, 1969) or pre-Kosovsky (Bobrovnik and Golovchenko, 1969) time. There are no reliable data supporting such assumptions. The presence of a sharp, gapping contact between the upper limestones and the underlying GAS, and the karst-like irregularity of the top of the GAS are used as the main arguments to support such breaks, besides the very fact that the Tyrassky Formation is highly karstified (which in "descending" karst would require exposure above fluvial base level). In fact such a contact can be formed without a break but under the artesian conditions by interstratal solution, and karstification does not necessarily require exposure of soluble rocks to the surface.

All of the above peculiarities of karst in the Tyrassky Formation can be explained by the artesian speleogenetic model. Artesian cave origin by waters ascending from the underlying Lower Badenian aquifer is not a special case (as adopted by Polkunov et al., 1979) but is characteristic of the entire region of the GAS and supra-gypsum limestones. "Ascending" karst development in the supra-gypsum limestone is clearest where the limestone directly overlies the Lower Badenian member, but it can also occur where there are karst conduits within the GAS. In the latter case, aggressiveness of water toward calcite is enhanced by the presence of H_2S and CO_2 generated by reduction of sulphates. That the caves in the supra-gypsum limestones do not display maze patterns like those in the GAS is explained by differences in the nature and distribution of initial fissure permeability.

The model of artesian speleogenesis leads to a unified regional interpretation of karst in the Miocene strata. Moreover, it explains the important role of karst in governing the exchange of water between aquifers and in the formation of sulphur deposits.

Biogeochemical processes in the formation of sulphur deposits

It is well accepted at present that all major sulphur deposits are epigenetic, formed by replacement of the parent gypsum/anhydrite with calcite and sulphur ores. This opinion is shared by most of the researchers that have studied Pre-Carpathian deposits (Aleksenko, 1967; Koltun, 1966; Koltun et al., 1972; Niec, 1992; Osmolski, 1973; Pawlowski et al., 1979; Sakseev, 1972; Sokolov, 1965, 1972; Kityk, 1979; Vinogradov et al., 1961). Replacement of sulphate rock with calcite and sulphur occurs in a process of redox reactions resulting in reduction of sulphate to sulfide and oxidation of organic carbon to CO_2 and water. In low-temperature diagenetic environments these reactions are driven by microorganisms, as shown by microbiological and geochemical (particularly isotopic) studies by Davis and Kirkland (1970), Feely and Kulp (1957), Ivanov (1964, 1972), Kirkland and Evans (1980), Ruckmic et al. (1979), Vinogradov et al. (1961), and others. Oxidation of reduced sulphur may occur either abiologically or (less common) microbially. The general processes of bacterial sulphate reduction and of sulphides oxidation are well known, but their stages and mechanisms are still controversial (Kushnir, 1988). The main processes and settings are briefly considered below.

The most important process in epigenetic sulphate transformation is sulphate reduction driven by microbes, a heterogeneous assemblage of *Desulfo-x*. The process can be described by the following simplified reaction:

$$SO_4^{=} + 2CH_2O \xrightarrow[\text{anaerobic bacteria}]{} H_2S + 2HCO_3^{-} \quad [1]$$

Sulphate reducing bacteria are strictly anaerobic and require a reduced environment (Eh < -100 mV) for growth, either in the bulk environment or in microenvironments that may be present, or maintained by bacteria themselves, within an otherwise more oxidizing milieu. The bacteria generally cannot metabolize saturated hydrocarbons, such as methane, but require specific organic compounds, such as organic acids or aldehydes (Kushnir, 1988; Machel, 1992). Transformation of methane into more simple oxygen-bearing compounds can be provided by aerobic fermenting bacteria that are widespread under natural conditions. It is assumed that transformation of organic matter can take place in anaerobic environments by bacteria that co-exist with sulphate-reducing bacteria and provide nutrients for them (Kushnir, 1988).

The solubility of H_2S in water is rather low. At pH = 6.5-9.0, hydrosulphides predominant in solution. Most of the H_2S exists as a gas phase. Calcium and bicarbonate commonly precipitates as $CaCO_3$, utilizing the HCO_3^- generated in the process of sulphate reduction:

$$Ca^{++} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \quad [2]$$

For calcite to precipitate continuously during the process of sulphate reduction it is necessary that H_2S be eliminated from the reaction zone, as its accumulation up to 500-700 mg/L would make the environment inappropriate for bacteria growth, and sulphate reduction would cease. Moreover, calcite is stable at pH generally higher than 7.0 (depending on the chemical environment). Excess H_2S can be eliminated by water flow or by oxidation in situ to elemental sulphur. Kushnir (1988) hypothesized that anomalous sulphate reduction can be performed by bacteria if environmental conditions deteriorate; at this sulphate is reduced to thiosulphate ($S_2O_3^{=}$). In this way sulphate-reducing bacteria can partially consume low-activity organics, including methane.

Isotopically light carbon in secondary calcite is one of the main points of evidence of its bioepigenetic origin. It inherits the isotopic composition of the initial organic compound. In the Pre-Carpathians, light carbon in epigenetic limestones of the Tyrassky Formation (σC^{13} = -32 to -65 ‰) clearly shows that the initial organic compound involved in sulphate reduction was methane. This origin is supported also by the presence of light carbon (σC^{13} = -32 to -42 ‰) in CO_2 in the air of caves that have only recently been aerated, and where sulphate reduction and CO_2 generation still occurs in the lower part of the GAS, or within the still-wet clay fill, such as in Zolushka cave (Klimchouk et al., 1984; Klimchouk and Jablokova, 1989). The CO_2 concentration in the air of such caves can be as high as 4.0% Thus, although methane cannot be utilized immediately by sulphate-reducing bacteria, it still serves as the initial organic compound. Models of the origin of sulphur deposits should stipulate conditions for methane transformation into more active forms.

Sulphate-reducing bacteria do not form elemental sulphur. Its formation is due to abiological or microbial oxidation of H_2S or to polysulfide dissociation. According to Machel (1992), abiological oxidation of H_2S is the single most important process forming epigenetic native sulphur deposits in low-temperature diagenetic environments:

$$2H_2S + O_2 \rightarrow 2S^o + H_2O \quad [3]$$

$$2HS^- + O_2 + 2H^+ \rightarrow 2S^o + 2H_2O \quad [4]$$

Hydrogen sulfide (and/or HS^-) reacts with O_2 not only to elemental sulphur but also to sulfite, disulphate, sulphate, and polysulphides. The reaction varies with pH, concentration of reactants, and the presence of impurities. In general, the formation and precipitation of elemental sulphur is favoured by the following conditions (Kushnir, 1988; Machel, 1992): (a) relatively high concentrations of total reduced sulphur ($S^=$); (b) relatively large $S^=/O_2$ ratios; and (c) relatively low pH (<6). With increasing pH, reduced sulphur is increasingly oxidized to sulphite, thiosulphate, and sulphate, rather then to S^o. This also explains the presence of barite and celestite as late mineral phases in many sulphur deposits, or in oxidized portions of these deposits. Moreover, at pH values between about 6 and 8.5, much if not most of the S^o that is generated by reactions [3] and [4] forms polysulfides rather then precipitating as a separate phase. Thus, for the formation of native sulphur by these reactions, the environments must be near-neutral to slightly acidic, with relatively low concentrations of oxygen, and low rates of oxygen supply. At high partial pressure of oxygen, or where oxygen is supplied at large rates, hydrogen sulfide (and/or HS^-) is oxidized to $SO_4^=$ (e.g. sulphuric acid) and no elemental sulphur is formed (Machel, 1992).

Where there is an excess of $SO_4^=$, oxidation of H_2S and formation of colloidal sulphur can occur in the absence of oxygen (Feely and Kulp, 1957):

$$3H_2S + SO_4^= \rightarrow 4S^o_{(colloidal)} + 2H_2O + 2OH^- \quad [5]$$

It is assumed that such sulphur precipitates together with calcite, to form a calcite/sulphur ore containing uniformly scattered sulphur. The concept of the formation of sulphur ores by reactions [1] and [5] has been widely accepted until recently, but Kushnir (1988) has pointed out that it is as yet unproved, and that thermodynamic analysis shows it to be unlikely.

In the presence of colloidal sulphur, the combined origin of calcite and sulphur occurs also in the following way:

$$2H_2S + 2Ca^{++} + 2H_2O \rightarrow Ca(OH)_2 + Ca(HS)_2 + 4H^+ \quad [6]$$

$$Ca(HS)_2 + 4S_{(colloidal)} \rightarrow CaS_{5\,(polysulfide)} + H_2S \quad [7]$$

$$CaS_5 + CO_2 + H_2O \rightarrow 4S_{(crystalline)} + CaCO_3 + H_2S \quad [8]$$

Polysulfides form as direct and indirect byproducts of bacterial sulphate reduction, or inorganically when H_2S dissociates into HS^- and then reacts with elemental sulphur that is derived from reactions [3] and [4] (Machel, 1992):

$$HS^- + (n-1)/8\ S_8 \rightarrow S_n^= + H^+ \quad [9]$$

The concentration and speciation of polysulfide is strongly pH-dependent. In slightly to moderate alkaline aqueous solutions (pH 7-9) they are stable as anions. At pH 8 to 9 the polysulfides $S_4^=$, $S_5^=$, and $S_6^=$, along with HS^-, are the predominant sulphur species in aqueous solution. At neutral to slightly acidic pH (pH < 7-6), polysulfide anions rapidly dissociate:

$$S_n^= \rightarrow S^o + S_{n-1}^= \quad [10]$$

Thus, elemental sulphur is "consumed" in the formation of polysulfides at pH > 6-7, and polysulfides release S^o upon a decrease in pH below this range, which leads to the precipitation of elemental sulphur (Machel, 1992).

Kushnir (1988) suggested the thiosulphate model of sulphur metasomatism, by which only anomalous sulphate reduction to thiosulphate occurs:

$$SO_4^= + \text{organic matter} \rightarrow S_2O_3^= + HCO_3^- + H_2O \quad [11]$$

Thiosulphate then migrates to adjoining zones where it is reduced to H_2S resulting in an increase of pH:

$$S_2O_3^= + \text{organic matter} \rightarrow H_2S + HCO_3^- + OH^- \quad [12]$$

At the boundary of the zones of different pH, calcite and sulphur precipitate:

$$Ca^{++} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \quad [13]$$

$$S_2O_3^= + 2H_2S \rightarrow 3S + H_2O + 2OH^- \quad [14]$$

It is assumed that this process leads to the formation of sulphur ores with uniformly scattered sulphur. The thiosulphate model is supported theoretically by thermodynamic analysis, but this is based on numerous assumptions and has not been proven by experiment.

Mechanisms of replacement of parent rocks

Soviet scientists have distinguished between two mechanisms of replacement of host gypsum/anhydrite with calcite or sulphur/calcite rocks: hydrogenic and metasomatic. Hydrogenic replacement occurs by precipitation of a new mineral in the place of a dissolved one. However, the mechanisms for metasomatic replacement is unclear, despite of the fact that sulphur/carbonate metasomatism is accepted by most researchers as a major ore-forming process. Sokolov (1972), who introduced and developed the concept of metasomatic origin of sulphur deposits, recognised that the conditions for metasomatism of sulphates to sulphur-carbonates, and even the process itself, are still poorly understood. Little progress has been made since then (Kushnir, 1988; Niec, 1992).

With regard to the conditions for exogenous sulphur formation, metasomatism is usually referred to as a process of replacement of sulphate minerals with the almost simultaneous formation of calcite and sulphur, as a result of biochemical and abiotic reactions. Replacement occurs in water-saturated zones of microporosity, with the host rock retaining its original volume and solid state (Korzhynsky, 1955; Lazarev, 1972; Sokolov, 1972). It is believed that replacement of ions occurs directly within the crystal lattice without the lattice being disrupted (Polkunov et al., 1979).

Not only is the process itself unclear, but also the mechanisms by which reactants are supplied to the metasomatic front and byproducts are removed. The process is postulated to occur in the microporous space of a rock, but studies have yet to evaluate this kind of porosity of a gypsum/anhydrite rock and matrix permeability. The chemistry and flow velocities of pore water in these materials are uncertain, and reaction rates are poorly understood. As the metasomatic front advances deeper into the sulphate rock, the inflow of reactants must, according to most schemes of ore formation, proceed through the newly-formed sulphur/calcite or calcite. As the result, the dynamics and chemistry of the pore solutions must change considerably, so that the conditions postulated for the process to start will change as well.

In general, the existing models for the process imply one of the following: either simultaneous or sequential input of a reducer and oxidizer to the metasomatic front, or the simultaneous presence of reducing and oxidizing environments in close proximity. Such conditions are impossible, or at least highly improbable, in zones of microporosity, especially if metasomatic front has propagated through a considerable thickness of rock. Many authors actually invoke concurrent or conjugate dissolution and precipitation. It is quite characteristic that most of authors, who postulate the process of metasomatosis in the origin of sulphur ore, discuss hydrologic and hydrochemical settings of the formation of sulphur ore (supply of reactants and outflow of reaction products) in terms of dynamics and chemistry of waters in the macrospace.

In the light of the above problems, it is questionable that metasomatism is a major process in the formation of calcite and sulphur-calcite epigenetic rocks, at least under hypergenic temperatures and pressures. The importance of macroporosity within the parent gypsum/anhydrite should be stressed as a media of transmitting reactants to and away from the sites of metasomatosis. Also, hydrogenesis nearly always takes place in the formation of epigenetic calcite and sulphur ore and is probably the dominant replacement mechanism. As shown below for the Pre-Carpathians, when an adequate hydrodynamic model for the origin of sulphur is presented, most of the geologic data commonly used to argue in favour of metasomatism are more likely to support hydrogenic replacement.

Water exchange in the Miocene sequence and the origin of sulphur deposits in the Pre-Carpathians

The pattern of water exchange is critical in any proper genetic model for the sulphur deposits. Such pattern forms the spatial and temporal framework within which the processes take place; it controls geochemical environments, the migration of reactants and reaction products between them. It is also important to consider the evolution of this flow pattern as the result of internal factors (such as the development of karst permeability) and external factors (such as changes in recharge/discharge conditions during neotectonic and geomorphic development).

As noted above, it is common in the regional hydrogeology of the Pre-Carpathians to consider the GAS to be an aquifuge and separating bed between the two limestone aquifers, preventing water exchange between them, except through windows where the GAS is absent. This concept has been part of all models suggested so far for the origin of sulphur deposits of the Pre-Carpathians. Several problems arise from this interpretation:

1. Large-scale sulphate reduction requires a stable supply of large amounts of dissolved sulphate into the reaction zone, which can not be provided if the GAS behaves as an aquifuge. The surface area of the sulphate contacting with water would be limited. If this scheme would be the case, then dissolution of sulphates would occur more or less equally in both the sub-gypsum and supra-gypsum aquifers. However, the concentrations of sulphate are normally small in the sub-gypsum aquifer and high in the supra-gypsum one.

2. If the GAS is impermeable, a uniform supply of hydrocarbons into the zone of sulphate reduction would be impossible. According to conventional hypotheses, hydrocarbons can penetrate the GAS only through tectonic faults and windows, which would produce localized zones of epigenetic calcite and sulphur-calcite. On the contrary, epigenetic calcite is distributed rather uniform even in the regional scale, and sulphur ores are uniformly distributed in the local scale of deposits.

3. The supra-gypsum aquifer is usually considered to be the zone of sulphate reduction. The generally accepted scheme also considers this aquifer to be the zone of H_2S oxidation, which occurs concurrently or sequentially with sulphate reduction. Attempts to constrain all stages of the sulphur formation processes into a single aquifer have forced investigators to make rather doubtful assumptions about paleohydrogeology. In other cases, the formation of sulphur is considered to be associated with windows into the GAS, or with marginal zones, where H_2S-bearing waters and oxygen-bearing waters from two different aquifers can mix (Aleksenko, 1967). This idea obviously contradicts the presence of sulphur ores above the GAS at considerable distances from margins or "windows". Moreover, this hypothesis ignores the fact that the local thinning and windows within the GAS are in most cases the result of its epigenetic replacement with sulphur ores or with barren limestones. The GAS was initially present, and if it's low permeability is implied, then it would prevent mixing of water and the formation of epigenetic calcite and sulphur ores.

4. According to the "window" scheme, the supply of reactants to the zone of sulphate reduction comes to the GAS from above. As the replacement front propagates downward from the top of the "impermeable" GAS, newly formed epigenetic rocks are incorporated into the upper limestone. Obviously hydrodynamic and hydrochemical conditions behind the replacement front must change considerably during the process, so that the supply of reactants and the outflow of reactions products would likewise change. This would cause the processes and lithologic patterns at the reaction front to change. However, no such evidence has been observed in the Pre-Carpathian deposits.

5. If metasomatic replacement of the GAS had actually occurred, then the metasomatic front would have had to propagate deeply into the supposed "impermeable" GAS for 20-30 m. As pointed out previously, it is doubtful that metasomatism could do so without the presence of macroporosity.

Thus, the notion that the GAS is impermeable not only contradicts the hydrogeologic data and ignores well developed karst in it, but it also casts doubt on some of the basic assumptions about sulphur genesis. The result has been 40 years of debate that continues even today.

The artesian hypothesis of speleogenesis introduced in the previous section explains the major peculiarities of water circulation within the Miocene sequence and supports the karst model for the origin of sulphur deposits for the Pre-Carpathians. The major points of this model are presented below.

1. Ascending water flow though the GAS, from the sub-gypsum aquifer to the supra-gypsum one, occurs in potentiometric lows where sufficient fissure permeability is present. These lows coincide with valleys entrenched into the capping clay aquiclude. The whole aquifer system discharges upward into the bottoms of such valleys. By this process, karst permeability develops in the GAS in the form of two- to four-storey cave systems (Figs 11 and 12). Maps of known maze caves show typical delineation of karstified areas (Fig. 10). The association of these "ascending" karst systems with old valleys explains why sulphur deposits that form after cave systems are also associated with old valleys (the "paleogeographic criterion" of Otreshko).

2. Waters of the sub-gypsum aquifer are commonly high in oxygen and calcium bicarbonate, and low in TDS. Gases (predominantly methane) enter the aquifer along faults from the adjacent foredeep and disperse various distances from the points or lines of input. Under aerobic conditions within the aquifer, methane is transformed under microbial mediation to simple organic compounds that can be utilized by sulphate-reducing bacteria.

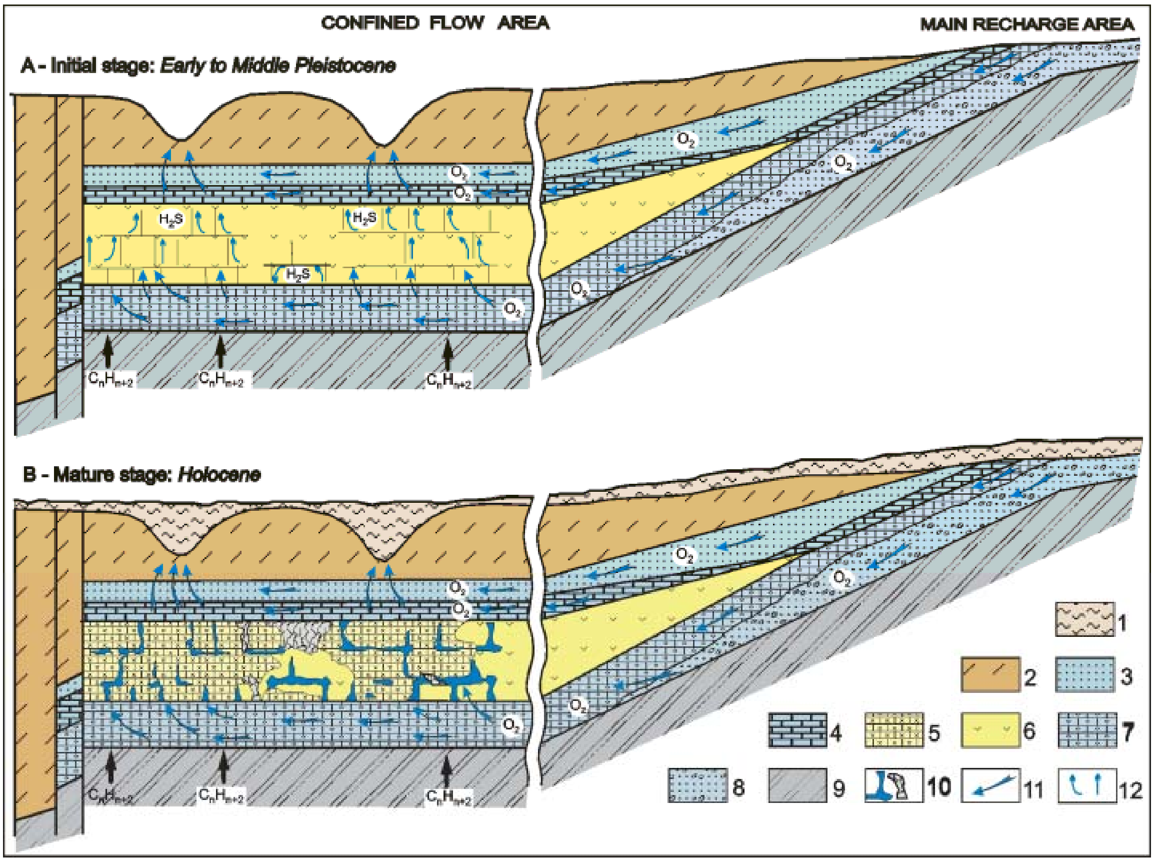

Fig. 12. Karst model of the formation of sulphur deposits in the Pre-Carpathians. A = initial stage, B = mature stage. *Quaternary sediments*: 1 = sands and loams. *Upper Badenian sediments*: 2 = clays and marls; 3 = sandstones; 4 = Ratynsky limestones; 5 = epigenetic sulphur-bearing and barren limestones; 6 = gypsum and anhydrite. *Lower Badenian sediments*: 7 = lithothamnion limestones; 8 = sands and sandstones. *Upper Cretaceous sediments*: 9 = marls and argillaceous limestones. 10 = dissolutional cavities; 11 = pattern of water flow in major aquifers; 12 = pattern of water flow through the gypsum/anhydrite.

3. Waters from the sub-gypsum aquifer ascend into karst fissures in the GAS and gain calcium sulphate composition. The TDS increases and the oxygen content and Eh decrease. The upper part of the GAS, near the contact with the overlying limestone, is the zone of active sulphate reduction. When conditions are favourable, replacement of the gypsum/anhydrite rock by calcite or sulphur-calcite takes place there. Excess H_2S escapes into the supra-gypsum aquifer and discharges along with water though the clay cap.

4. As sulphate reduction proceeds, the $SO_4^{=}$ content of the waters decreases, so that water at the upper contact again acquires (or increases) its solutional capacity with respect to gypsum. Dissolution of gypsum at the top of the GAS is concurrent with precipitation of calcite in the bottom of overlaying limestone (hydrogenic replacement). The newly formed epigenetic rock incorporates into the upper limestone horizon. In this way, the sharp, gapping contact is maintained between the GAS and epigenetic limestones, with clearly discerned dissolution features in the top of the GAS, which are peculiarities noted by many researchers. If sulphate reduction processes proceeds for a long enough time, or at high enough rate, the replacement front propagates downwards through the full thickness of the GAS, removing it entirely. Along the strike, as intrastratal water flow diminishes, epigenetic limestones may thin gradually with increasing distance from karst zones, from which reactants emanate. According to this model, reactant rise from below, so hydrochemical conditions remain rather stable as the replacement front propagates downward.

5. In the upper part of the GAS, replacement may occur also by metasomatic mechanism, encompassing the rock pillars between the conduits in dissolutional networks. The resulting features include relict structures inherited from the parent gypsum/anhydrite, abrupt transitions from one rock type to another along the strike, mineral complexes similar to those of the original rock.

6. Combinations of hydrogenic and metasomatic replacement of gypsum-anhydrite, as envisioned in the artesian karst model, explain virtually all major geological features in the supra-gypsum limestones. They also eliminate the seemingly contradictory aspects of structure and texture of epigenetic calcite and sulphur ores that have been the source of much argument by previous investigators.

7. If the vertical connectivity between fissure networks occurring in the lower part of the GAS and its higher horizons is poor, local conduit-fissure networks may form in the lower part of the GAS that allow back-circulation of water facilitated by natural convection. Thus water is able to flow through the GAS and return to the sub-gypsum aquifer (Fig. 12). This explains the local appearance of sulphate waters in the sub-gypsum aquifer, as well as local presence of epigenetic calcite and sulphur beneath the GAS. The latter have been one of the most contradictory points within previous models (Sakseev, 1966; Aleksenko, 1967; Kityk, 1979).

8. The karst model proposed here leads to three possible geochemical scenario of the origin of barren and sulphur-bearing limestones. That which of these situations takes place depends on parameters of local environment, which are controlled, to a considerable extent, by hydrodynamic conditions. Hence, they are dependent on karst systems development.

(a) In some areas, oxygen-rich groundwater flows laterally into the supra-gypsum aquifer from the main recharge area. Additional oxygen is supplied by water rising from the sub-gypsum aquifer through windows in the GAS defined by facies or tectonic. Where oxygen-rich water in the supra-gypsum aquifer encounters karstified zones in the GAS, it mixes with ascending H_2S-bearing water emerging from the GAS. If oxygen is supplied slowly and continually, then sulphur ore is formed by the "classic" mode of hydrogenic replacement (reactions [1], [3] and [4]). Zones of karst development are those of relatively low head toward which both sources of water are drawn.

(b) Where discharge from the artesian system is slow, reducing conditions and H_2S-bearing waters extend throughout the entire supra-gypsum aquifer above karstified zones in the GAS. High sulphate concentrations occur at the top of the GAS, where H_2S is oxidized according to the scheme proposed by Feely and Kulp (1977) to produce sulphur-calcite ores with uniformly scattered sulphur (reactions [1] and [5]). The framework of the karst model allows also other mechanisms for the formation of sulphur described earlier.

(c) Where conduit paths in the GAS are well developed, waters ascending through most transmissive conduits can still contain much oxygen, even in the upper part of the GAS. Mixing of these waters with H_2S-bearing waters from peripheral areas of slow flow can lead to sulphur deposition by oxidation of reduced sulphur compounds (reactions [3] and [4]).

9. Spatial and temporal variations of hydrodynamics within the Miocene aquifer system cause the groundwater exchange pattern to be complex and variable. Controlling factors are both external (variations in recharge and discharge to the system) and internal (permeability variations caused by karst development). Changes in pH and Eh occur in different parts of the system, as well as the migrating boundaries between geochemical environments. Thus, certain mechanisms of the formation and secondary transformation of sulphur can start or stop at various times and places within the system. This explains the lithologic diversity of sulphur ores and their varied relationships with barren limestones.

Regional pattern of karst evolution and the formation of sulphur deposits

During the late Pliocene and early Pleistocene the most active uplift occurred in the Rostochje and Opolje (northeast flank of the northwestern section of the GAS belt; see Fig.2), where widespread erosion almost completely removed the clay cap and the Tyrassky Formation. Elsewhere the initial surface stream pattern was initiated at that time. The formation of the old Pre-Dniester alluvial plain (7th terrace) is dated as late Pliocene. Stream channels migrated widely over this plane (Gofshtain, 1979). Simultaneously, other valleys formed north of the Pre-Dniester plain (Fig. 7), as well as on the Shchiretsky depositional plain in the northwest part of the GAS belt. The 6th Dniester terrace (early Pleistocene) is narrower then 7th but still much wider than the modern Dniester valley. Thus, as erosional valleys began to entrench into the clay cap, the regional pattern of potentiometric highs and lows in the Miocene artesian system was established. This caused intensified water circulation and initiation of karst systems of the "ascending" type.

In the interior of the platform fringe (Podol'sky area) inflow of hydrocarbons to the sub-gypsum aquifer and therefore sulphate reduction was slow and limited to a few areas. Therefore, sulphate reduction in zones of ascending karst development was uncommon. Epigenetic limestones are limited to certain zones where hydrocarbons were carried in along faults, allowing sulphate reduction to proceed. In the early Pleistocene, the uplift rate accelerated considerably in the Podol'sky area, causing the Miocene artesian system to rapidly lose its confinement. The resulting influx of oxygen-rich water was unfavourable to the origin of sulphur. With further deepening of drainage cave systems became relict.

In the northwest section of the GAS, within the Shchiretsky depositional plain, the uplift rate during Pleistocene was considerably lower than in the Podol'sky area. Distinct valley entrenchment into the clay caprock occurred only at the end of early-middle Pleistocene. Some entrenchments were caused by meltwaters from the waning Mindel glaciers, which covered this area (Gerenchouk et al., 1972). At this time, groundwater circulation through the Miocene sequence increased, as did karst development and sulphur deposition. In a few places (Rozdolsky deposit; Sokolov et al., 1969) erosional valleys entrenched as deep as the top of the Tyrassky Formation (Fig. 6), but in general they remained entrenched up to 30-40 m within the clay cap. Valleys were not deepened further, but instead were buried by late Pleistocene sediments of varied origin. Thus, in this region, conditions favourable to sulphate reduction and native sulphur formation in karst zones were maintained over quite a long time in rather stable hydrochemical environments. In many places such conditions persist even today.

Conclusions

1. The development of sulphate karst is one of the major prerequisites for the formation of epigenetic sulphur deposits. It is the source of dissolved sulphates needed for large-scale sulphate-reduction. This, likely, applies to most of epigenetic sulphur deposits associated with sulphate rocks, particularly to the Pre-Carpathian sulphur-bearing basin where the formation of sulphur deposits is related to speleogenesis in Miocene gypsum-anhydrite stratum (GAS).

2. Certain processes of the sulphur cycle, particularly bacterial sulphate reduction, enhance karstification in sulphate rocks by removing sulphate-ions from solution and maintaining the dissolutional capacity of waters.

3. Field data described in this paper show that the widespread acceptance of the GAS as an aquifuge is erroneous. The GAS does not prevent water exchange between the artesian Miocene aquifers of the Pre-Carpathians. The concept of the "aquifuge" role of the GAS brought about severe contradictions in previous models for the origin of sulphur deposits in this region.

4. Within karst zones, often quite large, the GAS aquifer has high conductivity that allows both vertical and lateral water exchange. Dissolution conduit systems in these areas provide paths for water exchange between the Miocene aquifers in the multi-storey artesian system.

5. In such multi-storey artesian system, vast two-to four-storey maze cave systems in the GAS developed where erosional entrenchment into the cap clay caused groundwater to ascend across the stratum. The recent model of artesian speleogenesis, combined with field data in the vicinity of sulphur deposits, suggest that relict maze caves in Podol'sky and Bukovinsky areas share the same origin as the dissolutional cavities in sulphur deposits, in the area of present artesian flow.

6. The proposed model for the genesis of sulphur deposits hinges on the ascent of groundwater from the sub-gypsum aquifer to the supra-gypsum aquifer through karst systems in the GAS. Such flow pattern provides the spatial and temporal framework within which the processes of the sulphur cycle take place, as well as it controls geochemical environments, the migration of reactants and reaction products between them. This model is well-compatible with the hydrogeologic settings of the sulphur deposits and with accepted biogeochemical processes of the sulphur cycle. It also explains why sulphur deposits are concentrated around buried valleys and karst zones and resolves many contradictions in the interpretation of geological features of the Tyrassky Formation. The major episode of sulphur-ore formation was from the early to middle Pleistocene, although in some areas it persists even today.

7. The karst model of the origin of sulphur deposits provides new criteria for predicting and prospecting for sulphur, as well as solutions to some of the engineering-geologic problems caused by mining of the deposits.

Acknowledgements

I would like to thank Kimberley I. Cunningham of the U.S. Geological Survey for his kind and generous assistance in translation of this paper to English. Josef E.Crawford of the Pennzoil Sulphur Company, Pecos, Texas, and Carol A.Hill of Albuquerque, New Mexico, added helpful suggestions. I am deeply indebted to Arthur N. Palmer of the State University of New York for his valuable editorial improvements to the paper.

References

Aleksenko I.I. 1967. Sulphur of the Pre-Carpathian. Moscow, Nedra, 303 p. (Russ.)

Andrejchouk V.N. 1988. Tectonic factor in the karst development of Bukovina. Sverdlovsk, 50 p. (Russ.)

Andrejchouk V. and Klimchouk A. 1993. Environmental change and human impact on karst in the Western Ukraine. In:, Environmental change and human impact in karst terrains, P.W. Williams, ed., *Catena Suppl.* **25**, Catena Verlag: 145-158.

Babinets A.E. 1961. Underground waters of the south-west of the Russian Platform. Kiev, Izd.AN USSR, 378 p. (Russ.)

Babinets A.E. and Tsapenko I.I. 1960. On conditions of the formation hydrogene sulfide enriched waters at the boundary between north-west outskirt of the Russian Platform and the Pre-Carpathian Foredeep. *Geol. zhurnal* **XX(6)**: 33-49. (Ukrain.)

Bobrovnik D.P. and Golovchenko Ju.K. 1969. On the study of karst in sulphur-bearing limestones and gypsum of Pre-Carpathian deposits of native sulphur. In *Geologija mestorozhdenij samorodnoj sery*. Moscow, Nedra: 238-245. (Russ.)

But Ju.S. 1962. Dynamics and regime of underground waters of Miocene sediments in the zone of junction between the Galitzko-Volynsky syncline and the Pre-Carpathian foredeep. In *Pytannja geologii Ukrainy*, Kiev, Vydav. AN USSR: 46-51. (Ukrain.)

Davis J.B. and Kirkland D.W. 1970. Native sulphur deposition in the Castile Formation, Culberson County, Texas. *Economic Geology* **65**: 107-121.

Dubljansky V.N. and Lomaev A.A. 1980. Karst caves of the Ukraine. Kiev, Naukova dumka, 176 p. (Russ.)

Dubljansky V.N. and Smol'nikov B.M. 1969. Karstological and geophysical prospectings of karst cavities of Pridnestrovsky Podolia and Pokut'e. Kiev, Naukova dumka, 151 p. (Russ)

Fedorova T.K. 1985. Physical/chemical processes in underground waters. Moscow, Nedra, 182 p. (Russ.)

Fedorova T.K. 1986. Aggressiveness of underground waters in the area of sulphur deposit. In *Metody otsenky i prognoza gidrogeologicheskikh uslovij pri inzhenernykh izyskanijakh*, Moscow, Strojizdat: 58-65. (Russ.)

Feely, H.W. and Kulp, J.L. 1957. Origin of Gulf Coast salt-dome sulphur deposits. *Amer. Assoc. of Petrol. Geol. Bulletin* **47**: 1802-1853.

Gajdin A.M. 1983. Hydrogeology of native sulphur deposits. *Sovetskaya Geologiya* **3**: 113-119. (Russ., res.Engl.)

Gajdin A.M., Klimchouk A.B. and Kovshikov H.H. 1985. Protection of geological environment at sulphur deposits. Moscow, NIITEHIM. 36. (Russ.)

Gajdin I.M., Klimchouk A.B., Antroptzev A.M. and Ostash L.I. 1991. Modification of water exchange under impact of mining. In *Water exchange in hydrogeological structures of Ukraine: Water exchange under disturbed conditions,* W.M.Shestopalov, ed., Kiev, Naukova dumka: 208-228. (Russ.)

Gerenchouk K.I., Demedjuk N.S. and Zdenjuk M.V. 1972. The Oksky continental glaciation on the west of Ukraine and its marginal forms. In *Kraevye obrazovanija materikovykh oledenenij*, Moscow, Nauka: 238-245. (Russ.)

Goleva G.A. 1962. Hydrogeological pecularities of the formation of sulphur deposits of the Pre-Carpathians. *Sovetskaya Geologiya* **2**: 88-99. (Russ.)

Gofshtain I.D. 1979. Neotectonics of the Western Volyno-Podolia. Kiev, Naukova dumka, 156 p. (Russ.)

Grinenko V.A., Mamchur G.P. and Srebrodol'sky B.I. 1966. Isotope composition ofcarbone of carbonates of sulphur deposits in the Pre-Carpathians. *Mineralogicheskij sbornik Lvovskogo universiteta* **20**, Lvov. (Russ.)

Ivanov M.V. 1964. The role of microorganisms in the genesis of native sulphur deposits. Moscow, Nauka, 367 p. (Russ.)

Ivanov M.V. 1972. Biogeochemistry of sulphur. In *Geokhimia i mineralogia sery*, Moscow, Nauka, 16-18. (Russ.)

Kirkland D.W. and Evans R. 1980. Origin of castiles on the Gypsum Plain of Texas and New Mexico. Trans-Pecos Region, southeastern New Mexico and west Texas. Dickerson P.W. and Hoffer J.M. (eds.). New Mexico Geological Society, 31st Field Conference Guidebook: 173-178.

Kityk V.I. 1979 (Ed.). Composition and reguliarities of distribution of sulphur deposits of the USSR. Kiev, Naukova dumka, 255 p. (russ.).

Klimchouk A.B., Jablokova N.L. and Ol'shtynsky S.P. 1984. Formation of air gas composition in caves of Podolia and Bukovina. *Doklady Akademii Nauk Ukr. SSR*, **ser. B, n. 2**: 138-143. (Russ., res. Engl.)

Klimchouk A.B. 1990. Artesian genesis of the large maze caves in the Miocene gypsum of the Western Ukraine. *Doklady Akademii Nauk Ukrainskoj SSR*, **ser. B, n.7**: 28-32. (Russ., res. Engl.)

Klimchouk A.B. 1992. Large gypsum caves in the Western Ukraine and their genesis. *Cave Science* **19, 1**: 3-11.

Klimchouk A.B. 1994. Speleogenesis under confined conditions, with recharge from adjacent formations. *Publ. Serv. Geol. Luxembourg* **XXVII**: Comptes Rendus du Coll. Intern. de Karstologie a Luxembourg: 85-95.

Klimchouk A.B., Aksem S.D., Shestopalov V.M. and Lisichenko G.V. 1985. Geological and hydrogeological conditions of karst development of Pridnestrovsky Podolia. *Fizycheskaja Geographija i Geomorphologija* **32**, Karst of Ukraine, I.L.Sokolovskij and A.B. Klimchouk (eds.), Kiev, Vyshcha Shkhola: 47-54. (Russ.)

Klimchouk A.B. and Andrejchouk V.N. 1988. Geological and hydrogeological conditions of the development of large gypsum caves in the Western Ukraine and their genesis. *Peshchery (Caves). Gypsum and Anhydrite Caves*, Perm, Perm University: 12-25. (Russ.)

Klimchouk A.B., Andrejchouk V.N. and Turchinov I.I. 1995. The structural prerequisites of speleogenesis in gypsum in the Western Ukraine. Kiev. Ukr.Speleol.Assoc., 106 p. (russ., engl.).

Klimchouk A.B., Jablokova N.L. 1989. Genesis of carbon dioxide of air in Ukrainian caves. *Proc. of the 10th Internatl. Congress of Speleology*, v.III, Budapesht: 800-801.

Koltun V.I. 1966. On the genesis of sulphur deposits of the Pre-Carpathians by lithological data. In *Geologia i geokhimia sernykh mestorozhdenij Predkarpatja*, Kiev, Naukova dumka: 12-20. (Russ.)

Koltun V.I., Roskosh Ja.T., Sen'kovsky Ju.M. and Jasinska A.A. 1972. Lithogenesis of sulphur deposits of the Pre-Carpathians. Kiev, Naukova dumka, 156 p. (Ukrain.)

Korzhynsky D.S. 1955. An essay on metasomatic processes. In *Osnovnye problemy v uchenii o magmatogennykh rudnykh mestorozhdenijakh*, Moscow, Uzdatel'stvo AN SSSR: 28-29. (Russ.)

Kutepov V.M. and Kozhevnikova V.N. 1989. Stability of karstified territories. Moscow, Nauka, 150 p. (Russ.)

Kutepov V.M. and Tsjurupa P.V. 1969. Engineering-geological conditions and map of Rozdol'sky deposit. In *Geologija mestorozhdenij samorodnoj sery*, Moscow, Nedra: 258-267. (Russ.)

Kushnir S.V. 1988. Hydrogeochemistry of sulphur deposits of the Pre-Carpathians. Kiev, Naukova Dumka, 1988. 179 p. (Russ.)

Lazarev I.S. 1972. On conditions of formation of sulphur occurences and onstages of mineralization at Gaurdaksky deposit. *Izvestija AN SSSR*, **ser.geol.,1**: 102-111. (Russ.)

Lein A.Ju., Ivanov M.V., Rivkina E.M. and Bondar V.A. 1977. Differences in isotope composition of carbon of pelitomorphic and crystalline limestones of sulphur deposits in the Pre-Carpathians. *Geokhimija* **4**: 578-588. (Russ.)

Machel H.G. 1992. Low-temperature and high-temperature origin of elementar sulphur in diagenetic environments. In *Native sulphur. Developments in geology and exploration*, G.R.Wessel and B.H. Wimberly (eds.), Littleton, Colorado: 3-22.

Mamchur G.P. 1972. Peculiarities of carbon isotopes distribution in carbonates of exogenous sulphur deposits and the possibility of their application for practical purposes. In *Geokhimia i mineralogia sery*, Moscow, Nauka: 240-252. (Russ.)

Merlich B.V. and Datsenko N.M. 1976. Conditions of formation of sulphur ores of Rozdol'sky deposit. Lvov, Izdatel'stvo Lvovskogo Universiteta, 218 p. (Russ.)

Miller L.J. 1992. Sulphur ore controls within the Salado and Castile Formations of West Texas. Native sulphur. *In Developments in geology and exploration*, G.R. Wessel and B.H. Wimberly (eds.), Littleton, Colorado: 165-192.

Niec M. 1992. Native sulphur deposits in Poland. *In Developments in geology and exploration*, G.R. Wessel and B.H. Wimberly (eds.), Littleton, Colorado: 23-50.

Osmolski T. 1976. Kras a geneza zloz siarki w Polsce. *Kwart. Geol.* **20, 3**: 559-571.

Osmolski T. 1973. Problemy genezy i wieku koncentracji siarki. *Kwart. Geol.* **17, 3**: 310-315.

Otreshko A.I. 1960. Paleogeographic criterion of prospecting for sedimentary deposits of native sulphur and possibilities of its application. *Trudy GIGHS* **6**: 64-68. (Russ.)

Otreshko A.I. 1966a. Principles and methods of predictions of native sulphur deposits formed amongst sedimentary formations. *Sovetskaya Geologiya* **6**: 7-19. (Russ.)

Otreshko A.I. 1966b. Some peculiarities of karst of sulphur deposits of the Pre-Carpathian basin. In *Geologija i geokhimija sernykh mestorozhdenij Predkarpatja*, Kiev, Naukova dumka: 76-79. (Russ.)

Otreshko A.I. 1974. The role of the pre-Carpathian in the formation of sulphur deposits of the Pre-Carpathian basin. In *Formatzionnyj metod v prognoze iizychenii mestorozhdenij gorno-khimicheskogo syrja*, Moscow, Nedra: 144-153. (Russ.)

Pawlowski S., Pawlowska K. and Kubica B. 1979. Geology and genesis of the Polish sulphur deposits. *Economic Geology* **74**: 475-483.

Peresyn'ko D.I. 1960. Comparative characteristics of hydrogeology of sulphur deposits of Central Asia and Pre-Carpathian. *Trudy GIGHS* **6**: 135-140. (Russ.)

Peresun'ko D.I. 1961. Karst of sulphur deposits. *Novosti karstovedenia i speleologii* **2**, Moscow: 63-64. (Russ.)

Pertzovich M.G. 1969. On the age of karst in sediments of Lower Tortonian of the Rozdol'sky deposit. In *Geologija mestorozhdenij samorodnoj sery*, Moscow, Nedra: 246-250. (Russ.)

Pisarchyk Ja.K. and Rusetskaja G.A. 1972. On the genesis of sulphur deposits of the Pre-Carpathians. In *Geokhimia i mineralogia sery*, Moscow, Nauka: 120-131 (Russ.)

Polkunov V.F. 1990. Mineral concentrations of native sulphur. In *Geotektonika Volyno-Podolii*, Kiev, Naukova dumka: 229-232.

Polkunov V.F., Denisevich A.I. and Kostrovskaja A.I. 1979. Karst at ore fields and deposits (the Pre-Carpathian sulphur-bearing basin). In *Composition i zakonomernosti razmeshchenia sernykh mestorozhdenij SSSR*, Kiev, Naukova dumka: 185-192. (Russ.)

Ruckmick J.C., Wimberly B.H., and Edwards A.F. 1979. Classification and genesis of biogenic sulphur deposits. *Economic Geology* **74**: 469-474.

Sakseev G.T. 1966. Podorozhnenskaya structure of the Pre-Carpathiansulphur-bearing basin. In *Geologia i geokhimia sernykh mestorozhdenij Predkarpatja*, Kiev, Naukova dumka: 50-59. (Russ.)

Sakseev G.T. 1972. Significance of carbon isotopes in carbonates for prospecting of sulphur in the Pre-Carpathians. In *Geokhimia i mineralogia sery*, Moscow, Nauka: 252-259. (Russ.)

Shestopalov V.M. 1981. Natural resources of underground waters of platform artesian basins of Ukraine. Kiev, Naukova dumka, 195 p. (russ.)

Shestopalov V.M. 1989 (Ed.). Water exchange in hydrogeological structures of the Ukraine. Water exchange under natural conditions: Kiev, Naukova Dumka, 288 p. (Russ.)

Sokolov A.S. 1965. About genesis of native sulphur deposits. *Lithology and mineral resourses* **2**: 51-59. (Russ.)

Sokolov A.S. 1972. Genetic classification of native sulphur deposits. In *Geokhimia i mineralogia sery*, Moscow, Nauka: 40-55.(Russ.)

Sokolov A.S., Vdovichenko G.M., Ivanov M.V., Karavajko G.I. and Karpenko V.I. 1969. Oxidation of sulphur ores in Rozdol'ky deposit. In *Geologija mestorozhdenij samorodnoj sery*, Moscow, Nedra: 197-214. (Russ.)

Sokolov D.S. 1962. Main conditions of karst development. Moscow, Gosgeoltekhizdat, 322 p. (Russ.).

Srebrodol'sky B.I. and Kachkovsky I.V. 1973. Vertical migration of hydrocarbonsand chemical elements as related with block movements in the Pre-Carpathians. *Izvestija AN SSSP* **ser. geol. 1**: 121-125. (Russ.).

Stankevich E.F. 1968. Conditions of sulphur formation in hydrodynamic zones of underground waters. In *Materialy rabochego soveshanija po prognozu mestorozhdenij samorodnoj sery v osadochnykh porodakh*. Kasan: 43-47. (Russ.)

Tkachouk L.G. and Koltun V.I. 1963. Some problems of karst in the gypsum/anhydrite horizon of Pridnestrovje. *Geol.Zhurnal* **XXIII, 4**: 68-73. (Ukrain.).

Tsjurupa P.V. 1960. Hydrogeological conditions of the Pre-Carpathian sulphur-bearing basin and of its major deposits. *Trudy GIGHS* **6**: 112-133. (russ.)

Vinogradov A.P., Grinenko V.A. and Ustinov V.I. 1961. Genesis of Pre-Carpathian sulphur deposits by isotope composition of S^{32}/S^{34} and C^{12}/C^{13}. *Geokhimija* **40**: 827-836. (Russ.)

Wallace C.S.A. and Crawford J.E. 1992. Geology of the Culberson ore body. In *Native sulphur. Developments in geology and exploration*, G.R. Wessel and B.H. Wimberly(eds.), Littleton, Colorado: 91-107.