

Diagenetic alteration of Badenian sulphate deposits in the Carpathian Foredeep Basin, Southern Poland: processes and their succession

Alicja KASPRZYK



Kasprzyk A. (2005) — Diagenetic alteration of Badenian sulphate deposits in the Carpathian Foredeep Basin, Southern Poland: processes and their succession. *Geol. Quart.*, 49 (3): 305–316. Warszawa.

The facies variation of the Badenian sulphate deposits in the Polish Carpathian Foredeep Basin reflects distinct depositional and diagenetic environments. In these environments the primary sulphate (mainly gypsum) was deposited and then underwent different pathways of diagenetic evolution, recognized on the basis of sedimentological, petrographic and geochemical studies. Diagenetic sulphate facies (anhydrite and secondary gypsum) formed in successive stages: syndepositional (the depositional stage), early diagenetic (at the surface and during shallow burial) and late diagenetic (during deeper burial and exhumation). Most anhydrite deposits show sedimentological and petrographic features characteristic of a diagenetic facies formed by replacement (anhydritization) of the precursor gypsum deposits. Four basic genetic models of anhydrite have been proposed: (1) syndepositional interstitial anhydrite growth *de novo*, (2) syndepositional anhydritization (*via* nodule formation and pseudomorphous replacement), (3) early diagenetic anhydritization (displacive anhydrite growth), and (4) late diagenetic anhydritization (replacive anhydrite growth). The succession of diagenetic processes and their paragenetic relationships within the Badenian sulphate deposits display a complex diagenetic evolution. Many controlling factors, such as a palaeogeographic setting, tectonic activity, geostructural constraints and physico-chemical changes of the pore fluids, related to sedimentary and diagenetic environments, have been involved in the sulphate diagenesis. The results may be applied to other ancient evaporite basins including the marginal gypsum deposits and anhydrite in the more buried, basinward part.

Alicja Kasprzyk, Polish Geological Institute, Holy Cross Mts. Branch, Zgoda 21, PL-25-953 Kielce, Poland, e-mail: alicja.kasprzyk@pgi.gov.pl (received: July 7, 2004; accepted: April 12, 2005).

Key words: Carpathian Foredeep, Badenian, sulphate deposits, anhydrite, diagenesis.

INTRODUCTION

The various depositional and diagenetic processes, involved in formation of Ca-sulphate deposits take place in a wide-range of environmental settings from marginal (subaerial and very shallow subaqueous) through shallow to deep subaqueous, and subsurface burial (Schreiber and El Tabakh, 2000). Nevertheless, anhydrite formed in these settings may sometimes produce similar lithofacies and crystalline fabrics (Ortí Cabo and Rosell, 1981; Rosen and Warren, 1990; Kendall, 1992; Rouchy *et al.*, 1994) and thus, the origin of many ancient anhydrite deposits remains controversial. Moreover, there is no agreement on a distinction between primary (depositional) and secondary (post-depositional) features of the sulphate rock in burial settings (Hardie, 1984; Hardie *et al.*, 1985; Spencer and Lowenstein, 1990; Kendall, 1992).

In many ancient evaporite formations, a complex succession of diagenetic processes related to burial have completely

obliterated the depositional pattern of the primary sulphate rocks. In the Badenian deposits of the Carpathian Foredeep, however, primary sulphate (gypsum) occurs at the basin margin, whereas anhydrite is mostly limited to deeply buried (basinal) areas, and thus the gypsum-to-anhydrite transition is readily accessible in core studies (Kubica, 1992; Kasprzyk, 1995, 2003; Kasprzyk and Ortí, 1998; Fig.1). The Badenian anhydrite has been previously interpreted both as a diagenetic facies related to burial (Venglynskyi *et al.*, 1982; Kubica, 1992) or as cumulate deposits precipitated from deep and high-salinity brines (e.g. Ney *et al.*, 1974; Garlicki, 1979; Liszkowski, 1989). However, Kasprzyk and Ortí (1998) concluded, on the basis of sedimentological and petrographic studies, that anhydrite deposits were formed both by syndepositional anhydrite growth and by anhydritization (replacement of gypsum) during early to late diagenesis. This interpretation has been reinforced by recent studies, which document distinct relationships between facies, diagenesis and palaeogeographic settings in the Badenian evaporite basin

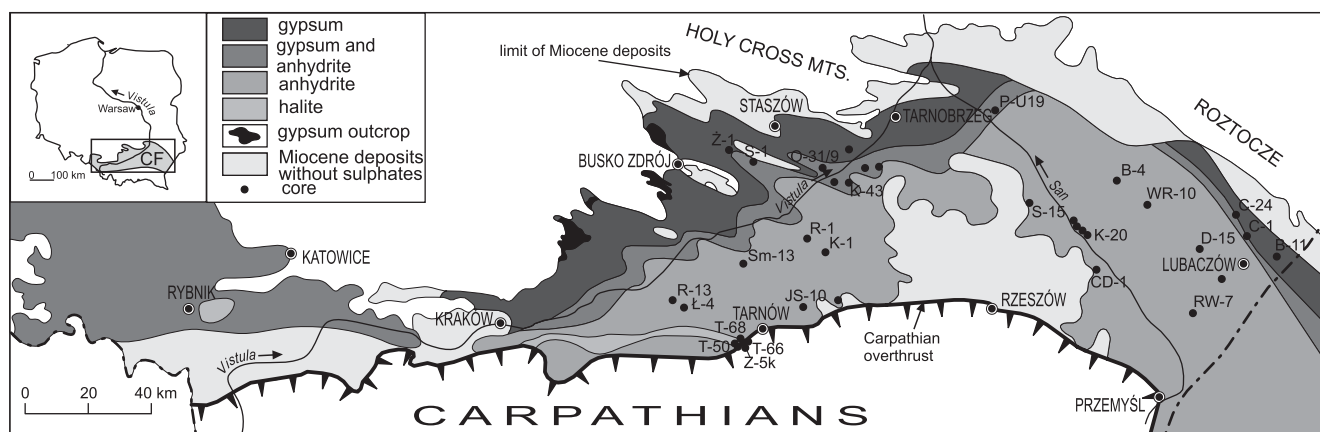


Fig. 1. Map of the major Badenian evaporite facies in the Carpathian Foredeep (CF) of Southern Poland

Cores: B-4 — Biszczka 4; B-11 — Budomierz 11; CD-1 — Chałupki Dębnińskie 1; C-1 — Cieszanów 1; C-24 — Czerków 24; D-15 — Dzików 15; JS-10 — Jastrząbka Stara 10; K-1 — Kaździolki 1; K-43 — Krzemienica 43; K-20 — Kuryłówka 20; Ł-4 — Łazy 4; O-31/9 — Okragła 31/9; P-U19 — Pysznicza U19; R-1 — Rydzów 1; R-13 — Rysie 13; RW-7 — Ryszkowa Wola 7; S-15 — Sarzyna 15; Sm-13 — Smęgorzów 13; S-1 — Strzelce 1; T-50 — Tarnów 50; T-66 — Tarnów 66; T-68 — Tarnów 68; WR-10 — Wola Różaniecka 10; Z-5k — Zawada 5k; Ż-1 — Żerniki 1

(Kasprzyk, 2003, 2005b). There is, however, still a poor recognition of the processes and controlling factors involved in the diagenetic alteration of sulphate deposits.

The aim of this work is to present a brief summary of my sedimentological and petrographic studies on the diagenetic evolution of Badenian sulphate deposits in the Carpathian Foredeep Basin, Southern Poland (Fig. 1). Here these results are combined with those of geochemical (trace element and isotopic) analyses of anhydrite samples, reported earlier (Bukowski and Szaran, 1997; Peryt *et al.*, 2002; Kasprzyk, 2003), to help interpret the depositional and diagenetic environments of the sulphate deposits and to construct the general patterns of anhydrite genesis in the Badenian evaporite basin. The present work emphasizes the importance of complex diagenetic processes in anhydrite formation. New information concerning gypsum-anhydrite relations and alterations comes from the study of numerous cores from different parts of the Polish Carpathian Foredeep (Fig. 1). For description of particular crystalline fabrics of anhydrite, the terminology of Ortí Cabo and Rosell (1981) is applied here.

FACIES DISTRIBUTION AND SUCCESSION

In the Polish Carpathian Foredeep Basin (the northernmost embayment of the Central Paratethys), the Badenian evaporites include a sulphate platform and an adjacent salt depocentre (Połtowicz, 1993; Peryt, 2000; Fig. 1). Shallow-water platform pelitic-sulphate deposits (gypsum, anhydrite, claystone, marl, clay), a few tens of metres thick, pass basinward into a sulphate-chloride facies (halite, anhydrite, gypsum, claystone) locally over 200-m thick.

In the northern peripheral part of the platform the dominant sulphate facies is primary gypsum that composes two members: a lower member (mostly autochthonous, selenitic facies) and an upper member (mainly allochthonous, clastic fine-grained deposits; Fig. 1; e.g. Kwiatkowski, 1972; Rosell *et al.*, 1998; Babel, 1999, 2005; Kasprzyk, 1999).

The primary gypsum is replaced by anhydrite and associated secondary gypsum (after former anhydrite) basinwards (>250 m burial depth; Fig. 2) (Kubica, 1992; Kasprzyk, 1995). In the gypsum-to-anhydrite transitional zone (abundant primary gypsum still preserved), the irregular (patchy) distribution of anhydrite within the primary gypsum, the presence of large anhydrite pseudomorphs after gypsum in the lower member as well as nodules and isolated, decussate laths of anhydrite in the gypsum are common features of initial anhydritization (cores: O-31/9 and S-1, Fig. 2). In completely altered (into anhydrite) sections, the vertical succession of lithofacies comprises nodular, nodular-mosaic and massive anhydrite, including a variety with stromatolitic features, in the lower part, that is overlain by laminated anhydrite and breccias (cores: WR-10, K-20 and D-15, Fig. 2). This succession is an equivalent to the gypsum sequence.

In the platform to basin transition, anhydrite deposits are usually <20 m thick and consist mainly of interbedded laminated anhydrite and breccias (cores: R-1 and RW-7, Fig. 2) (Kasprzyk and Ortí, 1998; Peryt, 2000). They pass laterally into finely laminated anhydrite and halite deposits (Figs. 1 and 2), interpreted as a deeper-water basinal facies (Garlicki, 1979; Połtowicz, 1993; Peryt, 2000).

The distribution of strontium through the anhydrite section allows differentiation between the two anhydrite members: (1) a lower member (predominant nodular and massive anhydrite) with low and homogeneous Sr values, and (2) an upper member (mostly laminated anhydrite and breccias) with a higher and more variable strontium content (Kasprzyk, 2003). The results reveal an apparent difference in the geochemical composition between the anhydrite sections located in different parts of the basin. This laterally variable geochemical composition related to facies changes across the basin most probably records a palaeogeographic control (reflecting different parts of the basin) on sulphate deposition and diagenesis.

The oxygen and sulphur isotope compositions of the platform anhydrite deposits are relatively homogeneous throughout the section and correspond well to the isotopic composition of the Badenian primary gypsum (Peryt *et al.*, 2002; Kasprzyk,

2003; Cendón *et al.*, 2004). A decrease in the $\delta^{18}\text{O}$ for the anhydrite of the upper member relative to the mean δ -value for the platform sulphates may reflect a general brine dilution. The high δ values found for some anhydrite samples may be related to processes involving either dissolution/precipitation or redox variations through the brine-sediment interface. There is no significant isotopic depletion of sulphur and oxygen in anhydrite associated with the halite deposits (Bukowski and Szaran, 1997; Kasprzyk, 2003), suggesting this sulphate is not a late-stage, residual precipitate supposed to have been formed in high-salinity, halite-saturated brines. Thus, there is no direct evidence of a reservoir effect on anhydrite formation. The results, however, do not exclude the possibility of sourcing of the dissolved sulphate by recycling of earlier marine evaporite successions in the Badenian basin (Cendón *et al.*, 2004).

FACIES ASSOCIATIONS

The sulphate facies distribution and succession (lower and upper members) reveal three distinct facies associations that record a range of depositional environments from nearshore to deeper basin (Fig. 2). The nearshore facies association shows structures (displacive sulphate nodules, chicken-wire and enterolithic patterns, microbial laminites and stromatolites; Fig. 2B, H–I) distinctive of marine-marginal sabkhas (e.g. Kendall and Harwood, 1996; Schreiber and El Tabakh, 2000). These facies include the basal sulphate nodules in the shoal sections (cores: S-1 and Ż-1), the sulphate microbial intercalations and the top laminated sulphate-siliciclastic-carbonate deposits at the landward margins of the basin (cores: WR-10 and B-11; Figs. 1 and 2). The shallow-water facies association displays common pseudomorphic structures of selenitic gypsum (Fig. 2G, I–K), some of which resemble crusts of vertically-oriented gypsum crystals in modern salinas (e.g. Warren, 1982; Ortí Cabo *et al.*, 1984). By analogy, bottom-nucleated selenites (now anhydrite or secondary gypsum) are interpreted to have been formed in marginal salinas some decimetres to a few metres deep, and affected by frequent fluctuations in the pycnocline (Kasprzyk, 2003; Bąbel, 2004). This facies association corresponds mainly to the lower member (Fig. 2). The deeper-water facies comprise laminated sulphate deposits and breccias of the upper member displaying redeposition features, such as graded bedding, convolutions, slump and contorted structures (Fig. 2A, C–F, L and M). Most of these features are considered as diagnostic of deep-water evaporite facies (Kendall and Harwood, 1996). Thus, this facies association in Badenian sections has been interpreted in terms of deeper-water, basin centre sulphate deposits (Kasprzyk, 1999; Peryt, 2000).

DIAGENETIC ENVIRONMENT

DIAGENETIC PROCESSES

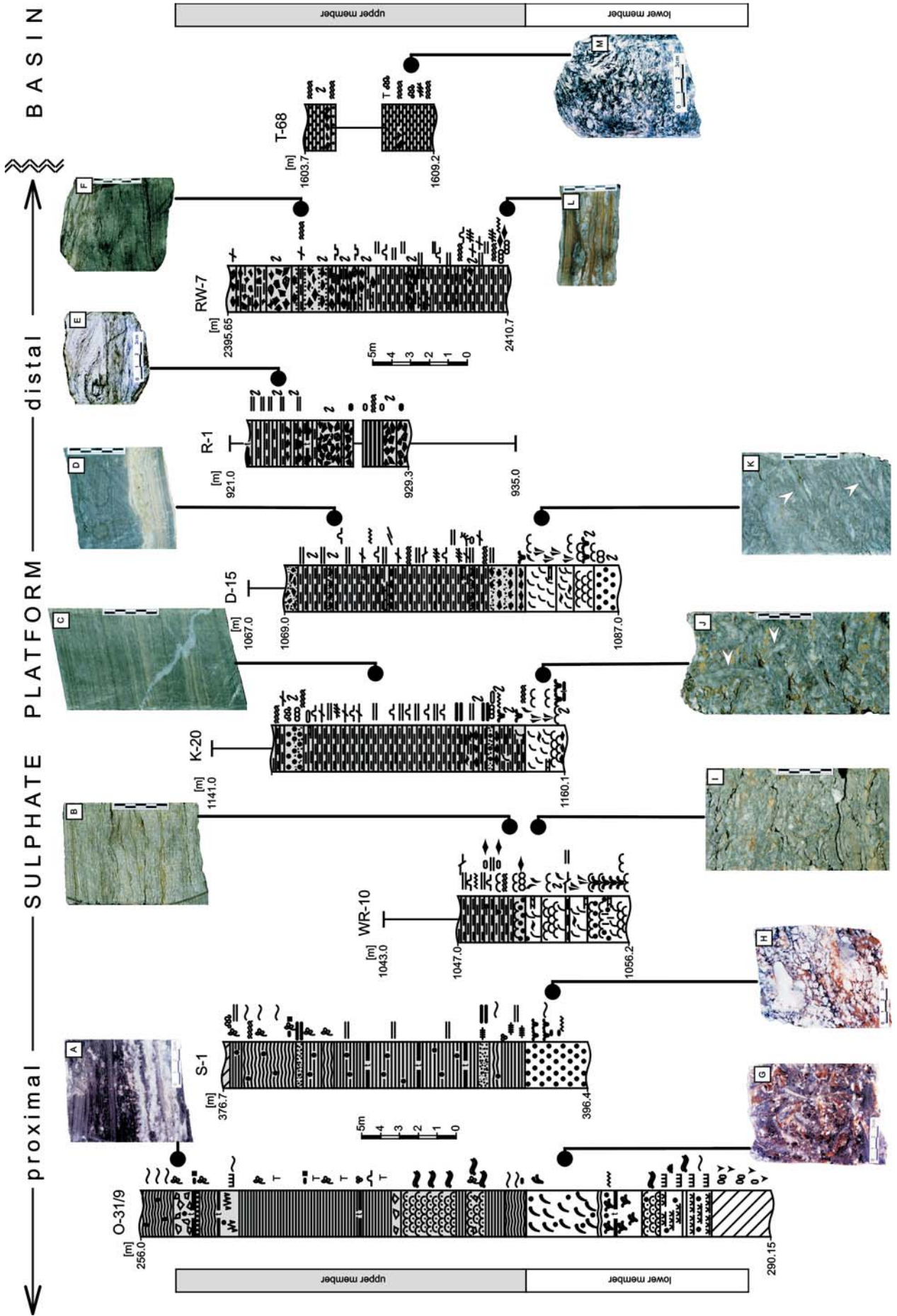
The Badenian sulphate deposits in the Carpathian Foredeep have undergone varying degrees of diagenetic changes at the

surface and in shallow to deeper burial settings. The sulphate facies variation and succession is reflected in different genetic patterns of anhydrite formation, depending on both palaeogeographic (related to different parts of the basin) and burial conditions. Depositional and diagenetic processes, that determined the genesis and successive alterations of the Badenian sulphate deposits varied with burial and exhumation (Fig. 3). The most important processes involved in sulphate diagenesis are: anhydritization, cementation, compaction, rehydration, replacement and recrystallization. The complex relations between these processes resulted in various petrographic and geochemical signatures, whereas their succession determined the preservation or obliteration of primary lithological features (Langbein, 1987; Spencer and Lowenstein, 1990; Kendall, 1992).

ANHYDRITIZATION

The nodular and nodular-mosaic anhydrite in the lower member displays crystalline fabrics characterized by: (1) expansive growth by means of nucleation of new anhydrite crystals inside nodules; (2) framework and preferentially mixed (fascicular and felted) microstructures; and (3) strong crystalline deformation and breakage by progressive growth and/or early compaction (Kasprzyk and Ortí, 1998). All these features are characteristic of syndepositional anhydrite in modern evaporite settings (Shearman, 1985; Rouchy *et al.*, 1994), and strongly suggest a sabkha environment and/or phreatic anhydritization processes (Figs. 3 and 4). Most anhydrite lithofacies of the lower member, displaying well-preserved pseudomorphs after gypsum crystals (Figs. 2 and 5D), are products of syndepositional anhydritization (*via* nodule formation) of original selenitic facies (Kasprzyk, 1995; Kasprzyk and Ortí, 1998; Peryt, 2000). Distribution of anhydrite in the gypsum succession is irregular and mainly limited to selenitic crystals boundaries and cleavage planes (Fig. 5A–C). Thus, the formation of anhydrite has been controlled by the porosity and lithology of the gypsum rocks.

In the laminated anhydrite of the upper member there is a lateral gradation, from the margin to the basin centre, of crystal-size, compactional deformations, displacive *vs.* replacive components, and amount of pseudomorphs, suggesting that anhydritization of gypsum could have started during early diagenesis and continued during burial (Figs. 3–4, 6 and 7). Pseudomorphs after clastic gypsum crystals are more distinct and larger in size in the platform successions when compared to the more basinal ones (Figs. 6C and 7A), suggesting original facies variation. These observations support the earlier interpretation of a progressive anhydritization process for the upper member, dependent on palaeogeographic and burial controls (Kasprzyk and Ortí, 1998; Kasprzyk, 2005b). According to this interpretation, in the distal successions the replacement of gypsum by anhydrite within the redeposited clastic sediments started during early diagenesis, as suggested by abundant displacive anhydrite components pushing aside the laminae and displaying intense deformation (Figs. 4 and 6D). The transformation continued (towards the margin of the basin) with increasing burial, resulting in large replacive anhydrite crystals only slightly deformed by compaction, and in random



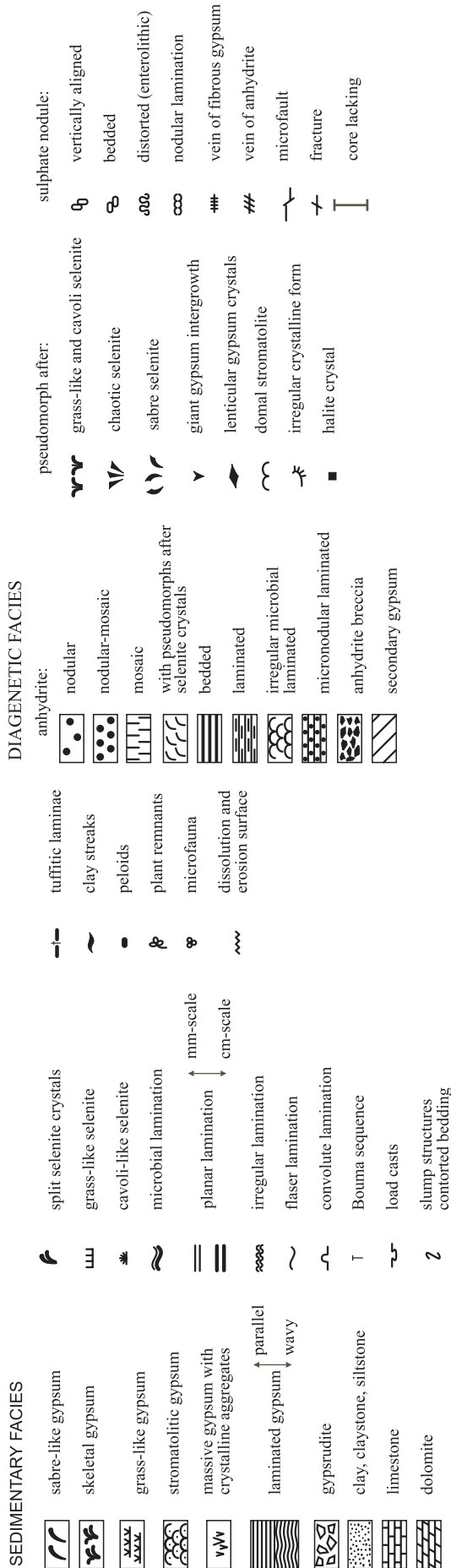


Fig. 2. Sulphate sections and lithofacies representative of various palaeogeographic settings through the Badenian evaporite basin

A — layer of syndimentary gypsum breccia in planar laminated gypsum; gypsum fragments are deformed, partly replaced by anhydrite (white) and randomly embedded in a clay-carbonate-gypsum matrix; **B** — irregular (crinkly) laminated anhydrite with sets of regular clay-anhydrite laminae at the top; **C** — regular laminated anhydrite crosscut by anhydrite vein (neptunian dike?); **D** — laminated anhydrite with a carbonate layer (light), laminae are regular at the bottom of the core while above they are broken and distorted; **E** — deformed, folded and disrupted (slump) sets of laminae: clayey-carbonate (dark) and anhydrite (light); **F** — laminated anhydrite (bottom) with fragments of *in situ* broken anhydrite laminae, at the top uniformly elongated; **G** — sable-like gypsum with small anhydrite nodules (white) replacing selenitic crystals from the outside; **H** — nodular anhydrite of chicken-wire pattern; **I** — irregular microbial laminated anhydrite (bottom) overlain by nodular-mosaic anhydrite with pseudomorphs after upright-grown selenitic crystals; **J-K** — anhydrite with distinct pseudomorphs after selenitic crystals (arrowheads) oriented randomly or uniformly; **L** — laminated anhydrite disturbed in part by pseudomorphs after lenticular gypsum crystals; **M** — distorted laminated anhydrite

anhydrite crystals scattered throughout and crosscutting the laminae without evident compactional effects (Figs. 4 and 6A–B). In the peripheral part of the basin, replacement by anhydrite was incomplete and original gypsum fabrics are well preserved.

CEMENTATION

In the lower member, anhydrite pseudomorphs after primary gypsum commonly occur (Fig. 2). This suggests that replacement was almost isovolumetric and was accompanied or directly followed by anhydrite cementation (Fig. 3), that allowed a preservation of original gypsum crystal morphologies (Hovorka, 1992; Kasprzyk, 1995). The early cementation seems to have been the main mechanism preserving the rigidity of pseudomorphs, which protected them against increasing pressure due to overburden or pore-water pressure (Shearman, 1985; Gunatilaka, 1990; Schreiber and Walker, 1992). The distribution of anhydrite in the Badenian gypsum indicates that cementation accompanied by dehydration started preferentially in zones of high microporosity, and therefore were dependent on the porosity and lithology of the former gypsum deposits. Replacement of gypsum crystals by preferentially aligned anhydrite laths (topotactic replacement) is most spectacular in the selenitic facies (Fig. 5A–C), suggesting that the gypsum lattice controlled the process (Langbein, 1987; Hovorka, 1992). Resulting pseudomorphs show coarsely crystalline, prismatic-aligned and cement-like palisade fabrics of anhydrite (Fig. 5D) (Kasprzyk and Ortí, 1998). These processes most probably commenced at the surface and were completed during shallow burial as documented in modern evaporite environments (Casas and Lowenstein, 1989; Fig. 3).

COMPACTION

One of the most important factors controlling both the lateral anhydrite fabrics continuum and the progressive anhydritization in the upper member was variable degrees of lithification of the precursor gypsum (soft sediment towards the centre, more compacted towards the margin; Kasprzyk and Ortí, 1998). For the sulphate of the lower member, compaction must have been preceded by cementation and thus compactional effects are negligible (Fig. 3). In the upper member the petrographic features of anhydrite, such as compactional deformation and displacive vs. replacive components, indicate varying degrees of sediment lithification at the time of anhydrite formation. In the basin margin, compaction seems to have preceded anhydritization, as de-

	Process/stage	Syndepositional	Early diagenetic	Late diagenetic
		SEDIMENTATION	crystallization of selenitic gypsum	
SEDIMENTATION	cumulative deposition of laminated gypsum/anhydrite			
	redeposition of clastic gypsum			
	dissolution surfaces			
	shallow	interstitial growth of sulphate nodules		
shallow	bacterial sulphate reduction and replacement: gypsum → pyrite			
	anhydritization of selenitic gypsum			
	sulphate cements			
	BURIAL	anhydritization of laminated gypsum (displacive anhydrite growth)		
compaction				
recrystallization				
pore infillings				
deep	anhydritization of laminated gypsum (replacive anhydrite growth)			
	intragranular anhydrite dissolution			
	anhydrite veins			
	EXHUMATION	rehydration of anhydrite		
replacement: gypsum/anhydrite → calcite/celestite/lutecite				
fibrous gypsum veins				

duced from the replacive anhydrite fabrics and the imperceptible deformation of anhydrite laths (Figs. 4 and 6A–B). It is assumed that compaction followed the syndepositional/early diagenetic anhydritization, and significantly affected the anhydrite fabrics towards the basinal settings (Figs. 3 and 6D). With increasing burial, little modification of those fabrics occurred due to additional compaction, pressure solution and some recrystallization. Compaction by burial, which might accompany or immediately follow dehydration of gypsum, resulted in further decrease in the stratigraphic thickness. The volume decrease, consequent to both the escape of the crystallization water and the porosity loss with progressive compaction, was more significant for the basinal successions, where fine-grained clastic gypsum deposits dominated (Fig. 2).

REHYDRATION

The rehydration genesis of some Badenian gypsum deposits is revealed by the distribution of rehydration features along fractures and strata boundaries of anhydrite rocks, and the common occurrence of corroded anhydrite relicts in gypsum (Figs. 2, 3 and 8). It can be assumed that, in the marginal parts of the evaporite basin, shallow burial and/or uplift and exhumation re-

Fig. 3. Depositional-diagenetic sequence of Badenian sulphate deposits

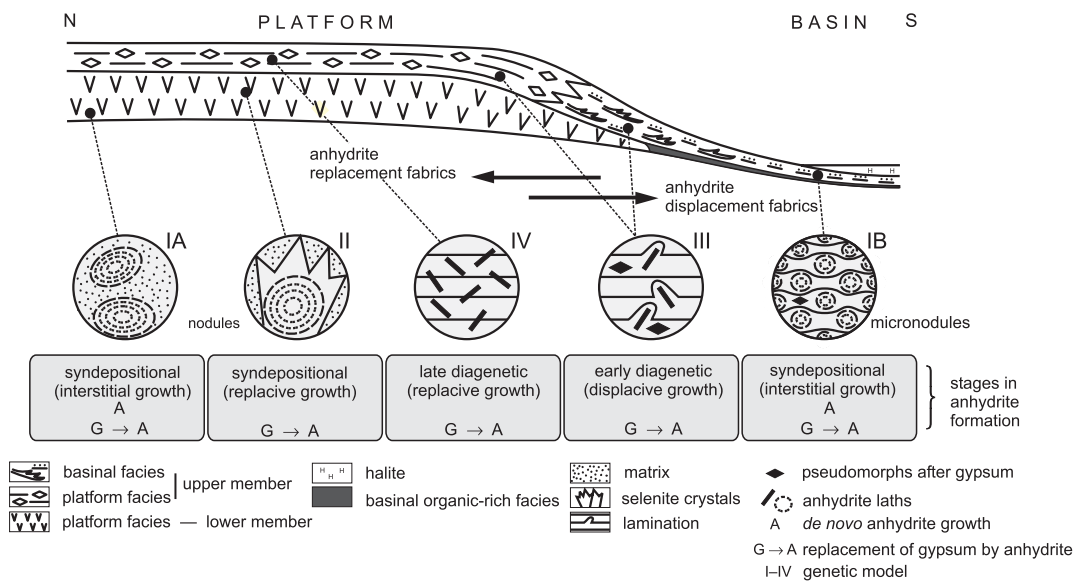


Fig. 4. Genetic models of Badenian anhydrite in the Carpathian Foredeep Basin (after Kasprzyk, 2005a)

I — syndepositional anhydrite growth *de novo*; II — syndepositional anhydritization; III — early diagenetic anhydritization; IV — late diagenetic anhydritization; displacive anhydrite fabrics are characterized by the presence of abundant anhydrite crystals pushing aside impurities and deforming the lamination; replacive anhydrite laths are scattered throughout, crosscutting the laminae

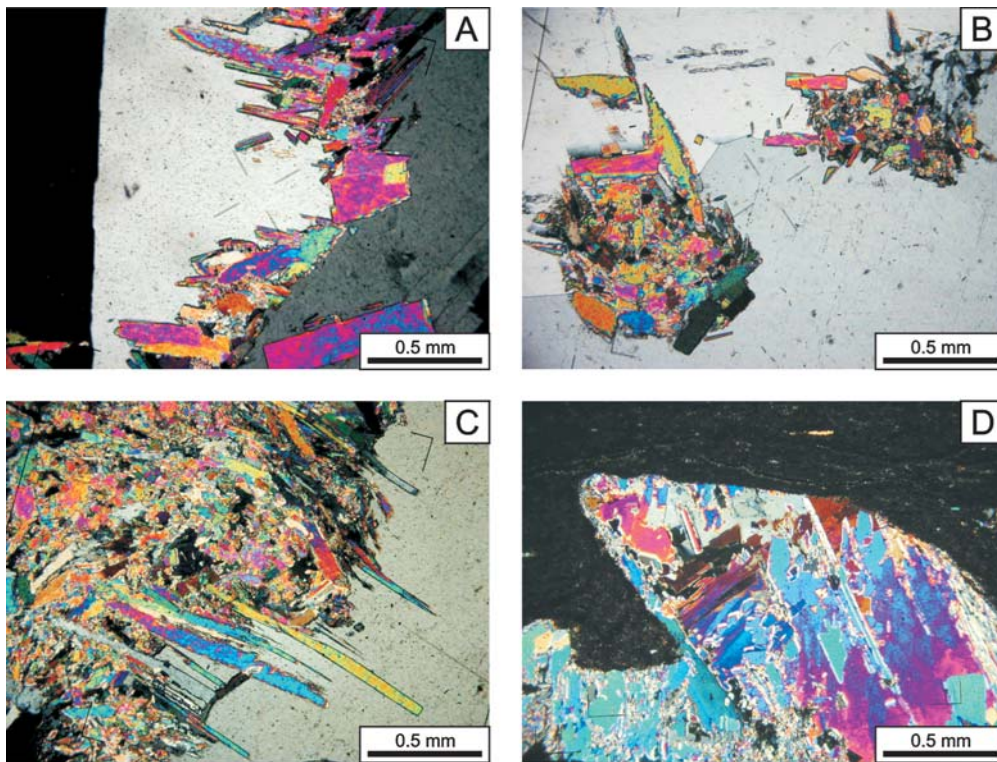


Fig. 5. Anhydritization of selenitic gypsum (platform facies, lower member)

A–C — initial replacement of gypsum by anhydrite showing microgranular and prismatic-aligned, palisade fabrics (topotactic replacement), anhydrite laths are oriented preferentially along the boundaries of selenitic crystals to form “veins” and nodular aggregates: **A** — core P-U19, depth 439.0 m, **B** — core Ž-1, depth 339.5 m, **C** — core P-U19, depth 451.6 m; **D** — anhydrite pseudomorph after large gypsum crystal, showing coarse-crystalline, cement-like palisade fabric, in clay-carbonate matrix (dark), core K-20, depth 1158.5 m; microphotographs, crossed polars

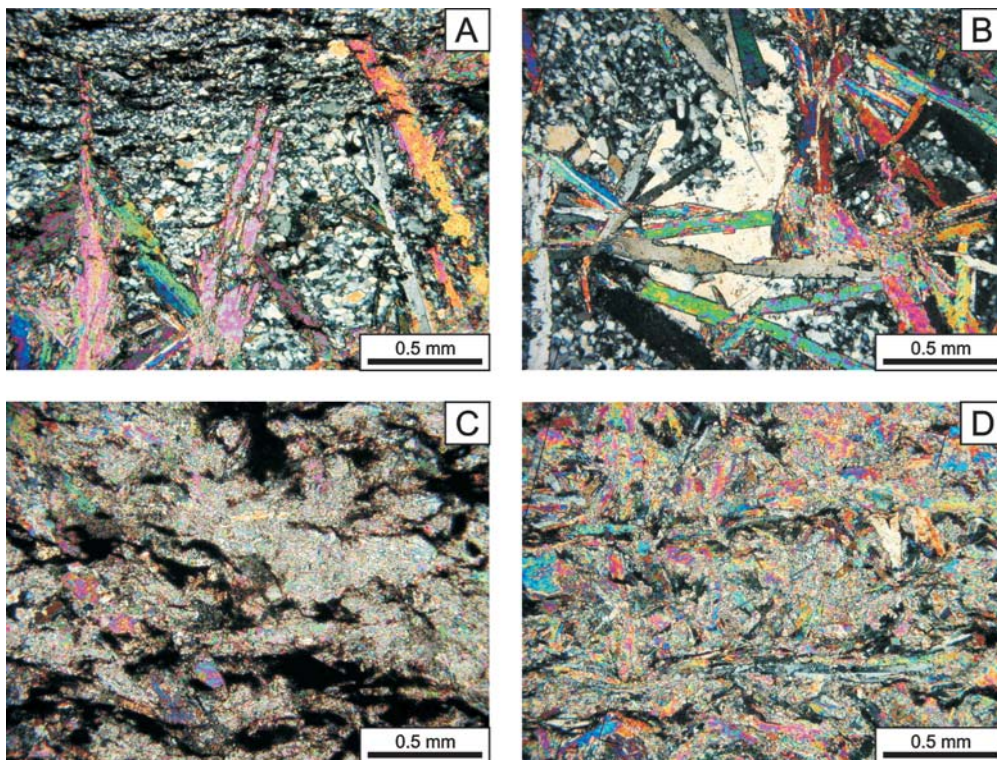


Fig. 6. Anhydritization of laminated clastic gypsum (platform facies, upper member)

A–B — decussate anhydrite laths crosscutting the clayey laminae and larger gypsum crystals (replacive fabric) in gypsarenite, core P-U19, **A** — depth 429.7 m, **B** — 434.7 m; **C** — anhydrite pseudomorphs after detrital gypsum in clay-carbonate matrix, core R-1, depth 927.6 m; **D** — irregular laminated anhydrite with elongated and deformed laths showing preferential subvertical or subparallel orientation (displacive fabric), core R-1, depth 922.3 m; microphotographs, crossed polars

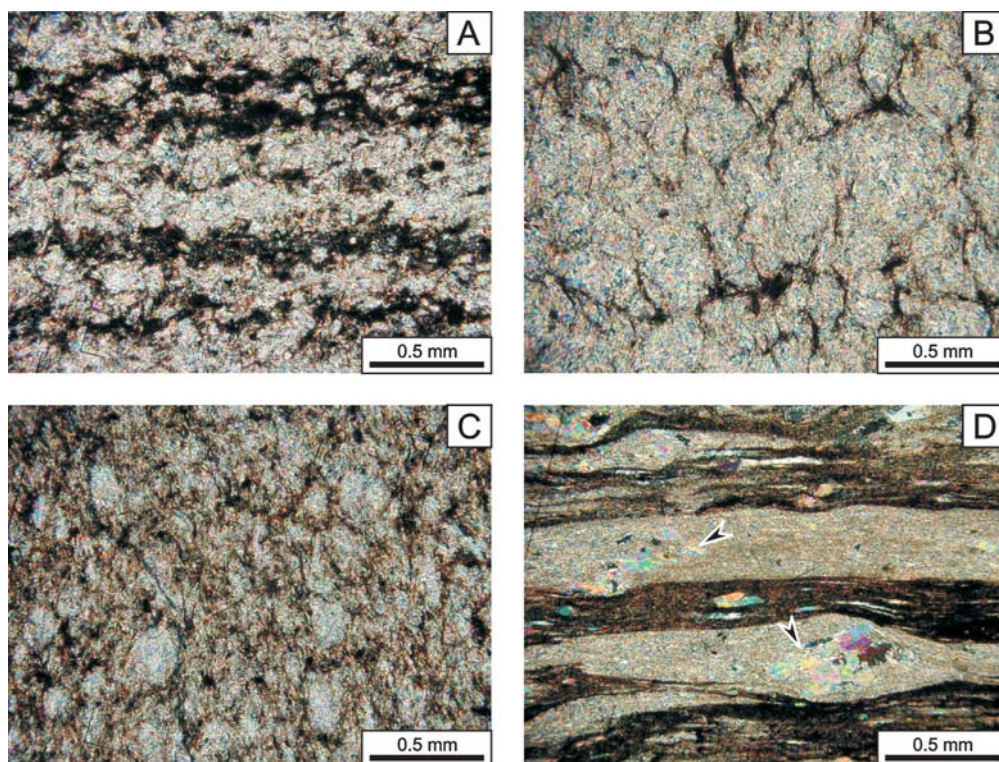


Fig. 7. Anhydritization of laminated clastic gypsum (basinal facies, upper member)

A — laminated anhydrite with pseudomorphs after detrital gypsum, core T-79k, depth 1427.3 m; **B, C** — micronodular laminated anhydrite with micronodules slightly rounded to aligned, some of which seem to be pseudomorphs after gypsum crystals: **B** — core T-66, depth 1486.9 m, **C** — core T-50, depth 1490.0–1494.0 m; **D** — irregular (flaser-like) laminated anhydrite with recrystallized in part pseudomorphs after halite crystals (arrowheads) grown displacively within clay-bituminous-anhydrite matrix, core T-79k, depth 2049.0–2053.0 m; microphotographs, crossed polars

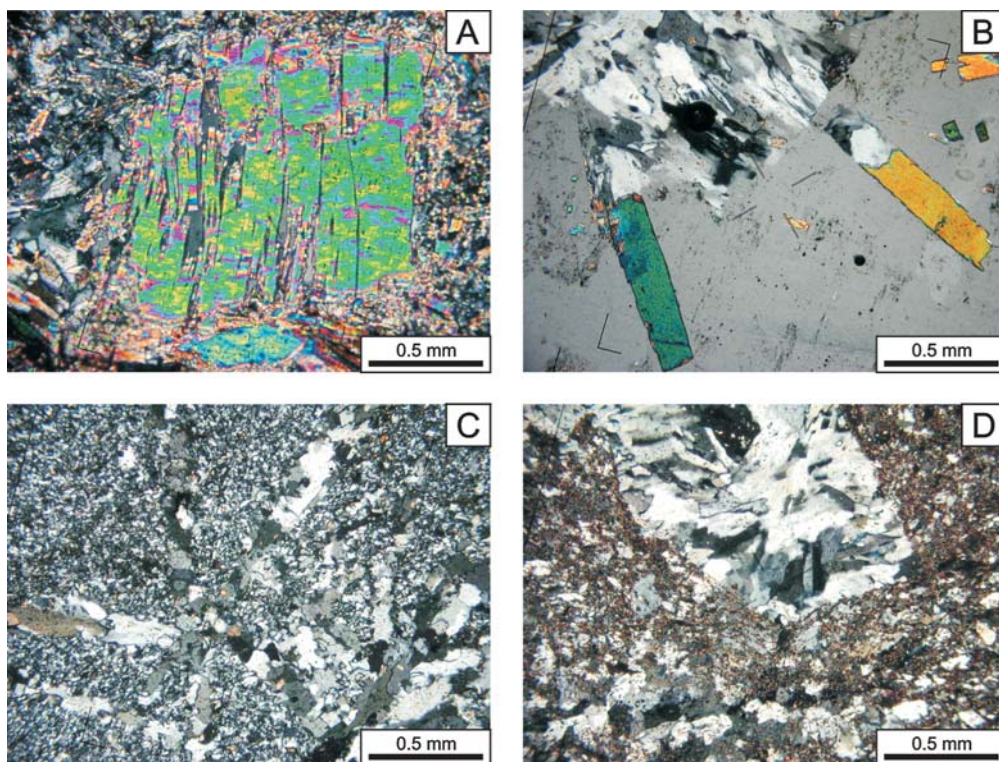


Fig. 8. Rehydration of anhydrite

A — relict anhydrite crystal replaced preferentially along the boundaries and cleavage planes by secondary gypsum, core B-11, depth 264.6 m; **B** — initial replacement of anhydrite laths by cloudy-ameboidal secondary gypsum within a selenite crystal, core O-31/9, depth 287.1 m; **C** — final stage of anhydrite replacement by secondary gypsum; pseudomorphs of cloudy-ameboidal secondary gypsum after randomly oriented anhydrite laths are distinct, core O-31/9, depth 257.9 m; **D** — pseudomorph of cloudy-ameboidal secondary gypsum after a large gypsum crystal in gypsarenite, core P-U19, depth 414.3 m; microphotographs, crossed polars

sulted in partial or complete rehydration of anhydrite to gypsum (secondary gypsum) at the surface by meteoric waters, or in the subsurface by low-salinity groundwaters. Uplift and exhumation were most probably determined by tectonic activity at the basin margin (Kubica, 1992). This rehydration, however, did not completely destroy the primary sedimentary and crystalline features (Fig. 2). Additionally, no significant difference in thickness of equivalent layers has been observed (Kasprzyk, 1995). The secondary gypsum displays microcrystalline, porphyroblastic or cloudy-ameboidal fabrics (terminology after Ortí Cabo, 1977; Ciarapica *et al.*, 1985; Fig. 8). The latter is characterized by lattice deformation and defects within developing crystals, suggesting relatively fast growth and local deformation by volume increase (Lugli, 2001). Microcrystalline aggregates appear commonly to be in optical continuity with the fine-grained primary gypsum matrix.

Effects of rehydration (secondary gypsum porphyroblasts and cloudy ameboidal aggregates, veins of fibrous gypsum) partly obliterated the anhydrite microstructures and crystal habits, but sporadically the secondary gypsum pseudomorphs still permit the distinction of former components, both anhydrite laths and primary gypsum crystals (Fig. 8B–D; Kasprzyk and Ortí, 1998). In that case, the replacement must have occurred with a negligible volume increase. The excess sulphate produced during rehydration has probably been expelled through permeable zones in the shallow subsurface.

REPLACEMENT AND RECRYSTALLIZATION

Many fabrics of the Badenian anhydrite display large laths affected by severe deformation and partial recrystallization (Fig. 9) at the crystal boundaries, where the anhydrite matrix replaces these laths (Fig. 9A). Similarly, large blocky anhydrite crystals composing pseudomorphs may be in part recrystallized, so that the original crystal boundaries are difficult to distinguish (Fig. 7D). This modification of early anhydrite fabrics most probably occurred during burial (Fig. 3). Replacement of sulphate by celestite (a type of “reaction pair” replacement in Spencer and Lowenstein, 1990) is common in the Badenian evaporite basin (Fig. 9D, G), suggesting an increased content of strontium in the diagenetic fluids. Although this replacement type can form by syndepositional interaction between the original mineral and the evaporating mother brine (Spencer and Lowenstein, 1990), the recognition of gypsum pseudomorphs with void-filling cement fabric and a celestite core suggests rather late diagenetic replacement (Fig. 3). Pseudomorphs of calcite and pyrite after gypsum crystals (Fig. 9E, F, H) must have involved fluctuating solution compositions and the introduction of a new solution. The presence of silica replacing the anhydrite fabrics (Fig. 9F) indicate that sulphate (gypsum, anhydrite) was easily affected by different phase replacement, i.e. replacement of sulphate by other minerals unrelated chemically to each other (“non-reaction pair” replacement in Spencer and Lowenstein, 1990), most probably during late diagenesis in both burial and at outcrop (Fig. 3). This kind of pseudomorphous replacement implies the introduction of a new solution dissolving gypsum without chemically reacting with it.

DIAGENETIC EVOLUTION

Gypsum in the Badenian basin has undergone syndepositional and diagenetic alteration to various degrees, depending on the local palaeogeographic and burial controls (Kasprzyk and Ortí, 1998; Fig. 2). These two main factors determined a complex paragenetic sequence and complex relationships between depositional and diagenetic processes, that may be resolved into three successive stages: syndepositional, early diagenetic, and late diagenetic, of Ca-sulphate formation and diagenetic evolution (Fig. 3). It should be noted, however, that there is a gradual transition from syndepositional to early diagenetic conditions, and therefore these terms have been frequently interchanged in the literature. Here, early diagenetic anhydrite is referred to as that anhydrite formed after the host sediment deposition and before its complete lithification in shallow (<250 m) burial environments, as defined earlier by Kasprzyk and Ortí (1998).

In the syndepositional stage, related to the sedimentary environment, deposition of selenitic and laminated clastic gypsum mainly took place. Deposition was accompanied by interstitial growth of sulphate nodules and/or anhydritization of selenitic gypsum expressed as replacive anhydrite growth (Figs. 3–5). All these processes must have continued during early diagenesis in the shallow burial environment. This stage also comprised precipitation of early sulphate cements in the lower member as well as bacterial sulphate reduction and replacement of gypsum by pyrite in the starved deep basin (Fig. 3 and 9E, F, H). The early diagenetic stage was characterized by intense sediment compaction of the upper member. That process continued following the syndepositional/early diagenetic anhydritization of gypsum deposit (displacive anhydrite growth), resulting in significant deformations (bending, breakage, reorientation) of the early anhydrite fabrics (Figs. 3, 6C–D and 7). At the basin margin, replacive anhydrite fabrics displaying negligible compactional effects and recrystallization features at the crystal boundaries suggest late diagenetic anhydritization (replacive anhydrite growth), accompanied or directly followed by partial dissolution and recrystallization of sulphate (Figs. 6A, B and 9A). During the late diagenetic stage, uplift, exhumation and/or erosion of sulphate deposits took place, probably related to tectonic activity at the basin margin. Tectonic fractures and joints provided high-permeability pathways for low salinity groundwaters that were diluting brines in the shallow subsurface. In this manner, the anhydrite rocks underwent a partial rehydration into gypsum (secondary gypsum). Although the time period during which rehydration of anhydrite occurred is difficult to define accurately, it is probable that this event was related to the late Badenian uplift of the basin postdating the evaporite deposition (Oszczypko, 1997). At the basin margins, anhydrite rocks were then exhumed, partly eroded and perhaps rehydrated into gypsum (Figs. 3 and 8). On the other hand, isotopic analysis of the crystallization water of secondary gypsum ($-74 \leq \delta D_{\text{‰}} \leq -113$; $-9 \leq \delta O_{\text{‰}} \leq -11$), corresponding to isotopically light water of a cold climatic period (Hałas and Krouse, 1982), indicate that the conversion of anhydrite back to gypsum occurred as sulphates reentered the meteoric realm and were bathed in cool and fresh pore fluids during exhumation or exposure. These data may

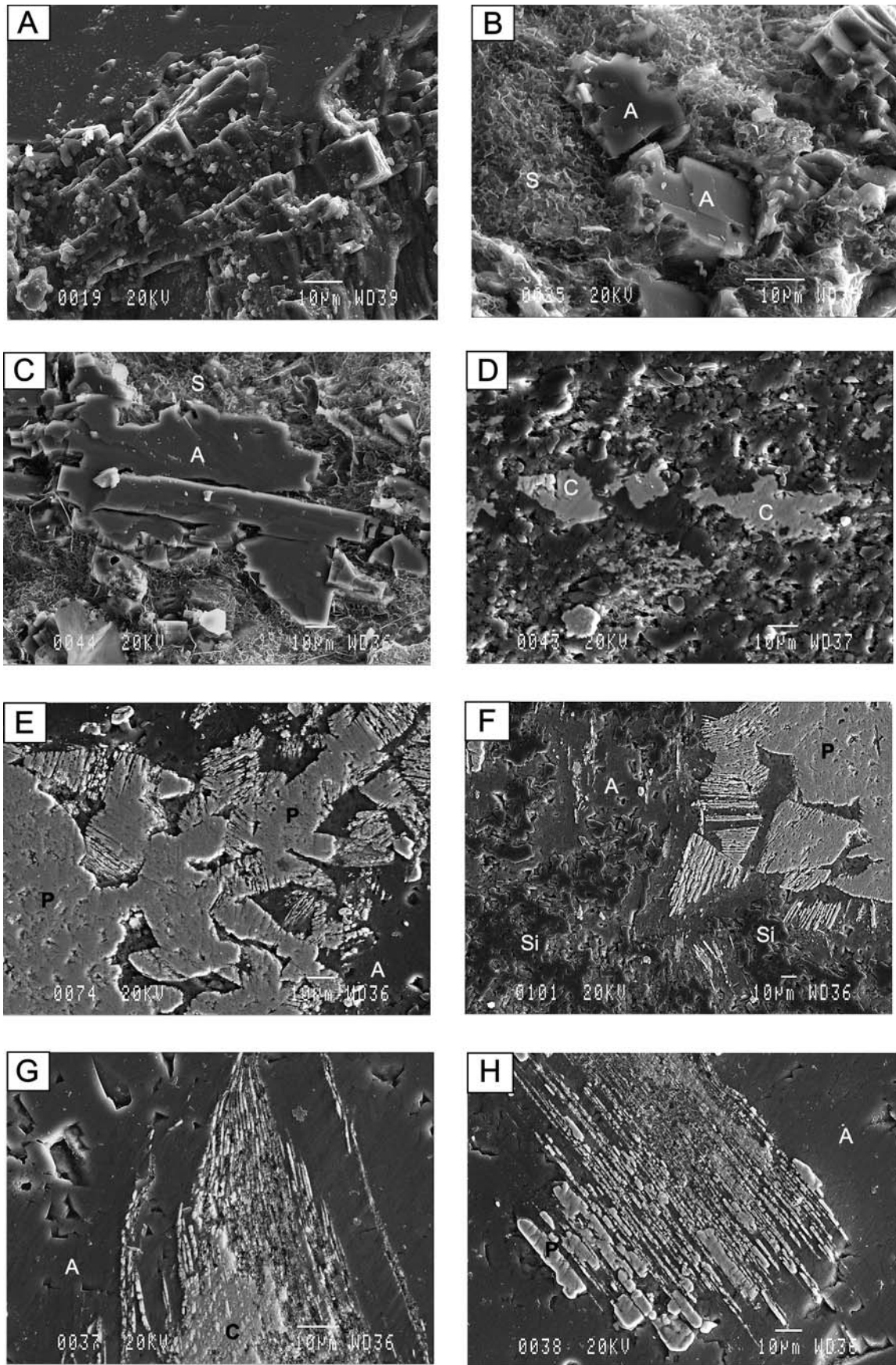


Fig. 9. Recrystallization and replacement of sulphate, SEM (SEI) images

A — anhydrite laths included into a macrocrystalline anhydrite crystal, core D-15, depth 1083.65 m, cleavage surface; **B–C** — anhydrite crystals (A) in a microcrystalline native sulphur (S), core D-15, depth 1081.4 m, cleavage surface; **D–H** — replacement of sulphate by celestite (C), silica (Si) and pyrite (P), note well-preserved pseudomorphs after primary gypsum crystals, background is presently anhydrite (A), core RW-7: **D** — depth 2410.1 m, **E–F** — 2410.65 m, **G–H** — 2410.45–2410.50 m, polished surfaces

suggest the origin of secondary gypsum or, alternatively, the isotopic exchange of its crystallization water, as a response to climatic cooling related to Pleistocene glaciation. Thus, the isotopic signature of Badenian secondary gypsum would reflect the recent history of its diagenesis. In any case, further investigations are necessary for better understanding of this problem.

A considerable contribution of low-salinity groundwaters or meteoric waters are suggested to be the main force in the water-rock interaction, including solution-reprecipitation phenomena. Thus, dissolution-reprecipitation processes resulted in the formation of anhydrite veins and other minerals (celestite, silica, calcite) replacing sulphate at a late stage (Figs. 3 and 9D, F–G).

ANHYDRITE GENESIS AND CONTROLLING FACTORS

Most Badenian anhydrite deposits display sedimentological and petrographic characteristics of diagenetic facies derived from subaqueous gypsum precursors. Three stages of diagenetic evolution: (1) syndepositional (the depositional stage), (2) early diagenetic (at the surface and during shallow burial), and (3) late diagenetic (during subsurface deep burial and exposure), each of them related to distinct palaeoenvironments, have been involved in anhydrite genesis and alterations (Figs. 3 and 4). The stratigraphic and lateral facies relations and the anhydrite fabrics succession record different genetic patterns for the two anhydrite members (Kasprzyk and Ortí, 1998; Kasprzyk, 2005a; Figs. 2 and 4). According to these patterns, in the lower member (restricted to the platform), anhydrite formed mainly by syndepositional anhydritization (*via* nodule formation and pseudomorphous replacement), whereas in the upper member (distributed throughout the platform and depocentre) successive stages (syndepositional, early diagenetic, late diagenetic) of anhydrite formation (both *de novo* growth and replacement of gypsum) occurred with increasing burial (Fig. 4).

The diagenetic evolution of Badenian sulphate deposits reflects both palaeogeographic and burial controls (Kasprzyk and Ortí, 1998). Additional factors that might also have influenced the genetic relations of gypsum-anhydrite and resulted in differentiation of the anhydrite pattern are: syndepositional tectonic movements controlling the basin morphology and hydrodynamics (geostructural constraints); temperature influencing the gypsum-to-anhydrite transition and the solubility products; the interplay between seawater influx, surface run-off and evaporative water loss, influencing a dynamic physicochemical regime in the shallow-water environments; and active bacterial sulphate reduction in anoxic bottom waters, thus favouring dissolution of gypsum and preservation of early diagenetic anhydrite due to the higher crystallization energy and lower solubility of the latter in the basinal settings. Gypsum is thought to be unstable in highly saline and O₂-poor waters (Sonnenfeld, 1984). Thus, in the deeper basinal environments of the Badenian basin, gypsum (the original sedi-

mentary product) could have been affected by anoxic bottom waters of high salinity, which exerted an important influence on anhydrite genesis. Accordingly, it can be assumed that the differentiated anhydritization pattern was related to physicochemical changes in depositional and diagenetic environments across the evaporite basin.

According to the proposed model, anhydritization of gypsum in the basin centre occurred mainly during early diagenesis (Fig. 4), which contrasts with the generally accepted idea that ancient basinal gypsum was transformed into anhydrite principally during deep burial (late diagenesis) (e.g. Langbein, 1987; Liszkowski, 1989; Kendall, 1992; Kendall and Harwood, 1996; Testa and Lugli, 2000). Additionally, there is no evidence of cumulative anhydrite formation by means of precipitation of the sulphate and settling in the brine column. In the Badenian basin, the influence of highly saline (chloride-rich), interstitial brines might have been fundamental to the anhydritization pattern (Kasprzyk, 1995, 2005b; Kasprzyk and Ortí, 1998).

CONCLUSIONS

In the Polish Carpathian Foredeep Basin the primary Ca-sulphate (gypsum) underwent alteration to various degrees, depending on the local palaeogeographic and burial controls. The signatures of successive changes in the deposits studied show a complex diagenetic evolution. This involves three stages: syndepositional (the depositional stage), early diagenetic (initial to shallow burial) and late diagenetic (subsurface deep burial and exhumation), each of them related to distinct palaeoenvironments. The comparison of platform and basinal successions suggests different patterns of anhydrite formation for the two sulphate members. The anhydrite of the lower member formed mainly by syndepositional anhydritization of gypsum rocks, whereas, for the upper member, successive phases, i.e. syndepositional *de novo* growth and early diagenetic to late diagenetic replacement of gypsum, were involved in anhydrite genesis. Many controlling factors, such as palaeogeographic setting, tectonic activity, geostructural constraints, physicochemical changes of the pore fluids, and so on, related to depositional and diagenetic (burial) environments, may have exerted an important influence on anhydrite genesis in the Badenian evaporite basin.

These results might be useful for studies of the facies and genesis of similar sulphate deposits in other ancient evaporite basins.

Acknowledgements. I greatly thank F. Ortí, J. J. Pueyo Mur and C. Taberner for helpful discussions. Special thanks are due to A. Gašiewicz, B. C. Schreiber and M. Narkiewicz for many constructive comments and remarks on an earlier version of the paper. The Polish Oil and Gas Exploration Company gave access to cores. The research was supported by the Polish Committee for Scientific Research.

REFERENCES

- BAŁEŁ M. (1999) — Facies and depositional environments of the Nida Gypsum deposits (Middle Miocene, Carpathian Foredeep, southern Poland). *Geol. Quart.*, **43** (4): 405–428.
- BAŁEŁ M. (2004) — Badenian evaporite basin of the northern Carpathian Foredeep as a drawdown salina basin. *Acta Geol. Pol.*, **54** (3): 313–337.
- BAŁEŁ M. (2005) — Gypsum facies and sedimentary evolution of the Badenian evaporite basin of the northern Carpathian Foredeep. *Acta Geol. Pol.* (in press).
- BUKOWSKI K. and SZARAN J. (1997) — Zawartość izotopów tlenu i siarki w anhydrytach z serii solonośnej Wieliczki i Bochni. *Prz. Geol.*, **45** (8): 816–818.
- CASAS E. and LOWENSTEIN T. K. (1989) — Diagenesis of saline pan halite: comparison of petrographic features of modern, Quaternary, and Permian halites. *J. Sediment. Petrol.*, **59**: 724–739.
- CENDÓN D. I., PERYT T. M., AYORA C., PUEYO J. J. and TABERNER C. (2004) — The importance of recycling processes in the Middle Miocene Badenian evaporite basin (Carpathian foredeep): palaeoenvironmental implications. *Palaeogeogr. Palaeoclimat. Palaeoecol.*, **212**: 141–158.
- CIARAPICA G., PASSERI L. and SCHREIBER B. C. (1985) — Una proposta di classificazione delle evaporiti solfatiche. *Geol. Rom.*, **24**: 219–132.
- GARLICKI A. (1979) — Sedimentation of Miocene salts in Poland (in Polish with English summary). *Pr. Geol.*, **119**.
- GUNATILAKA A. (1990) — Anhydrite diagenesis in a vegetated sabkha, Al-Khيران, Kuwait, Arabian Gulf. *Sediment. Geol.*, **69**: 95–116.
- HAŁAS S. and KROUSE H. R. (1982) — Isotopic abundances of water of crystallization of gypsum from the Miocene evaporite formation, Carpathian Foredeep, Poland. *Geochim. Cosmochim. Acta*, **46** (2): 293–296.
- HARDIE L. A. (1984) — Evaporites: marine or non-marine. *Am. J. Sc.*, **284**: 193–240.
- HARDIE L. A., LOWENSTEIN T. K. and SPENCER A. J. (1985) — The problem of distinguishing between primary and secondary features in evaporites. In: *Sixth International Symposium on Salt* (eds. B. C. Schreiber and H. L. Hamer), **1**: 11–39. Salt Institute, Alexandria, Virginia.
- HOVORKA S. (1992) — Halite pseudomorphs after gypsum in bedded anhydrite — clue to gypsum-anhydrite relationships. *J. Sediment. Petrol.*, **62**: 1098–1111.
- KASPRZYK A. (1995) — Gypsum-to-anhydrite transition in the Miocene of southern Poland. *J. Sediment. Res.*, **A65** (2): 348–357.
- KASPRZYK A. (1999) — Sedimentary evolution of Badenian (Middle Miocene) gypsum deposits in the northern Carpathian Foredeep. *Geol. Quart.*, **43** (4): 449–465.
- KASPRZYK A. (2003) — Sedimentological and diagenetic patterns of anhydrite deposits in the Badenian evaporite basin of the Carpathian Foredeep, southern Poland. *Sediment. Geol.*, **158**: 167–194.
- KASPRZYK A. (2005a) — Genetic patterns of Badenian anhydrite deposits in the Carpathian Foredeep, southern Poland (in Polish with English summary). *Prz. Geol.*, **53** (1): 47–54.
- KASPRZYK A. (2005b) — Constraints of anhydritization of Badenian gypsum deposits in the Carpathian Foredeep. *Biul. Państw. Inst. Geol.* (in press).
- KASPRZYK A. and ORTÍ F. (1998) — Palaeogeographic and burial controls on anhydrite genesis: a case study from the Badenian basin in the Carpathian Foredeep (southern Poland, western Ukraine). *Sedimentology*, **45**: 889–907.
- KENDALL A. C. (1992) — Evaporites and diagenesis: quantitative diagenesis. In: *Recent Developments and Applications to Reservoir Geology — Abstracts. North Atlantic Treaty Organization (NATO), Advanced Study Institute, Univ. Reading*.
- KENDALL A. C. and HARWOOD G. M. (1996) — Marine evaporites: arid shorelines and basins. In: *Sedimentary Environments: Processes, Facies and Stratigraphy* (ed. H. G. Reading): 281–324. Blackwell Sc.
- KUBICA B. (1992) — Lithofacial development of the Badenian chemical sediments in the northern part of the Carpathian Foredeep (in Polish with English summary). *Pr. Państw. Inst. Geol.*, **133**.
- KWIATKOWSKI S. (1972) — Sedimentation of gypsum in the Miocene of southern Poland (in Polish with English summary). *Pr. Muz. Ziemi*, **19**: 3–94.
- LANGBEIN R. (1987) — The Zechstein sulfates: the state of the art. In: *The Zechstein Facies in Europe* (ed. T. M. Peryt). *Lect. Not. Earth Sc.*, **10**: 143–188.
- LISZKOWSKI J. (1989) — A new halogenetic model for the origin of Lower and early Middle Miocene salt formations of the Carpathian region, eastern Central Paratethys (in Polish with English summary). *Pr. Nauk. UŚL.*, **1019**.
- LUGLI S. (2001) — Timing of post-depositional events in the Burano Formation of the Secchia valley (Upper Triassic, Northern Apennines), clues from gypsum-anhydrite transitions and carbonate metasomatism. *Sediment. Geol.*, **140**: 107–122.
- NEY R., BURZEWSKI W., BACHLEDA T., GÓRECKI W., JAKÓBCZAK K. and ŚLUPCZYŃSKI K. (1974) — Outline of paleogeography and evolution of lithology and facies of Miocene layers in the Carpathian Foredeep (in Polish with English summary). *Pr. Geol.*, **82**.
- ORTÍ CABO F. (1977) — Aproximación al estudio petrográfico de las microestructuras de las rocas de yeso secundario y a su origen. *Rev. Inst. Geol.*, **32**: 87–152.
- ORTÍ CABO F. and ROSELL L. (1981) — Fábricas cristalinas de la anhidrita nodular y laminada. *Acta Geol. Hisp.*, **16**: 235–255.
- ORTÍ CABO F., PUEYO MUR J. J., GEISLER-CUSSEY D. and DULAU N. (1984) — Evaporitic sedimentation in the coastal salinas of Santa Pola (Alicante, Spain). *Rev. Inst. Geol.*, **38/39**: 169–220.
- OSZCZYPKO N. (1997) — The Early-Middle Miocene Carpathian peripheral foreland basin (Western Carpathians, Poland). *Prz. Geol.*, **45** (10): 1054–1063.
- PERYT T. M. (2000) — Resedimentation of basin centre sulphate deposits: Middle Miocene Badenian of Carpathian Foredeep, southern Poland. *Sediment. Geol.*, **134** (3–4): 331–342.
- PERYT T. M., SZARAN J., JASIONOWSKI M., HAŁAS S., PERYT D., POBEREZHSKYY A., KAROLI S. and WÓJTOWICZ A. (2002) — S and O isotope composition of the Badenian (Middle Miocene) sulphates in the Carpathian Foredeep. *Geol. Carpath.*, **53** (6): 391–398.
- POŁTOWICZ S. (1993) — Palinspastic palaeogeography reconstruction of Badenian saline sedimentary basin in Poland (in Polish with English summary). *Geol. AGH*, **19**: 203–233.
- ROSELL L., ORTÍ F., KASPRZYK A., PLAYÁ E. and PERYT T. (1998) — Strontium geochemistry of Miocene primary gypsum: Messinian of SE Spain and Sicily and Badenian of Poland. *J. Sediment. Res.*, **68**: 63–79.
- ROSEN M. R. and WARREN J. K. (1990) — The origin and significance of groundwater-seepage gypsum from Bristol Dry lake, California, USA. *Sedimentology*, **37**: 983–996.
- ROUCHY J.-M., BERNET-ROLANDE M. C. and MAURIN A. F. (1994) — Descriptive petrography of evaporites: application in the field, subsurface and laboratory. In: *Evaporitic Sequences in Petroleum Exploration. TECHNIP Édition, Paris*: 70–123.
- SCHREIBER B. C. and EL TABAKH M. (2000) — Deposition and early alteration of evaporites. *Sedimentology*, **47**: 215–238.
- SCHREIBER B. C. and WALKER D. (1992) — Halite pseudomorphs after gypsum: a suggested mechanism. *J. Sediment. Petrol.*, **62**: 61–70.
- SHEARMAN D. J. (1985) — Syndepositional and late diagenetic alteration of primary gypsum to anhydrite. In: *Sixth International Symposium on Salt* (eds. B. C. Schreiber and H. L. Harner), **1**: 41–50. Salt Institute, Alexandria, Virginia.
- SONNENFELD P. (1984) — Brines and evaporites. *Acad. Press. Orlando*.
- SPENCER R. J. and LOWENSTEIN T. K. (1990) — Evaporites. In: *Diagenesis* (eds. I. A. McIlreath and D. W. Morrow): 141–163. *Geoscience. Canada*.
- TESTA G. and LUGLI S. (2000) — Gypsum-anhydrite transformations in Messinian evaporites of central Tuscany (Italy). *Sediment. Geol.*, **130**: 249–268.
- VENGLYNSKYI I. V., PANOVA G. M., ROSUMYEIKO S. V., POLKUNOV V. F., ROSKOSZ Y. T. and LEMYSZKO O. D. (1982) — Stratigraphy, facies and palaeogeographic conditions of the Miocene evaporite formation of the Volyn-Podolian plate, and Forecarpathian and Transcarpathian foredeeps (in Russian). *Ukrainian Academ. Sc. Lvov*.
- WARREN J. K. (1982) — The hydrological setting, occurrence and significance of gypsum in late Quaternary salt lakes in South Australia. *Sedimentology*, **29** (5): 609–637.