

DIAGENESIS OF THE MARLY-GYPSUM FORMATIONS, IGOUMENITSA AREA, N.W. GREECE

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Abstract

The Igoumenitsa area, in northwestern Greece, is composed of organic-rich clay evaporitic formations, of the Ionian zone. They have undergone diagenetic processes, which effect the mineralogical transformations. The purpose of this paper is the study of the mineralogical diagenesis and the possible implications to the geotechnical behavior of these organic-rich clay evaporitic sedimentary rocks. The diagenetic minerals reported in this study are: A: The authigenic swelling clay minerals, smectite and mixed layers of smectite. B. The two characteristic minerals phases of the sulfate diagenesis: 1. Bassanite (semi hydrated gypsum-CaO₄.1/2H₂O) and 2. Celestite (SrSO₄) that can be considered as an indicator of bacterial sulphate reduction, fluid flow and recycling of evaporites. The two authigenic minerals have derived from the evaporites, mostly by the dehydration of gypsum and by the action of pore water that is charged with the ions derived from the dissolution of pre-existent sulfates, halite and carbonates. C. The neoformation of the carbonate minerals aragonite and dolomite, due to probably bacterial sulfate reduction.

When organic-clay rich sediments, are associated to evaporites, the diagenetic processes become more complex and interacted. The diagenetic alterations of the gypsum/anhydrite rocks are related to the geotechnical behavior of the formation and may lead to possible karstification. That may cause problems in roads and tunnels construction on or through these evaporitic series.

Key words: diagenesis, evaporites, celestite, bassanite, mixed layers, karstification.

Περίληψη

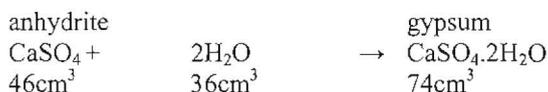
Η περιοχή της Ηγουμενίτσας στην βορειοδυτική Ελλάδα, συνίσταται από αργιλο-εβαποριτικές αποθέσεις πλούσιες σε οργανικό άνθρακα της Ιονίου ζώνης. Ο σχηματισμός έχει υποστεί διαγενετικές διεργασίες που επηρεάζουν τους ορυκτολογικούς μετασχηματισμούς. Ο σκοπός αυτής της εργασίας είναι η μελέτη της διαγένεσης των ορυκτών και οι πιθανές επιπτώσεις αυτής στη γεωτεχνική συμπεριφορά του σχηματισμού. Τα διαγενετικά ορυκτά του σχηματισμού που αναφέρονται σε αυτή τη εργασία είναι: Α. Αυθιγενή μεικτά αργιλικά ορυκτά σημηκτίτης και μεικτές άργιλοι του σημηκτίτη. Β. Τα δύο χαρακτηριστικά ορυκτά της διαγένεσης των θειικών ορυκτών 1: Ο βασσανίτης (ημιένυδρος γύψος CaO₄.1/2H₂O) και 2: Ο σελεσίτης (SrSO₄), που μπορεί να θεωρηθεί ότι είναι ένδειξη βακτηριακής αναγωγής των θειικών, ροής ρευστών και ανακύκλωσης των εβαποριτών. Τα δύο αυτά ορυκτά προέρχονται από τους εβαπορίτες και κυρίως από την διάλυση της γύψου, μέσω της

δράσης των πορικών διαλυμάτων, φορτισμένων με ιόντα από την προηγούμενη διάλυση θεικών, αλίτη και ανθρακικών. Γ. Ο νεοσχηματισμός των ανθρακικών ορυκτών αραγωνίτη και δολομίτη, πιθανών λόγω βακτηριακής αναγωγής των θεικών. Όταν με τους εβαπορίτες συνυπάρχουν αργιλικό σχηματισμοί με διασταλτά αργιλικά ορυκτά και οργανική ύλη, τότε οι διαγενετικές διεργασίες φαίνονται πολύπλοκες και ανταγωνιστικές. Οι διαγενετικές μεταροπές γύψου/ανυδρίτη σχετίζονται με την γεωτεχνική συμπεριφορά του σχηματισμού και μπορεί να προκαλούν καρστικοποίηση. Αυτό μπορεί να δημιουργεί προβλήματα στην κατασκευή δρόμων και σιράγγων στους εβαποριτικούς σχηματισμούς.
Λέξεις κλειδιά: διαγένεση, εβαπορίτες, σελεσίτης, βασσανίτης, μεικτοί άργιλοι, καρστικοποίηση.

1. Introduction

In nature, calcium sulfate occurs in different mineral forms: as gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite CaSO_4 , the two end members end as the interval, bassanite $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$. The transformation from gypsum to anhydrite and reverse depends on certain conditions as the temperature, the pressure and the amount of water available. Only anhydrite is stable above 58°C at a pressure of 100 kPa approximately. Gypsum is stable below 38°C in the presence of water. When water is not available anhydrite may still occur at these lower temperatures.

The transformation of anhydrite to gypsum, causes considerable volume change, as shown in the equation (Wittke 1990):



The specific volume of crystallized gypsum is 61 % greater than that of anhydrite. In contrast, anhydrite and two molecules of water possess a volume 11% greater than that of gypsum.

The anhydrite is metastable especially at small depths and tends to rehydrate to gypsum when it comes to contact with circulating groundwater within the near-surface zone (Murray 1964, Holliday 1970). This reaction involves a volume increase of 30-58 %, (Blatt et al 1980) which exerts pressures estimated between 2 and 70 Mpa. Volume changes are controlled by the porosities, before and after the diagenetic processes (Zanback and Arthur 1986). Therefore the phase transition between gypsum and anhydrite in both directions of the chemical reaction causes changes in volume between the original and the resultants minerals.

That adds to the potential hazards that increase even more with the associated marly clay deposits containing expansive clay minerals. It has been documented that expansive clay minerals intercalated with the dehydrating gypsum can absorb the liberated water of crystallization and expand to lift existing structures (Azam 1997). The volume-change behavior of incorporating expansive clay minerals depends on the form and amount of the present calcium sulfate (Azam 2003).

The deformation behavior of a dehydrating rock depends strongly on whether the system is drained or undrained. In the former case pore pressure does not built up and the rock may strengthen if the product phase are stronger than the reactants. In the later case, however, the rock will show a dramatic weakening and possibly embrittlement as pore pressure increases and the effective pressure is reduced to zero (Olgaard *et al.* 1995).

Gypsum and anhydrite, not to mention halite, are readily soluble in water. As gypsum is susceptible to rapid dissolution wherever there is active circulation of groundwater that is undersaturated with respect to calcium sulfate, substantial underground voids and cave system may develop. The spontaneous collapse of individual caverns allows upward migration of voids,

either by gradual caving of thinly bedded strata or occasionally by the sudden failure of more competent thickly bedded rocks, leading ultimately to subsidence of the overlying ground. Even more the complete dissolution of evaporitic minerals leads to problems concerning the residual deposits caused by gypsum removal and collapse.

Where there is a pore water flow, the high dissolution rate of gypsum and the aggressive nature of sulfate-rich water make the problem more intense. The diagenetic processes affect the porosity and permeability of the formation, which are of particular importance. The diagenetic alterations in evaporites have major impact on the geotechnical characteristics of the formation as in the case of tunneling (Georgiannou 2005) or road and bridge construction (Cooper and Sauders 2002, Johnson 2002).

2. Geological setting

The Igoumenitsa area formations belong to the Ionian Zone (NW Greece-Epirus region) that is part of the most external zones of the Hellenides. The rocks of the Ionian Zone range from Triassic evaporites and associated breccias through various series of Jurassic to Upper Eocene carbonates and to a lesser degree, cherts and shales followed by Oligocene flysch, (Rigakis and Karakitsios 1998).

The sub-evaporite formations of the Ionian Zone in Western Greece do not crop out nor were penetrated during drilling projects (BP 1971).

The wide Triassic evaporitic outcrops run parallel to the strike of the Hellenides thrust faults. They acted as the plane of decollement for thrust-sheet emplacement over much of the external Hellenides. Plio-Quaternary diapirs occur locally within the broad outcrops of the Triassic evaporites, as a result of local mobilization, due to thrust-sheet loading and resulting heating effects (Underhill 1988). Exposed diapirs are dominated by gypsum (halite was recorded only in boreholes). Surface exposures show a wide range of gypsum petrofabrics (Underhill 1988). The Ionian zone in Epirus constitutes a good example of tectonic inversion in a basin with an evaporitic substratum (Karakitsios 1995).

3. Materials and methods

The analyzed samples were provided from investigation boreholes carried out for the needs of geotechnical tests prior the construction of Egnatia motorway. The Egnatia is running across Epirus and Northern Greece from the starting-point at Igoumenitsa to Evros, being one of the largest road construction projects in Europe comprises motorway, bridges, tunnels and river and railway crossings.

For the needs of the technical project there have been carried out numerous examinations, geotechnical tests, reports and drilled several holes to investigate the substrate.

The examined samples were collected from 8 drillholes of Krystallopigi area northeast of the town of Igoumenitsa, relative to the construction of S1-S2 tunnels. The penetrated sedimentary formations can be described as clay organic-rich evaporitic formations, with intercalations of clay-evaporites and marly/silty claystones.

The samples were consisted by gypsiferous marly /silty-claystones in the upper part (approximately up to the depth of 50-60m) and evaporite rocks with clayerly intercalations in the lower part (up to the depth of 90 m). All samples have significant organic content. The samples were mineralogical analyzed by powder-XRD using the Siemens 5005 diffractometer with Ni-filtered CuK_{α} radiation on randomly oriented samples. Clay mineralogy was identified after treatments of air-dried, glycolated and heat-treated oriented samples of the $<2 \mu m$ fraction of selected samples.

SEM and microprobe analysis was performed on slides as well as on natural samples using the SEM JEOL JSM-5600 equipped with EDX OXFORD LINK_{TM} ISIS _{TM 300}

4. Results and discussion

4.1. Mineralogical analysis

The identified minerals can be divided to evaporites and non evaporites.

Gypsum and anhydrite are the principal evaporite mineral phases, bassanite and celestite found as accessory sulphates.

The non evaporite minerals are quartz, (present in all samples, indicating the importance of terrigenous input into the formation) feldspars, calcite, dolomite, magnesite and clay minerals.

The penetrated formations can be petrologically divided into two units.

The upper unit of approximately 50-60m depths is consisted by organic rich evaporitic claystones –siltstones partly sandy or granular, usually with considerable plasticity. The clay minerals percentage with few exceptions ranges between 25-75 %. The evaporitic portion of this unit is 35-50 %.

The lower unit of approximately 50-95 m depths is consisted by organic rich evaporitic deposits with intercalations of claystones. Evaporite minerals are predominant in the formation. The dominate evaporitic mineral is gypsum, anhydrite is up to 10 %, whereas bassanite has been identified in a few samples only, at the depth of 80-90 m. Celestite was found in the lower part unit samples.

Organic matter is present in all samples favored by the establishment of evaporitic sediments (Karakitsios 1998). Dolomite is present in most of the samples along with calcite. Its presence is expected by the act of groundwater and seawater flow within the upper most meters of the formation on carbonates and gypsum. In the process fine crystalline and geochemical distinct dolomite, is formed either as a replacement or cement (Machel and Mountjoy 1986).

4.1.1. Clay minerals

The clay mineralogy was performed on the clay fraction <2 μ m on selected samples of both units. The identified clay minerals and their proportion are kaolinite, illite, chlorite, smectite and mixed layers (Figs 1, 2, 3, 4), as shown in table 1. These clays are quite expected as they are associated with organic and evaporative environments (Chamley 1989, Tsioura-Vlachou 1991).

Part of the clay minerals is of terrigenous origin and another part is authigenic, as product of diagenetical procedures caused by the action of the pore water flow.

As smectite (montmorillonite) (Fig. 2) and mixed layers illite/smectite) (Figs 3, 4) and corrensite (mixed layers smectite/chlorite) (Fig. 1) are swelling clay minerals, their presence may have impact on the porosity and permeability of the formation.

Table 1 - indicative clay mineral proportions % within the clay fraction

Depth m	Illite	Kaolinite	Chlorite	Smectite-mixed/layers
10-15	30-60	30-40	0-12	0-16
40-50	50	28	16	5
60-70	49	30	15	6
80-90	45	35	12	8

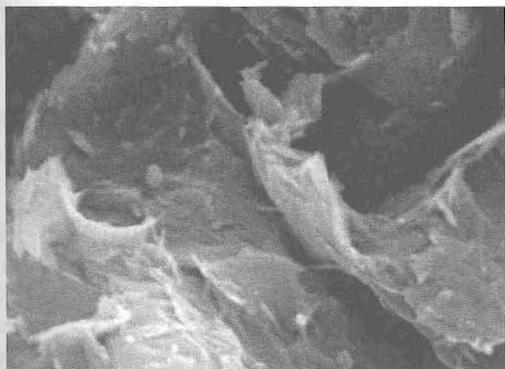


Figure 1 - Authigenic smectite/chlorite

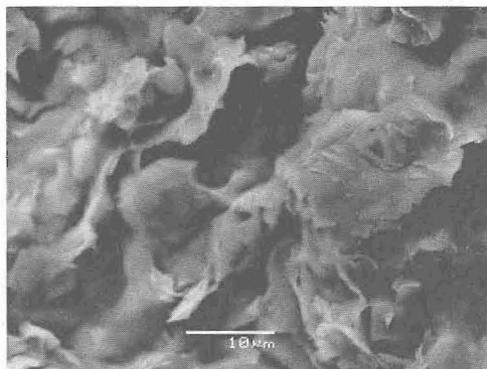


Figure 2 - Authigenic smectite

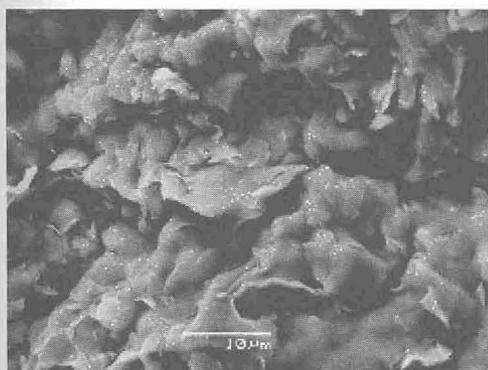


Figure 3 - Authigenic Illite (dust line) and illite/smectite filling pores

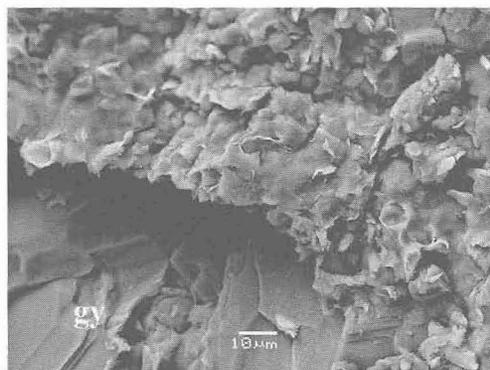


Figure 4 - Smectite and mixed layers on gypsum

4.1.2. Evaporite minerals

4.1.2.1. Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, bassanite $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, anhydrite CaSO_4

Bassanite is the middle member of gypsum - anhydrite phase.

Transformation of gypsum to bassanite or anhydrite occurs at relatively high ambient temperatures and/or high brine salinities (Hardie 1967). Gypsum crystals show various dissolution types as cavities (Figs 9, 13), patterns (Figs 5, 10), cracks (Figs 6, 13, 19), surface smoothing (Figs 9, 10).

They also are affected by physical stresses and deformed in the form of ductile (Fig. 15) or brittle (Figs 15, 16, 19, 20). Etching on the crystal surface of gypsum has been observed (Figs 5, 10). That can be attributed to the action of bacteria. Petrified bacterial rods were also observed (Fig. 9).

The association of dissolved sulfate and hydrocarbons is thermodynamically unstable in diagenetic environments hence redox-reactions occur whereby sulfate is reduced by hydrocarbons with concomitant oxidation of the organic compounds, either bacterially (bacterial sulfate reduction BSR) or inorganically (thermochemical sulfate reduction TSR), with similar products (Machel 2001).

The occurrence of bassanite has been observed only at certain samples of the evaporitic formation, especially at depths around 90 m, whereas the paragenesis of gypsum-anhydrite in various proportions is present in the whole length of the drilling holes. That suggests that special conditions are required for the formation of bassanite, as a middle member of the gypsum-anhydrite phase.

Experimental tests of dehydration of gypsum show that the transformation depends on the water pressure and the intermediated formation of calcium sulfate hemihydrated occurs at higher water

pressures than the calcium sulphate dehydrated (Badens et al 1998). The new phase, bassanite, shows also different technical characteristics than gypsum, as exceptional strengthening (Orgaard *et al.* 1995).

The development of pore fluid pressure in dehydrating rocks is a competition between the reaction, which produces water and the change in permeability caused by the reduction in solid volume.

In the examined samples bassanite may show a topotactic relationship with gypsum (Figs 7, 8), which suggest that a certain degree of recrystallization took place, (Moiola Glover 1965, Mees and De Dapper 2005). The initial development of bassanite around gypsum in pores was probably caused by an interaction with saline brines derived from the surface and/or from the formation itself. Bassanite-anhydrite transitions were not noticed, but cannot be excluded since they have been documented (Mees 1998). Bassanite occurs as isolated crystals (Fig. 8) or as aggregates (Fig. 7), as the nature of bassanite textures can change with depth and are determined by vertical variations in the nature of gypsum occurrences, temperature, water availability and salinity (Mees *et al.* 2005).

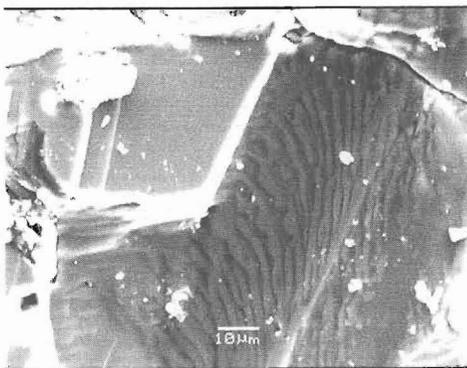


Figure 5 - Dissolution patterns of gypsum

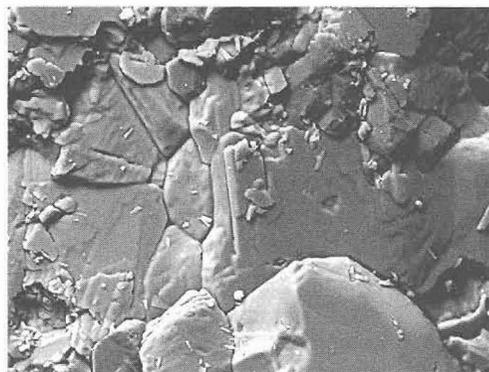


Figure 6 - Interlocking crystals of gypsum



Figure 7 - Bassanite (small crystals) on gypsum

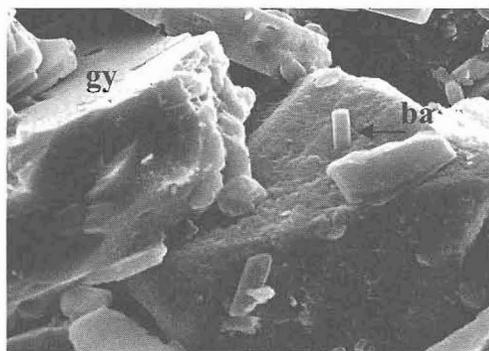


Figure 8 - Bassanite small crystals generating from gypsum

4.1.2.2. Celestite $SrSO_4$

The presence of celestite is not unusual in evaporite deposits. Celestite occurs as crystals-nodules-cements in many sedimentary rocks, particularly in evaporitic dolomites-limestones but also in dolomitic limestones and marls (Warren 1999).

Many mechanisms have been proposed for celestite formation (Scholle *et al.* 1990). It is formed more usually by the interaction of gypsum or anhydrite with Sr-rich waters (Kushnir 1986). The dissolution of calcium sulphate supplies SO_4 which then combines with Sr to precipitate as

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celestite. Generally, in a replacement a more soluble mineral will always be replaced by a less soluble, since the solubility products for anhydrite, gypsum and celestite are 10-4.6, 10-4.8 and 10-6.5 respectively (Ball *et al.* 1980), celestite should replace both anhydrite and gypsum.

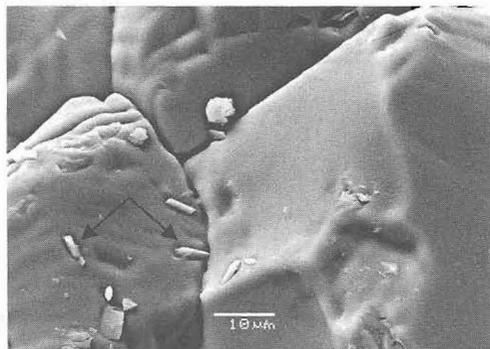


Figure 9 - Dissolution of gypsum and tiny petrified bacterial rods (arrows)

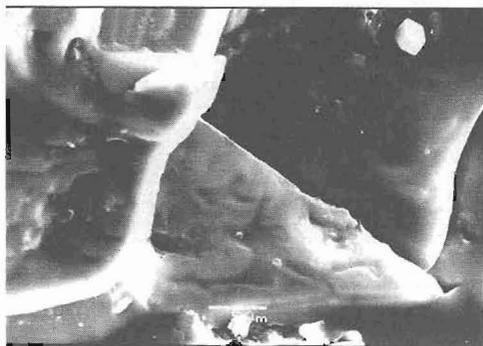


Figure 10 - Dissolution patterns of gypsum

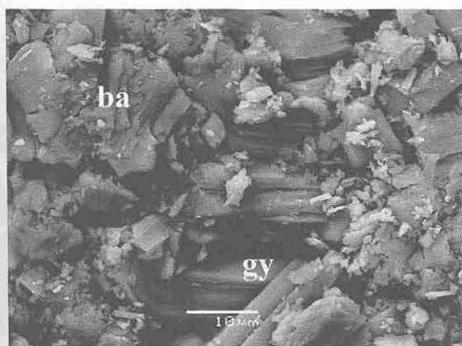


Figure 11 - Deformed gypsum (center) and bassanite

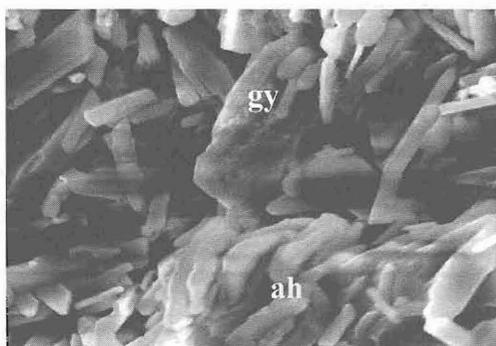


Figure 12 - Anhydrite small crystals and gypsum (center)

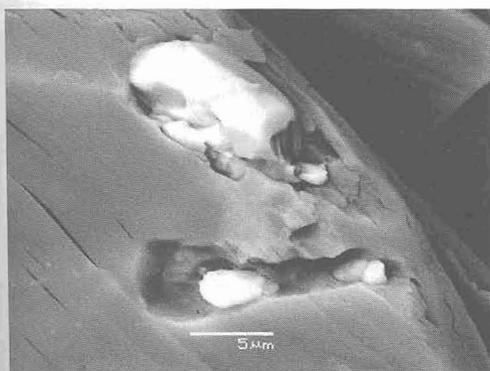


Figure 13 - Celestite crystals in vugs on gypsum

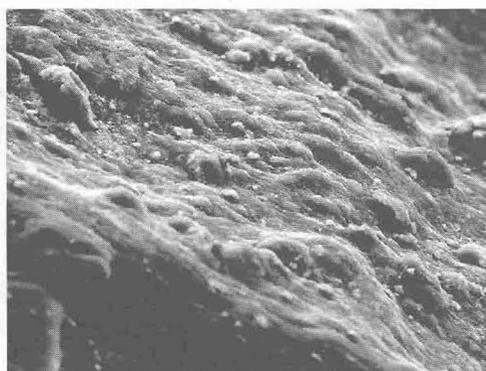


Figure 14 - Celestite crystals spread over gypsum

The presence of celestite (SrSO_4) suggests the alteration of anhydrite to gypsum. Anhydrite dissolution may be the main source for Sr (Jacobson and Wasserburg 2005). Sr rich waters may also derived during the conversion of gypsum to anhydrite (Kushnir 1982). Sr is believed to occupy the Ca sites in the vugs gypsum lattice, where it can be enriched ten times over the Sr content in enclosing dolostones (Carlson 1987). Dolomite is present in all the examined samples, in all boreholes (Fig. 10).

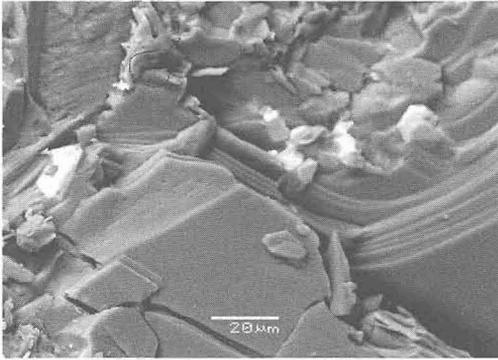


Figure 15 - Deformation (ductile) of gypsum, dissolution pits and celestite crystals

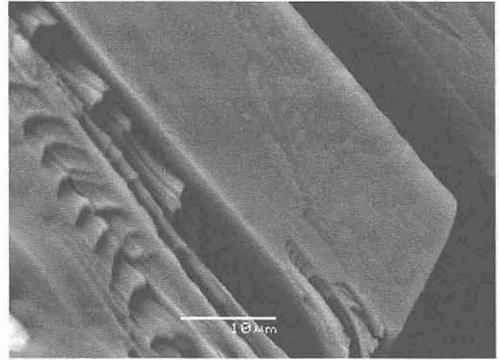


Figure 16 - Dissolution patterns and breakage of gypsum

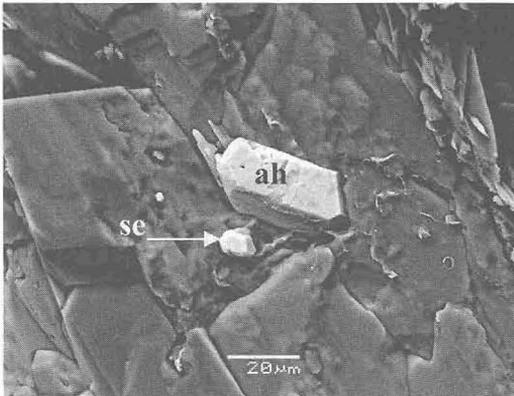


Figure 17 - Dissolution patterns on gypsum and isolated anhydrite, celestite crystals (white)

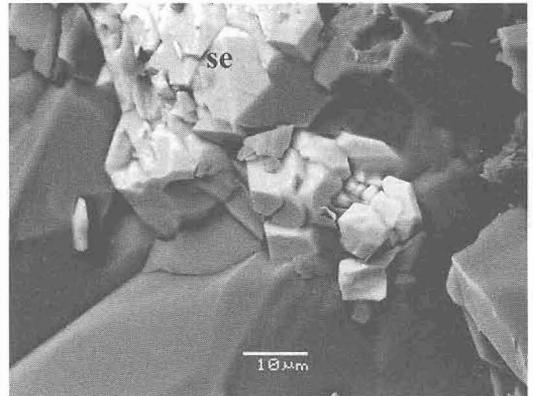


Figure 18 - Celestite (ce) aggregates on gypsum

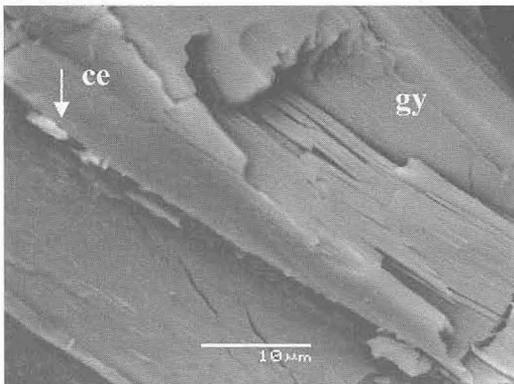


Figure 19 - Celestite (ce) developed on boundaries of deformed gypsum (gy)

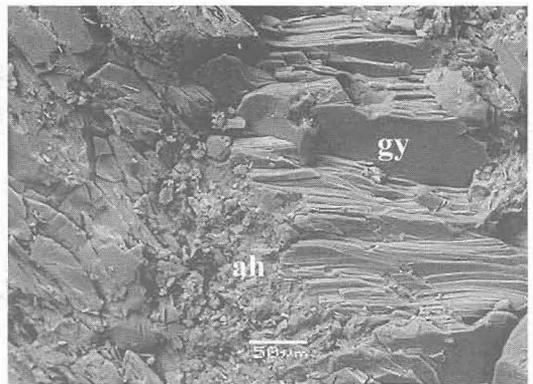


Figure 20 - Anhydrite (ah) crystals between gypsum (gy)

Celestite also, may have precipitated from SO_4 -enriched pore waters via the solution of calcium sulphate. That assumption is supported by the formation of tiny celestite crystals that fill in cavities created by the dissolution of the gypsum/anhydrite precursor (Warren 1999), (Fig. 1). Initial anhydrite incorporating Sr, becomes extremely slowly hydrated to gypsum which then

contains 0.40 g of SrO per mole, the rest of the strontium being found as tiny crystals of celestite spread all over the mass (Icart *et al.* 1965) (Fig. 14). Concluding, the precipitation of celestite in the formation may be attributed to:

- Water formed during the conversion of gypsum to anhydrite (Icart *et al.* 1965, Kushnir 1982, Warren 1999)
- Water that have leached Sr from feldspars and clays (Scholle *et al.* 1990)
- Water formed during the dolomitization of limestones (Wood and Shaw 1976, Carlson 1983)
- Water that have dissolved gypsum (Warren 1999)

All the above sources of Sr were available in the formation. In addition, pore water may have leached out the more soluble halite, which was detected in boreholes elsewhere (Underhill 1988) and in that case, Sr concentrations typically increase significantly with salinity (Hanor 2004).

According to microscopic studies two petrographic types of celestite crystals have been observed:

a) sub-idiotropic – tabular (Fig. 18) and b) prismatic crystals (Fig. 17). They may form aggregates (Fig. 18) or most like appear isolated (Figs 13, 14, 15, 17, 19,). Finely divided celestite crystals seem to have precipitate only from highly supersaturated brines with high Sr content (Kushnir 1986).

4.1.2.3. Carbonate minerals

Neof ormation of aragonite and dolomite

The neof ormed carbonate minerals detected in this study are aragonite CaCO_3 and dolomite MgCO_3 .

A strong relation between gypsum deposits and neof ormed carbonate minerals is well established, (Pierre and Rouchy 1988, Youseff 1989, Machel 2001).

It has been observed that bacterial sulfate reduction favored the precipitation of the carbonate phase. This can be attributed to an increase in alkalinity accompanied by sulfate reduction, (Peckmann *et al.* 1999). It is favored by the organic content of the formation, since the process of transforming sulfate minerals in the presence of organic matter to carbonate minerals and native sulfur is expected and attributed to sulfate-reducing bacteria (Thode *et al.* 1954, Peckmann *et al.* 1999).

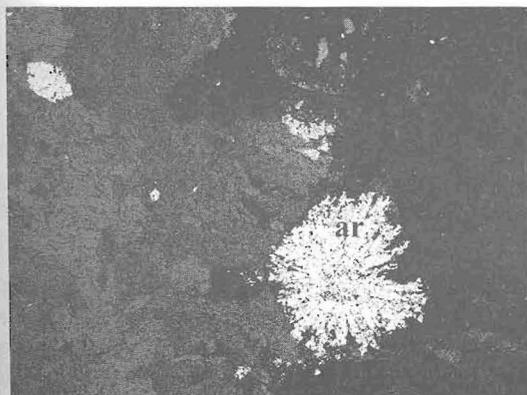


Figure 21 - Aragonite (ar) authigenesis

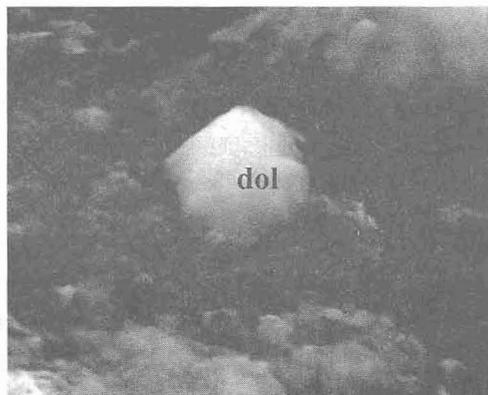


Figure 22 - Dolomite (dol) authigenesis

Aragonite crystals may display a radial habit (Fig. 21). Their formation may be attributed to the release of CO_2 by bacterial decomposition of organic matter, (Ricconi *et al.* 1996). They precipitate from pore water at elevated Mg/Ca ratio, that might favor the precipitation of aragonite

instead of calcite, (Peckmann *et al.* 1999). When Mg/Ca ratio increases, then dolomite will precipitate rather than aragonite or magnesite (Wright 1999). Saddle dolomite cement (Fig. 22).

The increase of magnesium levels in pore water can be attributed: a. to the dissolution of preexisting carbonates or b. to the bacteria desiccation. Magnesium is concentrated in bacterial cells and sheaths. When it is released due to desiccation, in hypersaline water with elevated concentrations of carbonate and sulfate ions, the Mg level, will be elevated (Wright 1999). The bacterial action seem to have impact on the sulfate phase reduction and the diagenetically neoformed minerals, (Machel 2001).

4.2. Porosity

The porosity of the evaporitic formations (lower part unit), that occurs at the depths of 50 to 95 m show variable values within a wide range. It appears low with interlocking gypsum crystals (Fig. 6) or clay minerals filling pores (Figs 3, 4), or higher with pore voids (Fig. 8). In various holes, the porosity was measured and found ranging between 0.31-5.20 %, 0.77-7.34 %, 2.98-8.83 % and up to 16.67-52.98 %. These values reflect the evaporite dissolution – diagenesis, and a potential karstification of the formation.

5. Conclusions

Evaporites are the most soluble of common rocks. They are readily dissolved to form the same types of karst features that are commonly found in limestone and dolomite that may include sinkholes, caves, disappearing streams, springs. Also contain evidence of paleokarst, such as dissolution breccias, breccia pipes slumped beds and collapse structures. Brecciation of the Triassic solution collapse breccias of the Ionian zone has been documented (Karakitsios and Pomoni-Papaioannou 1998). All these natural karst phenomena can be source of geoenvironmental problems. Considering that alternations in the forms of calcium sulfate under certain conditions, unlike the relatively slow formation of limestone karst, can take place in the time frame of engineering importance (Cooper and Sauters 2002), the construction of bridges and viaducts over actively dissolving gypsum karst is difficult.

Road construction over gypsiferous terrenes has to deal with these karst problems and poor ground conditions caused by collapsed strata. Further more the complete dissolution of gypsiferous beds can cause a residue of weak and brecciated strata, which also produces difficult conditions for construction. Where gypsum is present in bedrock either as massive beds or veins, it can be associated with sulphate rich groundwater that can be harmful even to concrete (Foster *et al.* 1995). Tunnels S₁ S₂ of the Egnatia Motorway were excavated through heavily fractured limestone and sheared sediments. The variety of the sedimentary formations and geological conditions resulted in considerable variability of tunnelling conditions and the need for extensive primary support measures and tests (Georgiannou 2005).

The four basic requirements for evaporitic karst to develop are: (1) gypsum or salt, (2) water unsaturated with CaSO₄ or NaCl, (3) an outlet for escape of the water, (4) energy to cause water to flow through the system, (Johnson 2002). All the above requirements are subsisted in the studied area:

Gypsum is present in all samples throughout the whole depth of the holes. Halite has been found elsewhere in deep holes in the formation and probably has been washed out in earlier stages. The porosity of the formation is considerable, although dissolution fights crystallization. The energy to cause water to flow through the system could be provided by the conversion of anhydrite to gypsum and by the diapirism of the basement. The intrusion of diapirs in addition, into cover sediments has impact not only on developing extensional structures but also on the mineral diagenetic process.

The same factors assisted by the mineralogical paragenesis and the organic content of the deposits, seem to control the mineralogical diagenesis. Authigenic mixed clay minerals as corrensite (chlorite/smectite) and illite/smectite were observed.

Diagenesis of the sulphate phase produces the sulphate minerals bassanite and celestite that can be considered as an indicator of bacterial sulphate reduction, fluid flow and recycling of evaporates.

The process of transforming sulfate minerals in the presence of organic matter results to carbonate minerals neofomation. Aragonite and dolomite were observed as neofomated carbonates, probably related to bacterial sulfate reduction.

When evaporitic minerals are incorporated with organic matter, clastics, carbonates and clays, via the pore water flow, the diagenetic mineral changes may become complex.

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