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Crystallization, Alternation and Recrystallization of Sulphates

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1. Introduction

Sulphates as well as silicates and carbonates are one of the most common minerals on the Earth's surface. They cover about 25% of continents surface (Blatt et al. 1980; Ford &Williams, 1989). Their recent sedimentary environments are the terrains of: the southern Mediterranean coast – coastal salt lakes of Marocco, Libya, Tunisia and Egypt, Gulf of Kara Bogaz (Caspian Sea), Persian Gulf – coastal sabkhas of UAE (special Abu Dhabi Emirate) and Qatar, Texas and California (Death Valley), salt lakes of South and Central Australia and salt lakes, salinas and salares of South America.

Annual total world production of gypsum in 2010 exceeded 146 million metric tones (http://minerals.usgs.gov/minerals/pubs/commodity/).

First of all, the sulphates are represented by two kinds of calcium sulphate - gypsum ($CaSO_4 \bullet 2H_2O$) and anhydrite ($CaSO_4$); mainly the first one creates deposits that are of economical value; it is used in the construction industry as bond material and to control the bonding speed, in casting and modelling and also in medicine (surgery and stomatology), during the production of paper. Its properties influence the parameters and quality of materials which it consist in. In construction/building industry the semi-hydrated gypsum is used as a result of frying in temperatures about 160°C (150-190°C) with sufficient amount of added water, the material bonds and hardens – the reaction is exothermic and the gypsum's volume increases of about 1%. Bassanite ($CaSO_4$ ½ H_2O), calcium sulphate semi-hydrate, is also known.

Rarely we can find the sulphates of: strontium (celestine), barium (barite), potassium (e.g. polyhalite), sodium (e.g. mirabilite, glauberite), magnesium (e.g. epsomite, kieserite), copper (e.g. brochantite, chalcanthite) and others. Most of gypsum and anhydrite on Earth are of evaporate origin, they are formed in specific order as a result of precipitation of the calcium sulphate inside the gradually drying sea basin (deep or shallow), lake, by the coastal lagoons, bays or sabkhas (indications of hot and arid climate). They are also the products of volcanic exhalations or low temperature hydrothermal processes, as well as of oxidation of sulphide deposits. The sulphates are also found above the salt mirror of diapirs, where they form the secondary deposit as the harder soluble residuum after the salt leaching – they constitute the main component of so-called gypsum or anhydrite-gypsum cap-rock.

The average precipitation rate of sulphates (gypsum and anhydrite) in the evaporite basin is ca. 0.5-1.2 mm/year and requires the evaporation of few to few tens cm high (2 m) column of water.

Probably, the oldest documented sulphate pseudomorphs are 3.45 billion years old and come from West Australia (Pilbara), cm-size growth and interpreted to replace gypsum (Barley et al., 1979; Buick & Dunlop, 1990); only slightly younger are pseudomorphs after swallowtail gypsum – 3.4 billion years old – from S. Africa, Kaapvall Craton (Wilson & Versfeld, 1994).

1.1 Gypsum: $CaSO_4 \cdot 2H_2O$

Crystal system: monoclinic, hardness: 2, density: 2.3-2.4 g/cm^2
soluble: in water, in HCl and in concentrated solution of H_2SO_4
contains impurities: Ba, Sr, deposit grains where it crystallizes, bituminous substances
habit: platy, columnar, fibrous, needle-like, lenticular; forms massive aggregates and twins - swallowtail (figs. 1.,2.,3.,6.,7. and 10.), usually colourless, might be coloured by Fe compounds

particular varieties:

- alabaster – fine-grained, sugar-like variety used in sculpture (fig. 4.),

- selenite – large well-crystallized varieties with dimensions reaching few m (fig. 5.); usually colourless

- spar – fibrous variety with semi-gloss, filling fissures and fractures (fig. 7.)

- desert rose – flower-like form of rounded gypsum aggregates (fig. 8.), occurring in the deserts as a result of ascent of the underground water rich in sulphates; it contains embedded sand grains built-in during the fast crystal growth.
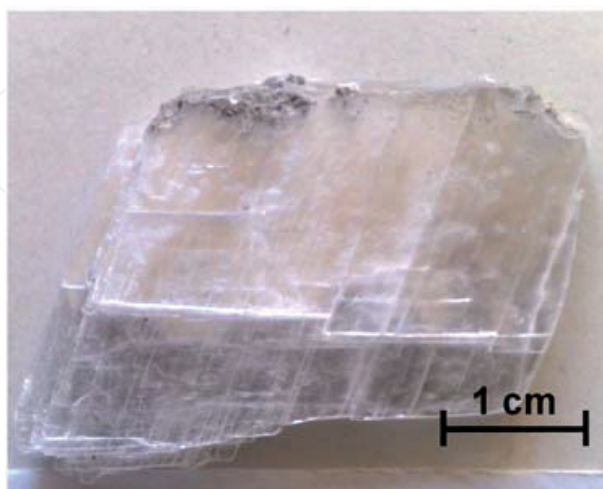

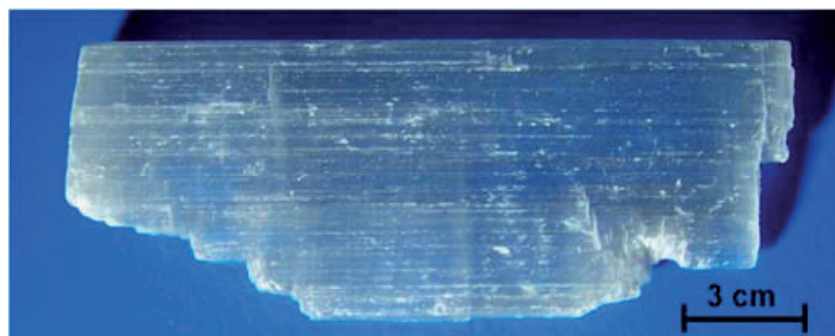Fig. 1. Platy gypsum (Petunia Bukta, Spitsbergen) phot. J. Jaworska

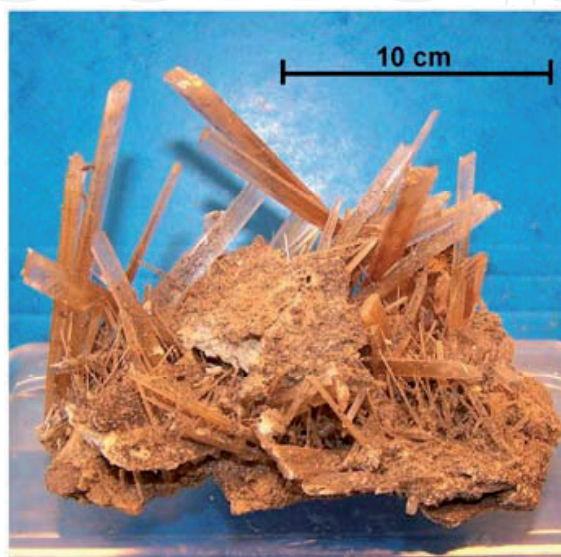Fig. 2. Fibrous gypsum (Germany) phot. J. Jaworska

Fig. 3. Columnar to needle-like gypsum (Polkowice, Poland) phot. J. Jaworska

Fig. 4. Alabaster (Ukraine) phot. J. Jaworska

Primarily, gypsum that crystallizes in the evaporite basins forms usually medium or coarse grains; sometimes the lamination occurs (fig. 15.), reflecting the changes in the basin (water composition, water level). Among the gypsum laminas, biolaminae appear; they are formed

in the neritic zones and can be either deformed by periodical droughts (mudcraks) or ruptured by crystallizing sulphates (teepee-like structures, see fig. 9). In deeper zones of the basin, sabre-like gypsum (fig. 14.) can crystallize; these are elongated gypsum crystals, 20-30 cm long, distorted in one direction due to the demersal current activity (they constitute the perfect indicators of paleocurrents). Selenite gypsum is an exceptional feature; it forms under stable conditions at the depth of few to several m (fig. 16.) and reaches the dimensions of 3.5-4 m usually, but even up to 10 m. In deeper zones, laminated gypsum forms; sometimes with the ripplemark remains or even turbidites and slump structure with fragments of older, more lithified gypsum.

Fig. 5. Selenite (Busko-Zdrój, Poland) phot. J. Jaworska

Fig. 6. Gypsum twins – swallowtail (Dymaczewo Stare, Poland) phot. J. Jaworska

1.2 Anhydrite: CaSO$_4$

crystal system: orthorhombic; hardness: 3.5, density: 2.98 g/cm^2
hardly soluble in: HCl and concentrated H$_2$SO$_4$
contains impurities: Ba, Sr

habit: platy, columnar, fibrous; the crystal size rarely exceeds 0.5-1 mm (fig. 11.); sometimes crystals grown in caverns and fractures appear; massive aggregates (fig. 13.), rare radiant aggregates exceptionally reach the length of few cm

usually colourless crystals

particular varieties:

- enterolithic anhydrite

- bluish, fibrous variety, resembling twisted viscera (regional mining name, see fig. 12.).

Recently, the gypsum precipitates from among calcium sulphates; whereas anhydrite crystallizes very rarely – the only locations of its recent crystallization are: the Persian Gulf coast, lakes: Elton and Inger, Death Valley and Clayton Playa (Nevada).

Fig. 7. Fibrous –spar gypsum in clay-slate (Niwnice, Poland) phot. J. Jaworska
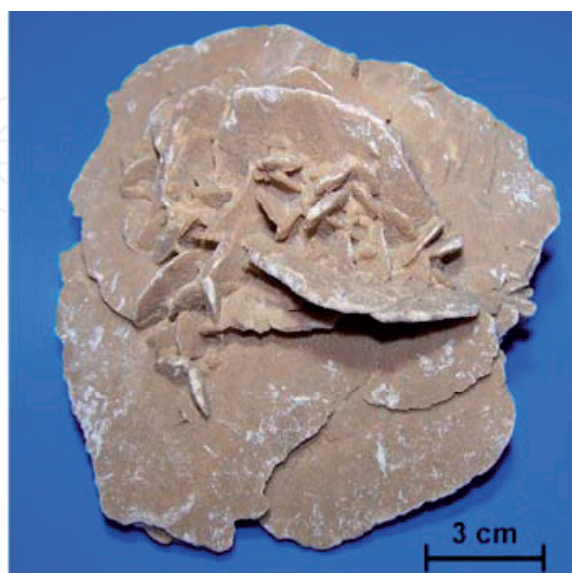

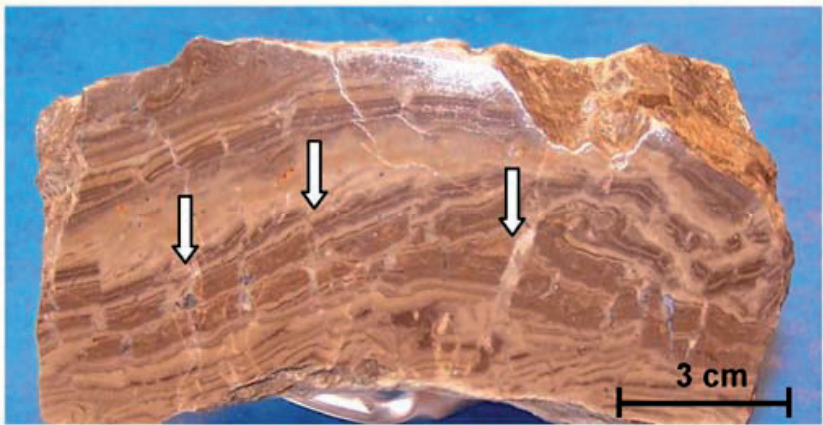Fig. 8. Desert rose; phot. J. Jaworska

Fig. 9. Biolaminas deformed by crystallizing sulphates (near Ostrówka quarry, Poland) phot. J. Jaworska
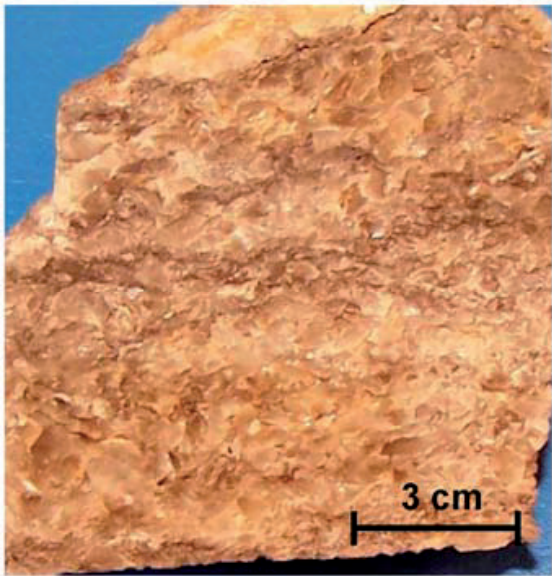

Fig. 10. Lenticular gypsum (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

Fig. 11. Anhydrite crystals (from Dębina salt dome, Poland) phot. A. Kyc

Fig. 12. Enterolithic anhydrite (Wieliczka mine, Poland) phot. J. Jaworska

2. Crystallization and alternation: Hydratation and dehydratation (gypsification, anhydritization)

2.1 Crystallization

In most of the cases during evaporation processes, the gypsum crystallizes first, than the anhydrite (higher concentration of solution, 5-6 times higher than the normal sea water

Fig. 13. Anhydrite rock - massive aggregates (Niwnice, Poland) phot. J. Jaworska

Fig. 14. Sabre-like gypsum (Nida region, Poland) phot. J. Jaworska

Fig. 15. Laminated gypsum (Niemeyer quarry, Germany) phot. J. Jaworska

salinity and in temperature about 40°C). Not until the concentration of solution reaches values close to NaCl concentration, the only phase of calcium sulphate which crystallizes and accompanies the rock salts is anhydrite; even if the temperature does not exceed 18°C. The thick rock salt deposits seldom form salt pillows together with salt swells and diapirs; their roof surfaces are located close to the Earth's surface (at the boundary of the salt mirror) and easily undergo leaching, leaving less soluble residue of - among the others - anhydrite grains and next - the anhydrite sandstone (fig. 19.), forming so-called cap-rock that forms the natural cover of the salt deposit. The anhydrite sandstone can – depending on the conditions - undergo further transformation typical for this very mineral (fig. 20.).
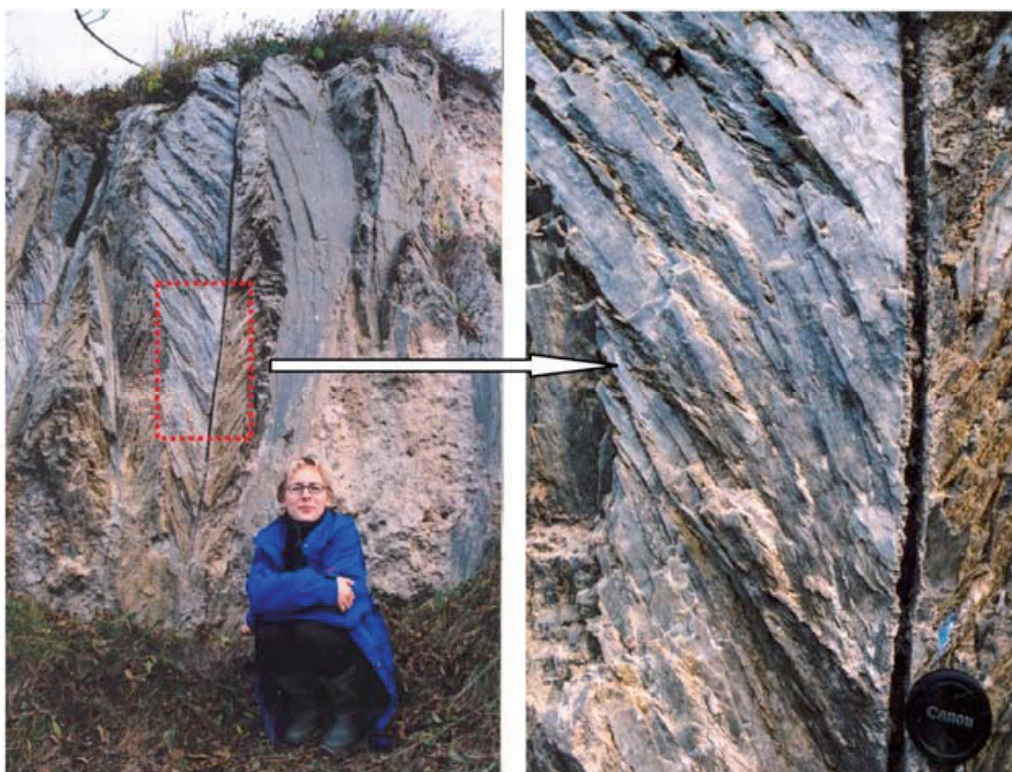

Fig. 16. Outcrop of 2.5-3 m selenite gypsums, regional named szklica (Nida region, Poland) phot. J. Jaworska
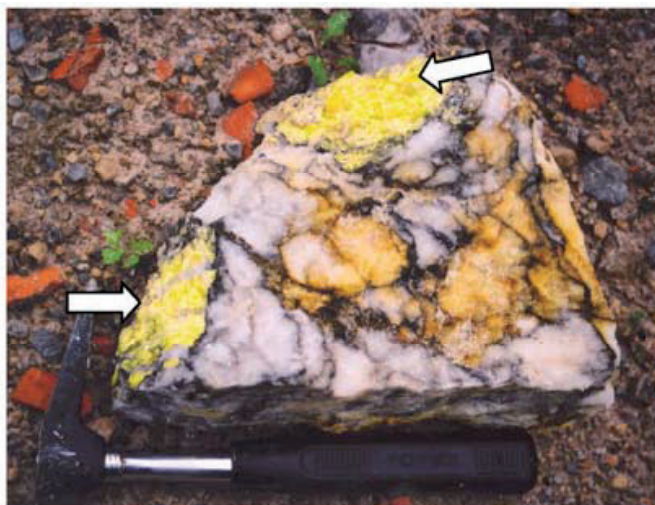
Fig. 17. Second native sulphur in gypsum rock (Niemeyer quarry, Germany)
phot. J. Jaworska

In the recent evaporation basins mainly the gypsum precipitates; anhydrite crystallizing under more extreme conditions occurs more rarely. Whereas among the sediments – particularly at the depths of few hundreds to few thousand meters – the anhydrite dominates. In many cases the anhydrite occurs as a product of the dehydration of gypsum; usually it is easily recognized pseudomorph of gypsum (e.g. selenite gypsum). The primary anhydrite, as well as the secondary one (dehydrate), as a result of tectonic processes, intense weathering of the overburden, climate changes etc., can be placed within the range of the underground or subsurface water (ground, meteoric) – where the hydration processes occur resulting in substitution of anhydrite by gypsum.

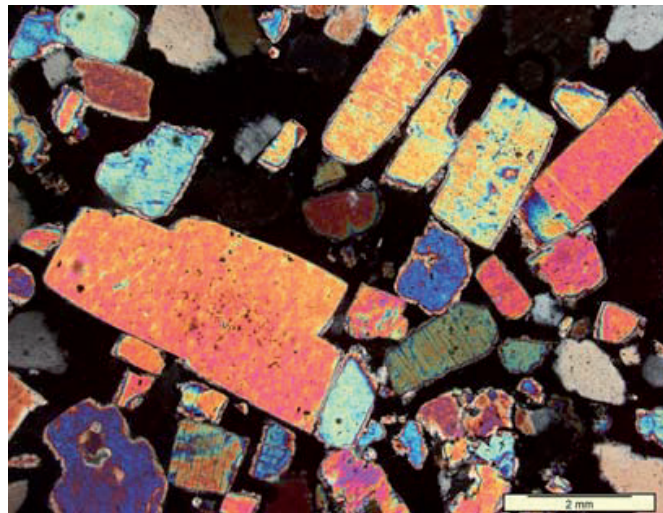Fig. 18. Gypsum-karst (Nida region, Poland). phot. J. Jaworska

Fig. 19. Anhydrite sandstone; microphoto, NX (cap-rock from Dębina salt dome, Poland) phot. J. Jaworska

2.2 Alternation

The sulphates – mainly the products of the hypergenic processes – very easily undergo the diagenetic processes, in which the dominant role is played by: hydration (gypsification) of anhydrite and dehydration (anhydritization) of gypsum; both processes are reversible and the reaction takes place as follows:

$$CaSO_4 \bullet 2H_2O \leftrightarrows CaSO_4 + 2H_2O$$

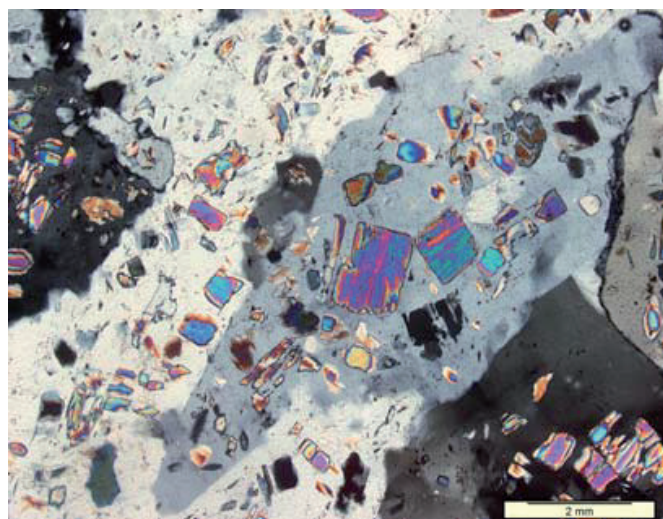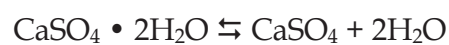$$gypsum \leftrightarrows anhydrite + water$$

Fig. 20. Lenticular gypsum with anhydrite inclusions; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

There are many factors affecting the start and course of this reaction:

1.   temperature and environmental pressure – depending on:

-     climate (for sulphates on the surface or close below it)

- depth of the deposits – thickness of the overburden,

- geothermal gradient of the area where the deposits occur – geotectonic environment and lithology of the overburden (thermal conductivity of the overburden),

2. chemical composition and concentration of solution, pore fluid pressure and the activity of water,
3. presence of micro-organisms and organisms (changes in Eh),
4. presence of cracks and pores in the sulphates as well as in the surrounding rocks.
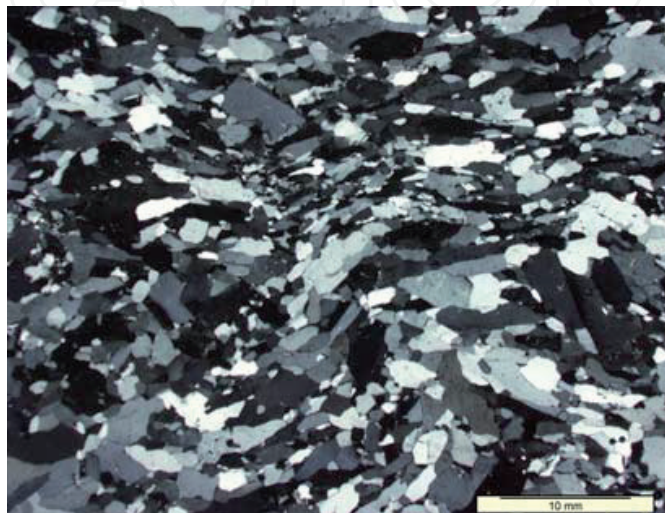

Fig. 21. Fine-crystalline gypsum; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

2.2.1 Conditions

Anhydrite under surface conditions or close to the surface can be formed as a result of intense heating (over 50°C) of primary gypsum by the sun under hot and arid conditions. When the gypsum deposits are buried, their transformation into anhydrite can theoretically start at the depth of about 450-500 m (Murray, 1964; Hardie, 1967; Jowett et al. 1993); those are the depths where temperature reaches 20°C, so the dehydration should not appear, however it is compensated by high overburden pressure (10 MPa; Kubica, 1972); on the other hand, according to Sonnenfeld (1984), gypsum can be found at the depth of 1200 m; and according to Ford and Williams (2007) even at 3000 m. The depth of the gypsum dehydration among others is modified by the geotectonic environment and the lithology of the overburden. The weakly heat conducting overburden, e.g. schists and gneisses, upon the areas seismically active, volcanic, causes the increase of the hydration speed – anhydrite can substitute the gypsum already at the depth of about 400 m; whereas well conducting overburden, e.g. rock salt of the cratonic areas, causes the process of transformation of the gypsum into anhydrite to occur hypothetically at the depth of even 4 km (Jowett et al., 1993). But the anhydrite gypsification process during the exhumation occurs usually at the depth of about 100-150 m (Murrey, 1964; Klimchouk &Andrejchuk, 1996). It starts either when the anhydrite appears in the area of influence of the ground water, or when it is exposed to rain water.
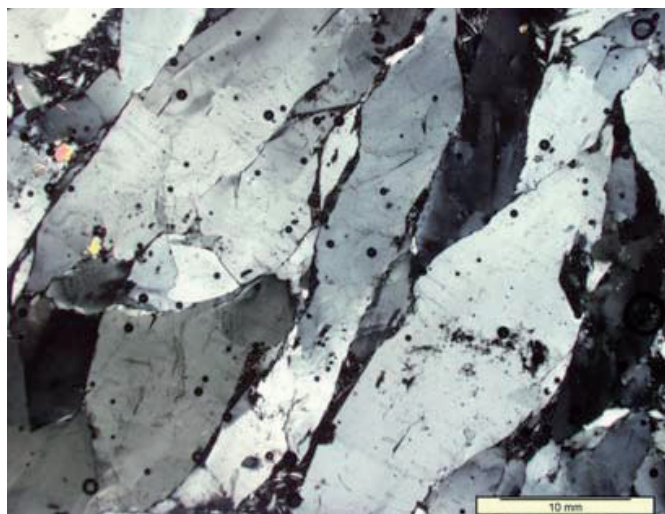
Fig. 22. Lenticular gypsum; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

The crystallization process of calcium sulphates, as well as their gypsification or anhydritization are affected by the solutions (and their pressure). The NaCl solution occurring in the pore fluids plays special role; it modifies the temperature of the gypsum-anhydrite phase transformation. If the composition of pore fluids corresponds to the composition of sea water, the water activity ($αH_2O$) is 0.93 and the transformation of gypsum into anhydrite occurs at the temperature of 52°C; however if the pore fluids are NaCl saturated, then the water activity reaches 0.75 and the transformation occurs at 18°C (Jowett et al., 1993). The temperature of gypsum-anhydrite transformation is increased by: the presence of alkaline metal ions (Conley and Bundy, 1958) up to 98°C and the solution of $CaSO_4$ up to 95°C, but with lack of the anhydrite nuclei (Posnjak, 1940). Additionally it is necessary to take into account the regime of pore fluids pressure; if it is hydrostatic, then the temperature of the gypsum transformation decreases along with depth from 52°C under surface conditions to about 40°C at the depth of 3 km, and in the case of the lithostatic regime – rises to about 58°C at 2 km (Jowett et al., 1993).
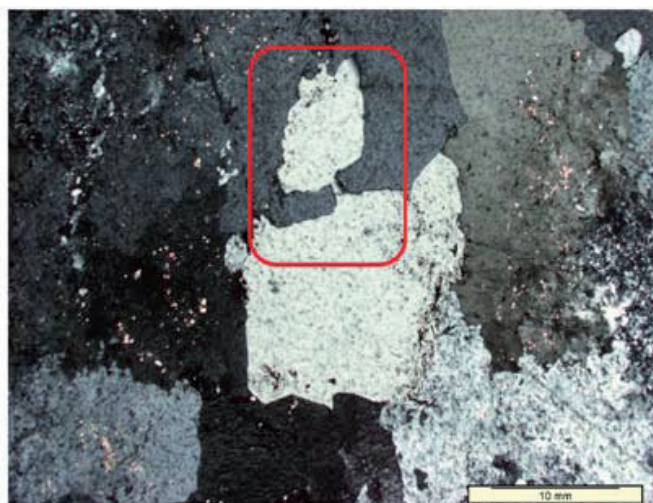
Fig. 23. Grain boundary migration between two gypsum crystals; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

Fig. 24. Large gypsum with kink folds; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

Fig. 25. 'Kink bands' and result of subgrain rotation in gypsum; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

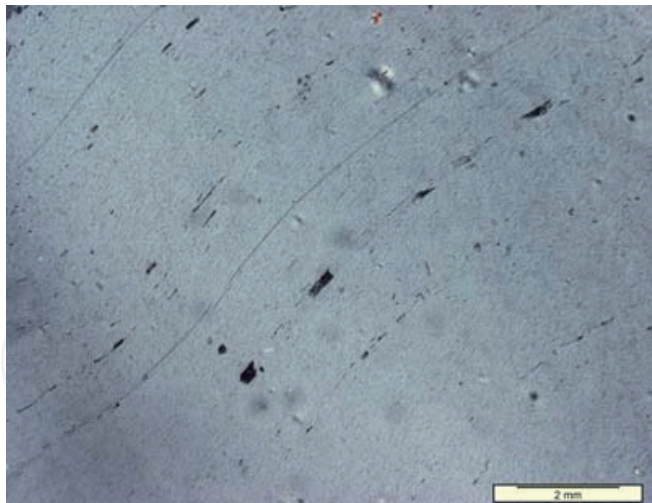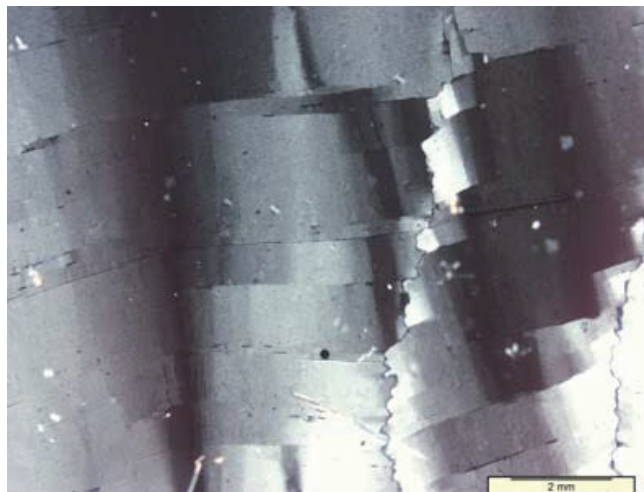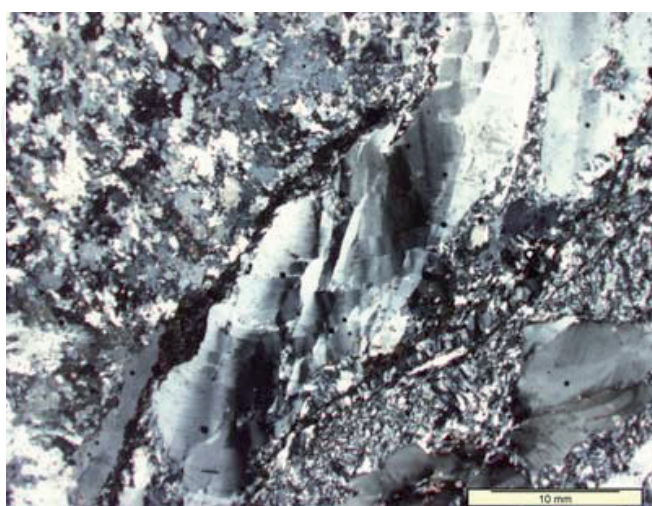Fig. 26. 'Kink bands' and result of subgrain rotation in gypsum; microphoto, NX (cap-rock from Wapno salt dome, Poland) phot. J. Jaworska

Shahid et al. (2007) comparing the crystallization and transformation conditions of sulphates in salt lakes and sabkhas in north Africa (Libia) and those from the Persian Gulf (Abu Dhabi) noted that while the climate is comparable, in the first case the anhydrite occurs very rarely, unlike in the area of the Arabian Peninsula. The main causes of this difference are the geochemical environment conditions: in the African sabkhas and salt lakes, the environment is more reducing and there is an occurrence of the organic material, the hydrogen sulphide releases and the sediment is dark; while sabkhas from the Persian gulf are more oxidised with lack of hydrogen sulphide - the sediment is light. The presence of fractures and joints in sediments/rocks surrounding the sulphates, as well as the microfractures and pores in the sulphates themselves strongly affect the start of the gypsification and anhydritization. Those free spaces allows the water to migrate and solutions to start and catalyse the course of processes.

2.2.2 Time

The anhydritization and gypsification (dehydration and hydration) under natural conditions can occur very quickly: within few years (Farnsworth, 1925) or even within one year (Moiola & Glover, 1965); and experiments showed that even within several/several dozen of days (i.e. Sievert et al., 2005), what depends on physical and chemical conditions under which the process occurs. We can see for ourselves the speed of these processes, when inside a brick (ceramic material) we note the anhydrite grains, which with infiltrating water are being gypsificated and expand destroying the material – the damage of walls occurs even within several years.

2.2.3 Volume

The volumetric change comes along with hydration and dehydration processes of the sulphates – the increase of volume of anhydrite by its gypsification is about 30-50% according to Petijohn (1957), and according to Azam (2007) - close to 63%. Whereas the gypsum anhydritization decreases its volume of about 39% (Azam, 2007); sometimes it occurs together with many alterations, especially of the primary rock structure. The different situation takes place in case of sulphate deposits which already contain water; according to Farnsworth (1924), 1000g of gypsum fills 431 cm^3, while the sum of anhydrite and water needed to form the same amount of gypsum fills 473 cm^3, 9% more – then under natural conditions, when the anhydrite deposit is porous/fractured and water supersaturated, the gypsification process can result not in increase but decrease of volume of the newly formed rock.

2.2.4 Models of gypsification and anhydritisation

According to Hardie (1967) there are three models describing transformation of gypsum into anhydrite (or backwards – anhydrite into gypsum):

1. dissolution of gypsum, and furthermore precipitation of anhydrite (during anhydritisation) or dissolution of anhydrite and later precipitation of gypsum (during gypsification);
2. direct dehydration of gypsum, that is loosing of the crystallization water (during anhydritisation) or adding the water – hydration of anhydrite (during gypsification). This mechanism results in change of the rock volume;

3. dehydration or hydration with mid stage, with participation of bassanite (mineral rarely occurring in nature). During the hydration, the reaction (occurring very slowly) is as follows:

$$4CaSO_4 \cdot \tfrac{1}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O + 3CaSO_4$$

bassanite   gypsum   anhydrite

2.2.4.1 Anhydritization

Petrichenko (1989) stated that the process of anhydritisation of gypsum began with its dissolution. This process is accompanied by the appearance of the nuclei of the new mineral phase – bassanite. During the second stage, bassanite transforms into anhydrite. The structural rearrangement of this mineral occurs, resulting in increase of thickness at the cost of length. Sheets (plates) of anhydrite crystals form with corroded edges. However in case of the presence of anhydrite "nuclei", the bassanite does not form, but anhydrite continues its crystallization at the cost of the calcium sulphate from dissolved gypsum. On the basis of examination of the inclusions in minerals, Petrichenko (1989) determined the conditions of the origin of anhydrite: this process takes place in the presence of concentrated brine solutions and under the conditions of high pressure and temperature, but not above 40-50°C.

Depending on time and speed of the sulphates transformation there are three kinds of the process: syndepositional, early- and late-diagenetic. The syndepositional anhydritisation occurring during the deposit formation, in shallow basin, sabkhas, in the subsurface environment, causes the substitution of gypsum to take place so fast that the anhydrite remain in its primary form. Anhydritisation during the later stages, according to the solutions of lower salinity, causes the primary sedimentary structures to disappear and the nodular structures to form – gypsum is substituted by incohesive mass of fine anhydritic strips and water, whereas the anhydritisation under the influence of highly concentrated brines can lead to the preservation of the primary gypsum pseudomorphs (Peryt, 1996; Warren, 1999), especially apparent in the coarse-crystalline gypsum forming "the grass-like selenite".

2.2.4.2 Gypsification

The process of hydration was described in detail by Sievert et al. (2005):

1. during the first quick phase, there is an initial partial dissolution of $CaSO_4$ and adsorption of hydratem Ca^{2+} and SO_4^{2-} ions at the surface of anhydrite;
2. during the second – the slower one, there is an increase of thickness of adsorbed layer
3. during the third phase, there is a crack formation in the absorber layer and counter migration of H_2O and Ca^{2+}, SO_4^{2-} ions;
4. during the fourth phase - the formation of gypsum nuclei at the surface of anhydrite occurs and in the end gypsum crystals are formed.

This process takes place in the presence of water (in the active phreatic zone), in temperatures below 40°C (process takes place faster in lower temperatures), and its speed depends on the presence of chemical activators, for example K_2SO_4, $MgSO_4 \cdot 7H_2O$ or H_2SO_4 (Sievert et al., 2005) and CO_2, which speeds and eases the hydration. At first, it covers the most fractured parts of the rock, taking place along the cracks and grain boundaries. As a

result of hydration, the anhydrite rock transforms into gypsum rock with fine-grained (alabaster), fibrous, porphyroblastic texture (Warren, 1999), coarse/lenticular-crystalline gypsum (sometimes with preserved relic of the anhydritic precursor) – they result from the dissolution of primary sulphates (fine-crystalline anhydrites); see fig. 21. and 22. The secondary gypsum can also be formed as a pseudomorph of the primary anhydrite (e.g. the floor of the cap-rock) or the coarse-crystalline gypsum (selenitic gypsum), which underwent anhydritisation and furthermore gypsification – in this case, despite the multi-stage characteristics of the diagenetic processes, the primary rock structure is preserved. There is an example of the Zechstein (Permian) sulphates, which were uplifted close to the surface as a result of diapirism, and further incorporated into a cap-rock, while being anhydritised and later gypsificated (Jaworska & Ratajczak, 2008).

2.3 Inclusions

Inclusions or remains of the primary precursor minerals (e.g. the remains of anhydrite in gypsum) can appear in the primary as well as in the secondary sulphates. Particularly valuable are the inclusions in the primary minerals which can be liquid, solid, gaseous, or even organic. They reach diameters between few and several hundred of μm. Sometimes they are arranged zonally, rhythmically – as the crystal grew. Among the inclusions:

a. solid – most often occur: clay minerals, quartz, chalcedony, barite, halite, carbonates - calcite, dolomite, magnesite
b. liquid – mainly the chlorine-sulphate solutions of various mineralization,

Part of the solutions can be saturated with gases (CO_2, N_2, CH_4, H_2 and H_2S), e.g. originating from the organic decomposition (Petrichenko et al., 1995). For example, in the badenian gypsum of Carpathian Foredeep, the presence of: fragments of characean algas, filamentous algas, and colony of unicellular cyanobacterium, insects, coccoids, and multicellular organisms – most probably fungi, has been confirmed. The good state of preservation of these microorganism tissues indicates anaerobic conditions during gypsum precipitation (Petrichenko et al., 1995). The detailed inclusion analyses led to a series of conclusions on the environment, chemical (basin type: open sea or inland ?; brine type: e.g. $Na-(Ca)-SO_4-Cl$ or $Mg-Na-(Ca)-SO_4-Cl$ or $Na-CO_3-SO_4-Cl$?) and biochemical conditions during the sulphate sedimentation; the variations of the solution chemical composition (e.g. indication of the fresh sea water inflow direction). In addition, the analyses of one-phase liquid inclusions provide information on the water temperature in the crystallization basin.

2.4 Calcitization

Sulphates, as well as gypsum and anhydrite can undergo calcification by:

a. bacterial reduction in deposits rich in organic substances – the most effective process,

- sulphates are altered by S-reducing bacteria to form H_2S, pyrite and other sulphides, native S and calcite (Holster, 1992)

b. infiltration of meteoric water rich in carbonate ions – occurs during the sulphates exposition onto water activity (Warren, 1999),

c. thermal reduction of sulphates – late diagenetic process, occurs in temperatures over 100°C, under atoxic conditions and with presence of the hydrocarbons (Machel, 1987).

Dissolution of sulphates in presence of hydrocarbons leads to biogenic SO_4 reductions and calcite precipitation according to reactions:

$$CH_4 + CaSO_4 \rightarrow CaCO_3 + H_2S + H_2O$$

Calcitization of the sulphates can be a multi-stage process (Scholle et al., 1992), which begins with (1) dissolution (or at least corrosion) of anhydrite, (2) hydration of anhydrite and gypsum formation, (3) dissolution of gypsum (this process can be accompanied by the formation of collapse breccia), and afterwards (4) precipitation of calcite inside free spaces and pores arisen after leached sulphates. Sometimes sulphur is the secondary product of calcitization of sulphates (see fig. 17.).

Generally, the gypsum – more easily than the anhydrite – can be substituted by calcite. In case where this process occurs in bigger scale, the post-gypsum limestones form. They can occur in the highest parts of the cap-rock, covering the upper parts of some diapirs - upon the area of Costal Gulf the shallowest subsurface cap-rock levels are usually formed as the calcitic deposits and therefore named as calcitic cap-rocks. However, the microscopic analyses of the cap-rock deposits demonstrated that among the secondary coarse-grained gypsum with the anhydrite remains, the calcification process starts exactly with these anhydrite inclusions, not with the gypsum.

2.5 Polyhalitization

The sulphate rocks can also undergo the polyhalitization process. It proceeds during the early stages of the diagenesis of evaporites as a result of infiltration of hot brines into the sulphate deposits (in the peripheral zones of the evaporite basins): halite saturated, with high contents of Mg^{2+} and K^+ (originating from the dissolution of the potassium salts in the local salt pans), sulphate-rich (Peryt, 1995 and 1996). This process starts from the edges of the grain/crystal and proceeds with deep embayments into the core – the anhydrite/gypsum grain disintegrates into smaller parts that undergo polyhalitization more easily (Stańczyk, 1970).

2.6 Dissolution and Karst

Sulphates – gypsum in particular – are common ingredients of the lithosphere and often occur close to the Earth's surface. Additionally, the gypsum easily undergo physical weathering (is soft and has ductile rheology), as well as chemical (dissolves in water). Gypsum dissolution rates reach 29 mm/year and have been measured in Ukraine (Klimchouk & Aksem, 2005). Therefore upon the areas of gypsum deposits karst processes and forms occur (fig. 18.). Gypsum-karst features commonly develop along bedding planes, joint or fractures; sometimes up to 30 m below the Earth's surface. The evidence is the presence of: caves, sinkholes, karren, disappearing streams and springs, collapse structures (Johnson, 2008). One of the longest reported gypsum caves is D.C. Jaster Cave (SW Oklahoma, USA) where main passage is 2,413 m long but total length of all the passages reaches 10,065 m (Johnson, 2008). Speleothems in gypsum caves may provide information

about paleoclimate and climate changes in the past, because in arid or semi-arid climates, the speleothems in gypsum cave are mainly composed of gypsum, whereas in contrast, in humid or tropical climate – of carbonate (calcite). The dating of speleothems could provide the paleoclimatic data relating to:

a. dry periods, when gypsum speleothems were deposited,
b. wet periods in arid zone, when calcite speleothems were deposited (Calaforra et al., 2008).

Gypsum-karst area could be dangerous and should be monitored due to the risk of danger. Some sinkholes and collapse structures, commonly being few hundreds m wide and tens of m deep, may cause the loss of human lives and damages, e.g. in Spain in Oviedo and Calatayud situated on cavernous gypsum area, direct economic losses by collapse events were estimated to be 18 mln euro in 1998 and 4.8 mln euro in 2003 (Gutiérrez et al., 2004 and 2008).

The process of the sulphates dissolution is visible not only in developement of karst features; it reveals itself in the smaller scale for example in development of stylolites as a result of pressure solution. The development of the stylolitization process has been usually described among the carbonate rocks - mainly limestones; in the evaporites the stylolites are exceptional. Bäuerle et al. (2000) took under consideration the problem of stylolites genesis in the main anhydrite deposits located in the salts of the Gorleben diapir (Germany). Detailed studies of these forms led to estimation of the amount of dissolved material thanks to the measurements of the maximum amplitudes of the stylolitic sutures visible inside the core. The calculations showed that over 26% rock mass were dissolved. Moreover the microscopic observations indicated the gaps in the sutures – the sutures were 'cut' by the anhydrite crystals formed as pseudomorphs after gypsum. This fact proves that the stylolitization had developed before the gypsum underwent anhydritization. In the article summary, the authors plotted the conditions of the stylolites formation in sulphates, especially in gypsum as the primary deposit where such forms appear. The process requires:

a. the presence of interbeds different than the sulphate rocks; the lithological heterogeneity,
b. the presence of overburden in which the increase of thickness and its chemical characteristics favour the conditions where the lower gypsum is under conditions balancing between pressure solution and the gypsum-anhydrite transformation.

3. Geochemystry of sulphates

The analysis of chemical (including isotopes) contents of the sulphate rocks leads to the conclusions regarding their genesis and diagenetic transformations; e.g. strontium and boron.

3.1 Strontium (Sr)

Sr can substitute Ca ions in minerals (mainly in carbonates and sulphates) or create their own minerals (celestine or strontianite), which very often occur dispersed in the marine sediments. High level of Sr characterizes the rocks formed during the final stage of

carbonates' sedimentation and during the first stage of calcium sulphates crystallization; generally in sulphates the Sr content increases in direct proportion to the brine concentration (Rosell et al., 1988). The primary gypsum precipitated from evaporated seawaters is expected to have a Sr content of 0.1-0.2% (Ichikuni & Setsuko Musha, 1978) and the one from K-Mg brines - the content of 0.97% Sr (Usdowsky, 1973). Butler (1973) thinks that gypsum precipitated from the celestine saturated solution should consist about 0.09% Sr, and anhydrite – about 0.24% Sr, but primary selenitic gypsum from the Eastern Betics basin contents strontium only between 493-625 ppm Sr (Warren, 2006) and primary Zechstein (Permian) anhydrites content 0.61% Sr (Polański & Smulikowski 1969).

Multimodal distribution of Sr compound in the primary sulphates (gypsum in particular) profiles indicates various sources of this element and multi-stage process of its concentration. The Miocene selenite gypsum from the southern border of the Holy Cross Mts. shows high Sr content (averagely 1300-1500 up to max. 2575 ppm); and scarce variations of the content indicate only episodic salinity fluctuations of the basin, probably connected with the inflow of fresh sea or meteoric water; the gypsum was formed in the sub-aqueous environment characterized by high salinity, whereas the laminated stromatolitic gypsum is characterized by high variations of Sr content (from max. 3695 to 179 ppm), simultaneously indicating high salinity fluctuations (Kasprzyk, 1993).

Strontium can also originate from diagenetic processes: bacterial sulphates reduction, dissolution and recrystallization – they may favour the liberation of strontium ions from the sulphate and could locally form higher concentrations within the other sulphate rocks (Kasprzyk, 1994).

Apparent decrease of Sr concentration occurs during rock transformation in the open system with unbounded circulation of the solution in free pore spaces, whereas the residual products of these transformations are often enriched in strontium. During the hydration of anhydrite, gypsum shows limited ability of Sr ions incorporation into its crystal lattice and is not able to incorporate them completely. Dissolution and recrystallization purify gypsum and anhydrite from impurities, and activate strontium lowering its content in newly created mineral comparing to the primary mineral, i.e. some secondary gypsums from Wapno Salt Dome consist only 159 ppm Sr (Jaworska & Ratajczak, 2008), primary anhydrite from which it has been created consist 1700 ppm Sr.

3.2 Boron (B)

B likewise Sr is a sensitive indicator of changing conditions in the evporite sedimentary environment, as its concentration in the sediment depends on the salinity.

Systematic increase of B content in the profile of sulphate sediments indicates progressive increase of basin salinity during the crystallization of successive generations of sulphates – evaporites containing the highest amounts of B originate from the most concentrated solutions. Any decrease/variation/fluctuation of this element concentration indicates fresh (sea or meteoric) water supply to the evaporite basin.

Sea water contains 4,45 ppm of boron, mainly in the form of undissociated ortho-boric acid. Solutions of this element deriving from the terrigenic sediments, submarine exhalations and

decomposing clay minerals (especially illite) constitute the source of borate ions in the sedimentary basins. Ions of BO_3^{2-} can isomorphically replace SO_4^{2-} and form their own minerals (borates, e.g. boracite).

The highest B concentrations are noted during the latest stages of evaporation – when the K-Mg salts precipitate accompanied (under favour conditions) by borates' crystallization. The B content in sulphate rocks (gypsum, as well as anhydrite) can fluctuate between 2 and 5500 ppm; in the Zechstein anhydrite the content ranges from 16 to 500 ppm, and in polyhalite reaches 800 ppm (Pasieczna, 1987) – generally, there are high B contents noted in polyhalite.

Sulphates can be analysed from the point of view of Mn and Fe contents; increased concentrations of both elements usually indicate the terrigenic deposit (siliciclastic sediments, clay minerals) supply into the sedimentary basin.

3.3 Isotopes

Another indication of the genesis and diagenesis of sulphates are the isotopic analyses of $^{87}Sr/^{86}Sr$ ratio, S ($\delta^{34}S$) and O ($\delta^{18}O$) in SO_4, and in the case of gypsum, also O ($\delta^{18}O$) of the crystallization water. $\delta^{34}S$ and $\delta^{18}O$ in SO_4 does not change despite of many transformations, the sulphate molecule maintain its primary isotopic composition, what allows to determine the primary sedimentary conditions, but dynamic and multiple transformation can affect the $\delta^{18}O$ of crystallization water, so in gypsum we have to indicate two $\delta^{18}O$ – in SO_4 and H_2O.

3.3.1 Sulphur (S)

The present-day $^{34}S/^{32}S$ ($\delta^{34}S$) ratio of sulphates in oceanic water is constant and reaches +20±0.5‰ with respect to V-CDT (Pierre, 1988) and the fractionation between dissolved sulphates in oceanic water and crystallized sulphates is negligible (Thode & Monster, 1965; Raab & Spiro, 1991). $\delta^{34}S$ was changing in the geological past and its general trends are known as the sulphur-isotope age curve (Claypool et al., 1980). This curve allows to define the time of evaporate crystallization.

3.3.2 Oxygen (O)

The present-day $^{18}O/^{16}O$ ($\delta^{18}O$) ratio of sulphates in oceanic water reaches 9.5±0.5‰ with respect to V-SMOW (Longinelli & Craig, 1967) but during crystallization of the oceanic sulphates, the $\delta^{18}O$ is raised up to 3.5‰ (Lloyd, 1968; Pierre, 1988) and $\delta^{18}O$ value of this sulphates reaches 13.0±0.5‰.

Primary gypsum and its crystallization water are formed in isotopic equilibrium with the mother brine (Sofer, 1978), but gypsum can easy loose its original crystallization water during further dehydration and hydration. During hydration sulphates interact with meteoric-, ground-, residual or sea water and gypsum absorbs this new, fresh or sometimes mixed primary water. In the areas of several-, several dozen of m long profiles consisting gypsum rocks, basing on the determination of $\delta^{18}O$ of their crystallization water, it is possible to indicate the type and range of individual water types which affected the sulphates. E.g. in profiles of the cap-rock of the Wapno and Mogilno salt diapirs (Jaworska, 2010) there is gypsum, which shows $\delta^{18}O$ of crystallization water indicating the influence of:

cold period - post-glacial water – $\delta^{18}O$ reaches values from -11 up to -13‰ in the lowest part of the profile (Wapno and Mogilno), recent (or similar to) meteoritic water - $\delta^{18}O$ reaches values of -9 to -10‰ (Wapno), cap-rock water - $\delta^{18}O$ reaches -4.3 to -6.6‰ (Mogilno), „mixing" water or warmer period water - $\delta^{18}O$ is -5.6‰ (Wapno) and from -6.9 to -8.7‰ (Mogilno).

The presence of water described as recent or originated from the colder periods inside the lowest and the middle parts of the cap-rock is very important for further management plan of such salt structure. The influence of present day water or the water from colder periods in the lowest part of the cap-rock indicates free flow of surface water into the area of so called salt mirror; the presence of this water in the middle part of the cap-rock indicates the occurrence of cracks, fractures and karst forms in cap-rock body. In consequence it means, that such cap-rock is not a hermetic cover and does not fulfil the requirements for a seal which protects the rock salt and salt mirror against inflow of freshwater. This information is of great importance for salt structures which are prepared for underground disposal of radioactive waste or for the storage of hydrocarbons, as well as salt mine.

3.3.3 Strontium (Sr)

The $^{87}Sr/^{86}Sr$ ratio of modern oceanic water is uniform and reaches 0.70901 (Burke et al., 1982) but has been changing in time. Main reasons of these irregular changes were contribution of Sr with high $^{87}Sr/^{86}Sr$ ratios from continents and input of Sr with low $^{87}Sr/^{86}Sr$ ratios from active mid –oceanic ridges (Veizer, 1989; Chaudhuri & Clauer, 1992). The general trends and variations of the marine Sr isotopes during the Phanerozoic carbonates are known (Burke et al., 1982) and this curve (the same as S-curve) allows us to study the age of evaporates precipitation. In evaporites the $^{87}Sr/^{86}Sr$ ratios reflect the isotopic composition of the brines or diagenetic fluids. Strontium does not fractionate (Holster, 1992).

Present-day strontium isotope ratio equilibrated between ^{87}Sr-depleted young oceanic basalts and hydrothermal activity along mid-oceanic ridges (ca. 0.7035) and ^{87}Sr-enriched continental sediments (from old continental granites) transported into the basin by wind and rivers (ca. 0.7119 and more; Chaudhuri & Clauer, 1992; Dickin, 2005). It is the same reason why primary Sr isotopic ratio of evaporites could not be the same as that of contemporaneous sea water – e.g. sediments may have deposited in closed basin with inflow of continental water and continental Sr - the Sr ratio of such sulphates is higher than the one of contemporaneous ocean water, so any variation of Sr isotopic composition may relate to the paleohydrology of the basin. Additionally, variations of Sr isotopic ratio may be explain by contamination with more radiogenic Sr or by diagenesis (Hess et al., 1986; Saunders et al., 1988; Chaudhuri & Clauer, 1992).

4. Recrystallization

In the classic approach recrystallization means the transformation of fine-crystalline minerals/rocks into coarse-crystalline ones and makes sometimes the continuation of the recovery process, when the mineral/rock or the whole material tries to loose the excess of the internal energy generated during the deformation/strain, when the crystal lattice defects

occur. During those processes the shape and size of grains change and the crystallographic axes rotate; they are also accompanied by progressive loss and disappearance of the primary rock texture/structure.

In the case of recrystallization of cap-rock gypsum, a reverse process can be generally observed (looking upwards) - the size reduction of the mineral grains (dominant or subordinate components).

The boundaries between adjacent fine gypsum grains are usually blurred and irregular, what results from transformation of the larger grains into smaller ones, which successively become individual.

The recrystallization of gypsum can occur via: grain boundary migration or subgrain rotation. The grain boundary migration is characteristic for the mineral grains with large variety of lattice defects density, whereas the subgrain rotation occurs in grains with uniformly dispersed defects (Passchier & Trouw, 1998).

4.1 Grain boundary migration

If the adjacent grains differs in defects density, the defect-poor one bulges into the defect-rich one; see fig. 23. It results in the removal of grains with many dislocations. It also enables the spontaneous crystallization and the growth of new grains - "nuclei" (either defectless or with few dislocations) inside the defect-rich grain; these fine new grains are called 'subgrains' as well.

4.2 Subgrain rotation

The deformation bands formed during the recovery tighten progressively, creating a grid determined by subgrain walls that developed successively within the grain. The subgrains are fragments of larger grain with fine boundaries. As a result of rotation, the crystalline axis of the subgrain becomes slightly misoriented relating to the axes of the adjacent subgrains or the main grain/crystal; the misorientation angle usually reaches max. 5° (FitzGerald et al., 1983; White & Mawer, 1988 fide Passchier & Trouw, 1998). During the rotation recrystallization the mylonitic and porphyroblastic/porphyroclastic rocks are formed.

Another (however not so common) mechanism of subgrain development can be observed in the rocks of the gypsum cap-rock - the process is called kinking and leads to formation of 'kink bands' (Means & Ree, 1988 fide Passchier & Trouw, 1998), which are represented by narrow accumulation of kink folds; see fig. 24. They are formed in brittle-ductile system and correspond to the initial shearing along the planes oblique to the dense anisotropic planes (sedimentary, metamorphic, lattice anisotropy) under the influence of parallel (to those planes) or close to parallel compression at rather high surrounding pressure (Dadlez & Jaroszewski, 1994). This process has been observed in few mm to few cm lenticular, cigar-shaped gypsum crystals; see fig. 25. and 26.

5. Summary

Sulphates are common minerals; they are easy crystallized, alternated and recrystallized.

Distinct variation of isotope ratios of sulphur, oxygen and strontium in the sea water sulphates in time enables their use to determine:

- the age of evaporite deposits;

- the sulphates' origin (marine or non-marine?, and primary or secondary minerals?) and

- in the case of gypsum (oxygen analysis of crystallization water), the determination of paleoclimatic conditions (also the time) when the gypsification occurred due to water particles accretion or isotopic composition exchange of water in gypsum.

The liquid inclusions analysis in the primary evaporites enables determination of chemical composition of primary solutions/brines from which the sulphates crystallized, as well as the temperature of water.

The analysis of the primary minerals remains constituting the impurities in the secondary crystals enables determination of the diagenetic processes taking place in the evaporite deposits (including the mineral precursor for the secondary crystal), and the direction and cause of diagenetic transformations (e.g. anhydrite gypsification: primary mineral – anhydrite, cause – presence of fresh or low-mineralized water in the deposit, e.g. as a result of tectonic uplift and exposition to the activity of shallow underground water).

The crystal shape, form and texture of gypsum and anhydrite sediments indicate the environmental conditions of their formation such as: basin bathymetry (shallow or deep zones of the basin), water oxygenation, either stability or dynamics of the environment (e.g. turbidity currents, sea-level fluctuations – in case of high variability and low thickness of separate sulphate lithotypes in the profile).

Trace elements analysis in sulphates:

1. Sr, B contents: constant increase of their contents in the profile indicate stable evaporation conditions; their variations episodes connected with the fresh water inflows to the evaporite basin and its dilution;
2. Mn and Fe contents: elevated concentrations of both elements indicate the supply of terrigenic sediments to the basin.

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