

The Environment of Miocene Salt Basins in Cis- and Transcarpathia

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Abstract. Miocene salt basins in Cis- and Transcarpathia formed in a semiarid climate that extended farther north than today. All these basins were lined by shallow shelves that became covered with gypsum, while more rapidly deepening parts became the sites of chloride precipitation. Virtually all precipitates are of marine origin, as they display the typical marine sequence of minerals; no continental evaporite minerals are present, nor is the full sequence curtailed as in leached and recycled marine evaporites. As rivers are rare in a semiarid climate, flash floods are the major suppliers of siliciclastic sediments. While the coarse fraction settles near the shores as gypsiferous sandstones, the fines float at the interface between inflow and resident brine. When they finally settle as a blanket, they retain permeability until compacted. If sea level is oscillating before or after an ice age, eroding gypsum of shelves can enter and get into contact with potash horizons, converting them from chlorides to sulfates. Economically, salt basins are not only major suppliers of halite and of potash fertilizer, but in many cases the surrounding porous strata, e.g., reef complexes, also contain hydrocarbons or lead-zinc deposits.

Key words: Miocene, evaporites, mineralogy Carpathian region

Occurrence

Miocene evaporites are mainly preserved in four circum-Carpathian areas. Cis-Carpathian locations encompass (1) a salt basin in eastern Slovakia abutting against the mountain range to the north, (2) a salt basin in Transylvania enclosed by the Carpathian arc and the Muntii Apuseni Mountains, and (3) small salt basins bounded by spurs at the end of the Carpathian arc. The Transcarpathian salt basin was covered by one continuous water surface and covered a large part of the northern foothills area in southern Poland and the adjacent Ukraine (Fig. 1).

All the basins faced south towards their entrance channels. Basins facing south or east require a lower entrance sill to entrap and concentrate resident brines than basins facing west or north. This is due to the vertical component of the Coriolis effect.

Extent of peri-Carpathian salt basins

Miocene salt basins extended much farther north than salt basins do today along western margins of continents. The wider belt of a semiarid climate was caused by an increased diameter of the subtropical anticyclones, which produce a string of high-pressure cells along the Horse Latitudes.

Salt basins require a climatic regime, in which

$$E/t > (P + G + R)/t \quad (1)$$

i.e., in a unit of time (t) the water loss through evaporation (E) is greater than the combined atmospheric precipitation (P), groundwater (G) and river (R) discharge. A Mediterranean climate, marked by winter rains and a long dry season, was defined by W. Koeppen (1931) to represent a ratio of

$$1 < P(T + k) < 2 \quad (2)$$

whereby P and T are atmospheric precipitation and temperature, and k is a constant.

As the jet stream slows down due to a reduced solar energy intake, it assumes a meandering pattern with wider amplitude. This is apt to get the high-pressure cells stuck in one place for some time and the adiabatic heating in them is reduced.

A reduced intake of solar energy translates into a cold spell with reduced winter rains in a shortened wet season, while the dry season is lengthened. The amount of annual water loss is thus increased despite the cooler climate.

The Miocene salt basins vary slightly in their age, which indicates that cold spells were repeatedly interrupted by slightly warmer periods, when some of the depressions would either freshen or dry out. The climatic oscillations also affected the sea level, which became



Fig. 1. The present distribution of Miocene Ciscarpathian and Transcarpathian salt basins.

slightly variable, be it through melting of the margins of incipient polar ice caps and glaciers, or a change in the thermal expansion of the water masses.

Onset of precipitation

Aragonite is the most common marine carbonate, while primary calcite occurs in lacustrine environments. Above a Mg/Ca ratio of 11.75 aragonite is the only stable phase (Berner, 1975). It reaches a maximum at a molar Mg/Ca ratio of 5.0; in seawater this ratio stands at 5.05. It is the only phase precipitated, once the Mg-concentration exceeds 243 ppm, even though it is thermodynamically unstable at surface temperatures and pressures (Sonnenfeld, 1984). Aragonite [CaCO_3] begins to precipitate in seawater at 1.8-fold concentration (McCaffrey *et al.*, 1987). However, it is always produced by bacterial activity and does not occur in a sterile environment (Billy *et al.*, 1976).

No bicarbonate can remain in solution at a 3-4-fold concentration of a brine derived from seawater (Wattenberg, 1936). At gypsum saturation, reached at about 3.8-fold concentration (McCaffrey *et al.*, 1987), the partial pressure of carbon dioxide has dropped below $10^{-3.7}$ (Stumm & Morgan, 1970) or about 2×10^{-4} .

Gypsum is not a straight precipitate of the inflowing sulfate and calcium ions. Anaerobic sulfur bacteria destroy over 90% of all incoming sulfate ions to get at the oxygen (Butler *et al.*, 1973). Thiobacteria and cyanophyta that live along the interface of the resident brine and the inflow produce new oxygen by photosynthesis. They need warm, sunlit shelves to prosper. Their oxygen reconverts the hydrogen sulfate generated by anaerobic sulfur bacteria back into sulfate ions.

A surplus of hydrogen ions and an excess of cations resulting from hydrogen sulfide removal raise the pH and increases the stability of CaCO_3 . Bicarbonate ions,

unstable in hygroscopic brines of high pH, turn into CO₂. Concentrating marine brines can entrap only minimal quantities of CO₂, but fluid inclusions in many halites, sylvites and carnallites contain some. No bicarbonate ions remain in solution at gypsum saturation and CO₂-solubility drops below 200 ppm (Sonnenfeld, 1984). Carbonate minerals cease to precipitate and the brine is virtually anoxic, containing less than 4 ppm of oxygen (Kinsman *et al.*, 1974).

One or several pink horizons (called "bacterial plates") develop within the mixing zone between surface waters and bottom brines. They are mainly composed of oxygen producing cyanophyta and thiobacteria, which reoxidize hydrogen sulfide into sulfate ions. Reconstituted sulfate ions convert aragonite into gypsum; gypsified algal stromatolites are common in modern shallow lagoons. Blue-green algae and bacterial photosynthesizers continue to flourish in gypsum layers, because gypsum is transparent to ultraviolet radiation. Gypsum precipitation depends on algal oxygen supplies and is restricted to water depths within the photic zone, to shallow shelves and shoals.

As the inflow concentrates, carbonate sedimentation retreats to the entrance or to supratidal parts of the shore as beach rock. Gypsum precipitates in subtropical lagoons at a brine density of 1.115 g/cm³, or 4.5-fold concentration, at a rate of about 0.5-1.0 mm/yr. Hite and Buckner (1981) estimated an average of 0.8 mm/yr. Initially, gypsum spreads throughout the lagoon. As long as the subsidence does not drop the bay floor below the photic zone, the brine exchange equilibrates in the gypsum field and the system continues to accumulate gypsum. Gypsum precipitates on shallow shelves and shoals, but precipitation ceases where the net subsidence rate drops the bay floor below the photic zone. Gypsum scavenging can then take over unless halite precipitation coats the bottom.

The original gypsum contains a fraction of celestite [SrSO₄], built into the crystal lattice or forming small druses. Its solubility is over twenty times smaller than that of gypsum, but it has largely been leached during the conversion of gypsum to anhydrite. At most ambient temperatures prevailing in the subtropical belt, namely, at any water temperature above 18°C (Braitsch, 1964), a brine saturated for halite is hygroscopic enough to convert gypsum to anhydrite. Gypsum is then a very unstable mineral. Most of the trace elements trapped in the crystal lattice of gypsum are also removed during the dehydration of the gypsum. That is particularly true of traces of base metals.

Limestones, such as reefs, marginal to a salt basin can become dolomitized by the interaction of meteoric with evaporitic waters (Magaritz & Peryt, 1994). Indeed, most of the limestones situated paleohydrologically down

slope from an evaporite basin, are dolomitized, but also those are dolomitized in which a porous limestone bed in a salt basin allows meteoric waters to encroach.

Saturation for individual solutes is achieved when the ratio between the cross sectional area of the entrance strait and the brine surface area exceeds a given amount: for gypsum this is about 10⁶, rises for halite to 10⁸ and for carnallite to 10⁹ (Lucia, 1972). The inflow/outflow ratio likewise determines the degree of saturation: for gypsum it is greater than 4.69, for halite 8.69, for sylvite 13.21, for carnallite 13.81 and for tachyhydrite 16.13 (Sonnenfeld, 1984). It follows that gypsum flats, as indicators of an evaporitic environment, are much more common than salt basins.

A simple calculation of prevailing evaporation rates of modern marine embayments and declining rates of concentrating brines shows that the water surface has to be a multiple of the area in which the chlorides precipitate. Commonly, the ratio between gypsum precipitating shelf and halite precipitating depressions is in the range of 2.5-4.0 (Sonnenfeld, 1984). In contrast to gypsum, rock salt deposition requires a prograding transgressive phase (Friedman, 1980; Jauzein & Hubert, 1984), attaining a maximum during potash precipitation (Matthews, 1975)

The thickness of the salt basins

Thick evaporite sequences are thus the product of syn-sedimentary subsidence; alternating evaporite minerals of different solubility are due to oscillating subsidence rates (Jauzein & Hubert, 1984). Where the sea floor remained reasonably flat without grabens and other depressions, such as e.g. throughout the Pannonian plain, the Tyrrhenian, Aegean and Adriatic Seas including the post-Miocene Po Valley depression, the brine produced only gypsum and all other solutes flowed out as undercurrent throughout the entrance straight. Busson (1984) referred to a basin arrested in such a position as an "aborted evaporite basin". He cited the Upper Cretaceous gypsum flats of the Maghreb in Northwest Africa as an example, coeval with an anoxic event in the ancestral tropical Atlantic Ocean. Most of these gypsum flats show textures indicative of a shallow-water environment. Invariably they also show a positive $\delta^{34}\text{S}$.

The rate of salt precipitation is at least two orders of magnitude greater than the rate of synsedimentary subsidence. It thus could fill rapidly all synsedimentary depressions. During storms, flash floods, or even winter rains, much of the salt redissolves, only to be added to the next precipitation cycle. All major salt basins contain several such cycles. The amount of salt that is preserved is thus strictly a function of the rate of synsedimentary subsidence and the continuity of marine water supplies. It is not a function of the relative aridity.

Brine depth

Each salt basin has started as a shallow pan, in which gypsum eventually reached saturation. The depth of salt basins, formerly equated with salt thicknesses disregarding any synsedimentary subsidence. Davies and Ludlam (1973) defined an evaporite basin merely as "a basin with water depth great enough relative to water transparency, wave fetch, and other hydrographic parameters, to permit development of a stable, chemically controlled, density stratification, where photosynthesis below the chemocline was slight or non-existent."

Hovorka (1987) presented evidence of water depths in the 10-metre range, or only 5-10 m (Adams, 1969), shallowing to 2-10 m in many parts, since influx repeatedly could dissolve evaporite rock (Adams, 1970). Amieux (1980) estimated the water depths of Lower Oligocene evaporites in the Alsace to have been in the centimeter to meter range on the basis of gypsarenite levels, desiccation cracks, and erosion of white gypsiferous dolomite. On the basis of the proportionality of precipitate to mother liquor, Strakhov (1962) assigned a brine depth of 2-6 m to both the potash deposits west of the Urals and the ones in the Alsace.

The subsiding salt basins on either flank of the concurrently rising Carpathian Mountains apparently form a couplet of compensating vertical movements along normal faults. They are obviously instigated by events in the upper mantle, such as a lateral displacement of mass, yielding a mass deficiency under the rising mountains and an excess dragging down the subsiding basins. However, our knowledge of the causes of vertical movements in the earth crust is far inferior to that about the horizontal displacement of plates.

The source of the precipitates

Virtually all the precipitated salts are of marine origin because of the full upward sequence of anhydrite/gypsum, halite, K-Mg-salts, halite and gypsum. They do not represent leached and recycled evaporites. Neither are they evaporites of continental origin, as they would then display a different mineralogical sequence.

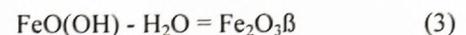
A survey of available quantities of halites and K-Mg-salts precludes a continental source, even by redissolving more ancient (Permian?) deposits. Much of the basement is formed by rocks metamorphosed during mid- and late Paleozoic orogenic events and thus has been eliminated long ago as a source of leached evaporites.

Each peri-Carpathian salt basin is framed by anhydrites that originally represented gypsum shelves. Concentrating brines could slide from these into synsedimentary subsidence centres. Halite and other components of the solute were either deposited in these subsidence centres or expelled through the bottom outflow.

The brine concentrates further in depressions within the basin and quickly reaches halite saturation. The bulk of the solute is represented by sodium chloride and thus its precipitation depletes the sodium and leaves only a very concentrated mother liquor mainly containing KMg-chlorides. The total absence of magnesium sulfate salts, so prevalent in seawater, even though they are less soluble than sylvite and carnallite, indicates the early development of a massive sulfur deficiency in the brine (Borchert & Muir, 1964) due to sulfate reduction by anaerobic bacteria. Once saturation is again reached, potassium chloride minerals start precipitating, which are originally of two types:

(1) the slowly nucleating sylvite [KCl] accumulates under the protection of the inflow that separates it from the atmosphere. Here, beneath the cover of the inflow, the N-hydrides (e.g., urea, ammonium chloride) derived from the decomposition of proteins increase the pH, decrease the solubility of potassium chloride and raise that of magnesium chloride (Seidel, 1917; Emons, 1967) until it becomes infinitely soluble. At the same time, bivalent iron compounds, derived from the decomposition of chlorophyll and hemoglobin are also protected. The primary sylvite is thus white in colour.

(2) the resident brine comes in contact with the atmosphere beyond the inflow wedge. Here the N-hydrides are destroyed and the rapidly nucleating carnallite [KCl.MgCl₂.6H₂O] precipitates. Primary carnallite is much more common than primary sylvite, because the area covered by the inflow is much smaller than the exposed water surface. The abundant organic nitrogen in fluid inclusions of carnallite confirm the original presence of N-hydrides and gives the rock its nickname "popcorn salt." The dissolved bivalent iron compounds settle out at the same time as goethite [FeO(OH)]. In the intensely hygroscopic brine this goethite quickly converts to hematite as



The carnallite becomes thus shot through with hematite needles and platelets. Consequently, primary carnallite is red.

Downward circulating waters can leach MgCl₂ out of red carnallites leaving a red sylvite behind at some reduction in volume. They can eventually recrystallize the sylvite and expel all hematite to the crystal boundaries, leaving the sylvite crystals themselves clear. Since an addition of MgCl₂ to sylvite requires a volume increase, it is much rarer and occurs only as a carnallite coating. The ultimate in leaching is reached when all K-Mg-chlorides are removed, leaving a red halite. However, a red halite also occurs in thin halite veins in shales, where the iron has been leached out of the vein walls.

Most marine evaporite basins that reached halite saturation also produced intercalated potash horizons, even

though the precipitation of K-phases requires a more than 90-fold concentration of the brine (McCaffrey et al., 1987). They are usually found in two positions within the basin:

(1) K-Mg-chlorides reduce their solubility upon cooling and thus precipitate on the basin floor, wherever there is a cool groundwater discharge. They then form an intimate mixture with the halite slush present. Such a rock is called sylvinite or carnallite, respectively

(2) K-Mg-chloride brines have a tendency to rise upon cooling and to float against the shelf margin. Because of the rotation of the earth, they abut preferentially against gypsum shelves on the western or north-western side of depressions. They then form pure layers that are gradually thickening westward towards the shelf edge and are abruptly terminated by the reach of ancient rain wash.

As the halite is compacted, the permeability of a basin floor is bound to decrease over time, causing a decrease in leakage through the basin floor and, thereafter, the appearance of the more soluble salts near the top of a chloride sequence (Casas and Lowenstein, 1989; Sanford and Wood, 1991).

It should be mentioned here that the control of K-Mg-chloride facies by decomposition products of proteins or of chlorophyll is an organic steering process of precipitation, in line with the organic control of gypsum precipitation.

Basins with steep sides, delineated by normal faults with substantial throw, do not produce gypsum shelves. They show a gypsum deficiency, e.g., the Lower Cretaceous Sergipe Basin of Brazil, Khorat Basin of Thailand, Cuanza Basin of Gabon or Sannakon Basin of Laos. The calcium stays in solution and the hydrogen sulfide derived from inflowing sulfate ions escapes. The sequence then goes beyond carnallite to tachyhydrite [$\text{CaCl}_2 \cdot 2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$], which can be seen as a Ca-carnallite (Wardlaw, 1972). Tachyhydrite does not contain any organic decomposition products, but may contain some sergipite [$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$] (Sonnenfeld and Kühn, 1993). Basins with such steep sides and no shelves do not occur in the Carpathian realm.

The ratio of the individual evaporite facies confirms a continuous inflow/outflow regime, inasmuch as there is a distinct shortage of precipitates of higher, compared to those of lower solubility. The existence of a continuous inflow is indicated by an absence of a frequent drying out of the basin, of an outflow by the absence of an isochemical distribution of precipitates. That does not preclude frequent redissolution events by flash floods or by storms mixing surface waters into the brine along deep drafts of seiches.

Bromine in evaporite deposits

Bromine is incorporated into the halite and sylvite lattices, substituting for chlorine. In carnallites it substitutes preferentially in MgCl_2 and this depletes surrounding halite. The amount of substitution increases with brine concentration. Where bromine has been leached out of a crystal lattice, the metallic sodium is left behind as platelets and produces a blue colour in halite, metallic potassium a violet colour in sylvite (Sonnenfeld, 1995), and in both cases an increased porosity.

Siliciclastic sediments

Siliciclastics are fining towards the shores of evaporite basins; chemical weathering yields a lateritic soil. Alternate freeze-thawing in a rich dew and exfoliation or spalling comminute surrounding soil. Limonitic coatings become red hematitic coatings in the dry air, hence the ubiquitous occurrence of "red beds" composed of clays and silts around marine evaporite basins.

Semiarid climates are marked by a dearth of rivers and creeks. The main supplier of clastic sediments are flash floods. These bring material from farther inland and deposit coarse sediments onto gypsum shelves, producing gypsiferous sandstones or arenaceous gypsum. The contribution of silt and clay from nearshore areas is unusually large. These fines are swept out along the interface between surface inflow and resident waters (Sonnenfeld & Hudec, 1985). They settle slowly as a blanket soaked in local brine onto the preexisting halite surface, which may be corroded by partial redissolution. As such the fines can carry with them totally unabraded estuarine fossils that give the false impression that they may have lived far out into the salt basin. The clay layers are mainly composed of members of the Mg-chlorite family and thus represent a sink for magnesium. In Paleozoic evaporites these clays are often converted to illite.

Beyond the reach of the clay laminae there occurs a thin gypsum layer that is witness to the temporary freshening of the brine down to the sediment surface. Farther out into the basin, only a corrosion surface may mark the flash flood.

A resumption of the brine concentration then covers the clay layers with new halite before the interstitial brines could be expelled. That leaves a pipeline of a porous and permeable sediment layer sandwiched between impervious halite, until compaction collapses the porosity and laterally expels the brine.

In the Carpathian realm the rise of the Carpathian Mountains during the salt deposition led to chaotic breccias at the basin margins and to frequent spreads of clay horizons. However, the orogenic movements did not split

existing basins. Instead, they merely accentuated the sills between basins that were originally interconnected by narrow channels. For instance, it is today almost impossible to judge whether the Ciscarpathian salt basin in northeastern Slovakia was ever connected through a narrow passage to the Transcarpathian basin in southeastern Poland, or whether the individual small salt basins along the Muntii Apuseni were once part of a larger depression.

Epigenetic alterations

Salt basins that were unable to compact before they were affected by major sea level oscillations, remained open to an input of meteoric waters long after they were covered by other sediments. This happened worldwide to all Neogene salt basins, before that to Permian ones, and before that to Infracambrian ones. There must be a connection to the pre- and post-glacial nervousity of sea level. In other ages, only salt basins were affected that were tectonically disturbed and opened up to influx of meteoric waters, e.g., the salt basins in the Zagros Mountains of Iran and the Salt Range of Pakistan. Coeval undisturbed salt basins on the Angara Shield remained undisturbed.

In the Carpathian realm it is not so much the tectonic effect of the rising Carpathian arc (although this may have contributed), as the nervousity of the sea level due to the early manifestations of the Plio-Pleistocene ice age. This contrasts with the Permian sea level oscillations that affected salt basins primarily in the aftermath of an ice age.

As the sea level drops, the gypsum shelves become exposed to rain and runoff. Any gypsum converted to halite by hygroscopic halite-saturated brines is reconverted back to gypsum by the runoff. Although gypsum solubility is small in pure rain water ($1.017 \text{ m}^3/\text{m}^3$ of rainwater at 20°C or $1.0086 \text{ m}^3/\text{m}^3$ at 30°C), its solubility increases more than fourfold as soon as some halite dissolves with it. Such a brine can then diffuse into the still permeable clay layers and reach K-Mg-salts that are thickest at the outer limit of rainwash.

The reaction of sylvite and carnallite with incoming brines saturated with calcium and sulfate ions, but also containing rising amounts of sodium and chloride ions, leads to a series of secondary K-Mg-sulfate minerals and some calcium chloride. The first to be leached is MgCl_2 , which, as magnesium sulfate, replaces gypsum laminae. This produces a reciprocal relationship between thicknesses of gypsum and kieserite [$\text{MgSO}_4 \cdot \text{H}_2\text{O}$]. The chloride ions thereby combine with the calcium to form the highly soluble CaCl_2 . A secondary dehydration converts the gypsum back to anhydrite.

It is noteworthy that kieserite cannot be produced in the laboratory below 110°C (Braitsch, 1964), a tempera-

ture unlikely to have been attained either on the brine floor or in shallow, uncompacted layers immediately below it. The geothermal gradient would have produced a rock temperature of this magnitude only at a depth of 2,000-2,500 m. There is no evidence that the salt basins were ever buried that deep.

Once also the potassium chloride fraction of carnallite dissolves, the gypsum laminae marginal to the shelves are replaced by polyhalite [$\text{K}_2\text{SO}_4 \cdot 2(\text{MgSO}_4 \cdot \text{H}_2\text{O})$] or in rare cases syngenite [$\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4$] after sylvite [KCl].

Further conversion of the potash horizons leads to a kainite hat [$(\text{KCl} \cdot \text{MgSO}_4)_4 \cdot 11 \text{ H}_2\text{O}$] by cooler brines descending from above and to langbeinite [$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$] by warmer brines ascending from below. At a temperature of 83°C kainite is unstable and with halite generates kieserite, sylvite and langbeinite, as well as MgCl_2 (aq) (Herbert, 1995). A whole series of KMg-sulfates can be produced by a further input of Ca-SO_4 -brines laced with Na-Cl-brines. Eventually all potassium and magnesium is removed and replaced by sodium.

Retroconversion of sulfatic minerals can also occur. In that case, carnallite is white as well as sylvite, and thus almost indistinguishable from primary deposits.

Since the conversion of KMg-chlorides to KMg-sulfates could have occurred only as long as access to the KMg-layers was provided by an incompletely compacted clay layer, the conversion must have occurred very early. It is, therefore, a moot point to argue whether the KMg-sulfates are secondary or primary. Many conversions of carbonate minerals occur along the Persian Gulf within one cycle of seasons and primary versus secondary minerals often cannot distinguished.

Economic considerations

The conversion of KMg-chlorides to KMg-sulfates reduced the total volume of potash deposits present and often produced convolute bedding planes. It usually increased the tenor of potash layers and thus rendered them more profitable to mine for fertilizer.

It is interesting to note also, that on their former margins most evaporite basins contain significant hydrocarbon deposits. Evaporite basins generate about three orders of magnitude more organic matter than do the open ocean. Due to the metabolic activity of microorganisms, especially prokaryotes (Rothschild *et al.*, 1994), organic matter is converted into hydrocarbons even in the halite precipitating part of the basin. The hydrocarbon deposits are frequently crude oils near the halite margin, because sodium chloride catalyzes the liquification of organic matter. This is the case both at the southern margin of the Carpathian arc as on its northern rim. Gypsum, on the other hand, fosters the gasification of organic matter.

Heavy metal concentrations and biogenic enrichment in microbial environments, such as algal mats (Taher *et al.*, 1994), are common in salt basins. Since primary gypsum is shot through with algal layers on account of the transparency of gypsum to ultraviolet rays, are lodged in crystal lattice errors in gypsum.

Conclusion

Miocene salt basins in Cis- and Transcarpathia formed in a semiarid climate that extended farther north than today. These basins were lined by shallow shelves that eventually were covered with gypsum, while more rapidly deepening parts were the site of chloride precipitation. Virtually all precipitates are of marine origin, for they display the typical marine sequence of minerals; no continental evaporite minerals are present, nor is the full sequence curtailed, as is the case in leached and recycled marine evaporites. As KCl- and MgCl₂-brines become less dense upon cooling, they rise and form wedges against the shelf, due to the Coriolis effect, preferentially on the northwest side of the basin. Inasmuch rivers are rare in a semiarid climate, flash floods are the major suppliers of siliciclastic sediments. While the coarse fraction produces gypsiferous sandstones near the shores, the fines float out at the interface between inflow and resident brine. When the fines finally settle, they retain permeability until compacted. An oscillating sea level before or after an ice age bares the shelves. Eroding gypsum of shelves can enter and get into contact with potash horizons, converting them from chlorides to sulfates. Economically, salt basins are not only major suppliers of halite and of potash fertilizer, but often also contain in surrounding porous strata, e.g., reef complexes, either hydrocarbons or lead-zinc deposits.

References cited:

- Adams, S. S., 1969. Bromine in the Salado Formation, Carlsbad, New Mexico. - *New Mexico Bureau of Mines and Mineral Resources, Bulletin* No. 93, p. 1-122.
- Adams, S. S., 1970. Ore controls, Carlsbad potash district, Southeast New Mexico. - In: Rau, J. L., and Dellwig, L. F., editors., *Third Symposium on Salt*, 1, 246-257.
- Amieux, P., 1980. Exemple d'une passage des "black shales" aux évaporites dans le Ludien (Oligocène inférieur) du bassin de Mormoiron (Vaucluse, Sud-Est de France). - *Centre des Recherches d'Exploration-Production Elf-Aquitaine, Bulletin*, 4, 281-307.
- Berner, R. A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from seawater. - *Geochimica et Cosmochimica Acta*, 39, 489-504.
- Billy, C., Blanc, P., and Rouvillois, A., 1976. Aragonite et association bactérienne en milieu marin. - *Laboratoire de Micropaléontologie (Université Pierre-et-Marie-Curie), Travaux*, 6, 91-109.
- Borchert, H., and Muir, R. O., 1964. *Salt Deposits, the Origin, Metamorphism and Deformation of Evaporites*. - Princeton, N.J.: Van Nostrand-Reinhold, 338 p.
- Braitsch, O., 1964. The temperature of evaporite formation. In: A. E. M. Nairn, ed., *Problems in Paleoclimatology*, p. 479-490.
- Busson, G., 1984. La sédimentation épicontinentale des bassins salins accomplis et des bassins évaporitiques avortés: effet sur la sédimentation océanique contemporaine et contiguë dans le cas du Crétacé saharien et Nord Atlantique. - *C. R. Acad. Sci., Paris*, [II] 299: 213-216; Paris.
- Butler, G. P., Krouse, R. H., and Mitchell, R., 1973. Sulphur isotope geochemistry of an arid supratidal environment, Trucial Coast. - In: Purser, B. H., ed., *The Persian Gulf*, p. 453-462. New York: Springer Verlag.
- Casas, E., and Lowenstein, K., 1989. Diagenesis of saline pan halite: comparison of petrographic features of modern, Quaternary and Permian halites. - *Journal of Sedimentary Petrology*, 59, 724-739.
- Davies, G. R., and Ludlam, S.D., 1973. Origin of laminated and graded sediments, Middle Devonian of western Canada. - *Geological Society of America, Bulletin*, 84, 3527-3546.
- Emons, H. H., 1967. Untersuchungen an Salzsystemen in gemischten Lösungsmitteln. - *Third International Kalisymposium, Proceedings*, 1, 257-268. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig.
- Friedman, G. M., 1980. Review of depositional environments in evaporite deposits and the role of evaporites in hydrocarbon accumulation. - *Centre des Recherches Exploration-Production Elf-Aquitaine, Bulletin*, 4, 589-608.
- Herbert, H. J., 1995. Zur Geochemie und geochemischen Modellierung hochsalinärer Lösungen. Habilitationsschrift, University of Kiel.
- Hite, R.J., & Buckner, D.H., 1981. Stratigraphic correlations, facies concepts, and cyclicity in Pennsylvanian rocks of the Paradox Basin, in Wiegand, D.L., (ed.), *Geology of the Paradox Basin*, Rocky Mt. Assoc. Geol., Field Conf. Guidebook, pp. 147-159.
- Hovorka, S. D., 1987. Depositional environment of marine-dominated bedded halite, Permian San Andreas Formation, Texas. - *Sedimentology*, 34, 1029-1054.
- Jauzein, A., and Hubert, P., 1984. Les bassins oscillants: Un modèle de genèse des séries salines. - *Science Géologique, Bulletin*, 37, 267-282.
- Kinsman, D. J. J., Boardman, M., and Borcsik, M., 1974. An experimental determination of the solubility of oxygen in marine brines. - In: Coogan, A. H., ed., *Fourth Symposium On Salt*, 1, 325-327.
- Koepfen, W. P., 1931. *Grundriß der Klimakunde*. - Berlin: de Gruyter.
- Lucia, F. J., 1972. Recognition of evaporite-carbonate shoreline sedimentation. - In: Rigby, J. K. and Hamblin, W. K., editors, *Recognition of Ancient Sedimentary Environments*. Society of Economic Paleontologists and Mineralogists, Special Publication No. 16, 160-191.
- Magaritz, M., and Peryt, T. M., 1994. Mixed evaporitic and meteoric water dolomitization: isotope study of the Zechstein Limestone (Upper Permian), southwestern Poland. - *Sedimentary Geology*, 92 (3-4), 257-272.
- Matthews, R. D., 1975. Evaporite cycles in the Devonian of Michigan. - *Ontario Petroleum Institute, 14th Annual Conference*, Paper No. 11, 13 p.
- McCaffrey, M.A., Lazar, B., and Holland, H. D., 1987. The evaporation path of seawater and the coprecipitation of Br and K with halite. - *Journal of Sedimentary Petrology*, 57, 1928-937.
- Rothschild, L. J., Giver, L. J., White, M. R., and Mancinelli, R. L., 1994. Metabolic activity of microorganisms in evaporites. - *Journal of Phycology*, 30 (3), 431-438.
- Sanford, W. E., and Wood, W. W., 1991. Brine evolution and mineral deposition in hydrologically open evaporite basins. - *American Journal of Science*, 291, 687-710.
- Seidel, A., 1917. *Solubilities of Inorganic and Organic Substances*. - 2nd edition, Princeton, N.J.: Van Nostrand-Reinhold, 367 p.
- Sonnenfeld, P., 1984. *Brines and Evaporites*. - Orlando, Fla.: Academic Press, 61 pp.
- Sonnenfeld, P., 1995. The color of salt. - *Sedimentary Geology*, 94, 267-276.
- Sonnenfeld, P., and Hudec, P. P., 1985. Origin of clay films in rock salt. - *Sedimentary Geology*, 64, 113-120.

- Sonnenfeld, P., and Kühn, R., 1993. Ein Vorkommen von kristallwasserhaltigem Kalziumchlorid im Tachhydrit des Sergipe Beckens, Nordost-Brasilien. - *Kali und Steinsalz*, 11 (5/6), 187-189.
- Strakhov, N. M., 1962. *Principles of Lithogenesis*. - Akademiya Nauk SSSR, Moscow (transl.: Consultants Bureau, New York, 1967-1970, 3 vols).
- Stumm, W., and Morgan, J. J., 1970. *Aquatic Chemistry*. - New York: Wiley Interscience, 583 p.
- Taher, A. G., Abd El Wahab, S., Krumbein, W. E., Philip, G., and Wali A. M., 1994. On heavy metal concentrations and biogenic enrichment in microbial mat environments. - *Mineralium Deposita*, 29 (5), 427-429.
- Wardlaw, N. C., 1972. Unusual marine evaporites with salts of calcium and magnesium chloride in Cretaceous Basins of Sergipe, Brazil. - *Economic Geology*, 67, 156-168.
- Wattenberg, H., 1936. Kohlensäure und Kalziumkarbonat im Meere. - *Fortschritte der Mineralogie, Kristallographie und Petrographie*, 20, 168-195.