

GENESIS OF MARINE EVAPORITES - A SUMMATION

PETER SONNENFELD

University of Windsor, Windsor, Ontario, Canada N9B 3P4

(Manuscript received September 27, 1991; accepted on March 25, 1992)

Abstract: Evaporite minerals precipitate in a temperature range of +32 °C to -54 °C in concentrating brines with a density of 1.1 - 1.4 g/cm³, as evaporation rates decrease and precipitation accelerates. Soils of nearly all ages contain pseudomorphs after individual evaporite crystals; however, there are only Proterozoic and Phanerozoic bedded evaporite deposits. Within a marine basin, gypsum precipitates on shoals and shelves, halite in deeps, and K-Mg- or Ca-Mg-chlorides preferentially on the western flank. The mean rate of halite accumulation exceeds rates of subsidence and yields a shallowing basin. A density stratified brine with high pH and low Eh in its bottom waters uniformly distributes chloritic clay markers supplied by flash floods, but tends to dissolve coarse siliciclastics. Na-carbonates and -sulfates occur only in lacustrine setting or in nests with marine beds, where meteoric waters have infiltrated. Cyclicity of deposition in a key feature of all evaporite basins. Permian and Neogene potash deposits have been heavily sulfatized by a meteoric water influx along clay markers and anhydrite laminae. Salt diapirs pierce overlying strata wherever these are exposed to tectonic stresses or to bending moments along continental margins; cratonic basins are rarely affected.

Key words: formation of evaporite minerals, brine chemistry, evaporite basins.

Introduction

Evaporites contain minerals precipitated from naturally occurring marine or continental brines that were concentrated to saturation by evaporation or by freeze-drying.

The sequence of primary precipitation is identical in all Phanerozoic marine evaporite basins. Laws of physics and chemistry of brines have thus remained constant, biogenic influences on precipitation did not change, and the ionic composition of seawater (whatever its salinity might have been) has never deviated far from present values (Holland 1984; Sonnenfeld 1987).

Climatic constraints

Evaporites form in arid and semiarid lands, where annual evaporation exceeds atmospheric precipitation and runoff, i.e., in two subtropical belts of high evaporation and two subpolar belts of low precipitation. Both subarctic and intracontinental deserts give rise only to groundwater-derived soil encrustations and to lacustrine evaporites.

A brine evaporates as long as the pressure of air is lower than that of the brine. This difference declines as the brine concentrates; concurrently, the surface tension rises, rendering it more difficult for water molecules to escape. Evaporation thus slows down as brines concentrate. A brine saturates for halite at an atmospheric humidity of less than 76 %, for potash at 46 %; further concentration requires an even lower humidity. The degree of aridity thus sets an effective limit to evaporation and concentration of residual brines.

Atmospheric precipitation and river and groundwater discharge decrease with increasing aridity. Leaves, pine cones, fern pinnules, and tree trunks, found well preserved in halites, indicate a discontinuous vegetation cover rather than a desert, even near major marine evaporite basins, and an annually variable

with occasional flash floods.

Enhanced solar radiation in warm periods imparts more energy to atmosphere and oceans, tightens the anticyclonic whorls of subtropical atmospheric and marine circulation, reducing their diameter. Evaporation from the oceans increases, humid conditions spread, dry belts contract, and evaporite deposition declines. An early Holocene rise of 5 °C in the mean equatorial air temperature increased the water carrying capacity of tropical winds more than these winds could hold in subarctic regions even where the temperature rose by 20 °C; rains fell over wide areas, diluting any surface brines.

Conversely, a lower radiation intake translates into less evaporation over equatorial seas, less latent energy transported as water vapor into higher latitudes, and less global rainfall. Less energy transmitted to the Hadley cells increases the diameter of the subtropical Highs; the width of the Horse Latitudes expands and with it the subtropical dry belts. With rising aridity the rainfall becomes more variable; temperatures, rates of evaporation, and sea level fluctuate more in cooler periods. In addition, winds blowing out to sea from a chilled land surface warm up over water and maximize evaporation losses. Expanding belts of dryness roughly coincided with Pleistocene glacial periods, narrowed belts of deserts with interglacial times. However, aridity maxima lagged slightly behind temperature minima.

A slight drop or rise in sea level along a gently sloping coastline either exposes broad shelves or inundates a beach. This causes large changes in evaporation losses and in the water surface subject to evaporation. A drop in water temperature of 1 °C lowers the sea level enough to critically reduce the cross sectional area of shallow straits and the water exchange through them. Because of climate and sea level variability evaporites are more plentiful during dry, cold periods, less in periods of high insolation. In that respect they are antithetic to the optimal spread of land plants and with it of peat and coal belts.

Evaporite minerals

Evaporite minerals precipitate when there are not enough free water molecules to act as solvent. Seawater contains 92 water molecules per ion, but a brine saturated for NaCl only 4.5. The brine dries out, i.e., the solvent is lost, at a salinity of 350–400 ppt and an air temperature of about 32 °C. All dissolved salts precipitate in polar regions by freeze drying at about -54 °C. This gives a range of about 86 °C for all changes in natural brine composition between the eutectic point (when the solution solidifies) and the eutonic point (when it dries out). Evaporites precipitate at essentially atmospheric pressures.

Saturated brines precipitate aragonite at 1.100 g/cm³ and reach the eutonic point at a density of 1.3995 g/cm³ with the complete solvent removal, giving a range of less than 0.3 g/cm³. There is no record of a marine evaporite basin having precipitated all its solute right to the eutonic point, even when the open water body dried out. In all instances the terminal concentrate escaped or was diluted.

Continental evaporites

Groundwater-derived evaporites

Groundwater-derived gypsum and halite crystals, crusts and efflorescences are known since the Archean era, 2,550 Ma B.P.; earlier ones are all replaced by other compounds as pseudomorphs, molds and casts (Sonnenfeld 1984). They occur in semiarid and arid soil horizons of any latitude and almost any period. Efflorescences are found in microenvironments such as mine outlets, tunnels, lava caves, or tomb stone surfaces.

Groundwater that rises to the surface evaporates and precipitates crusts and crystals in the soil. More soluble components leapfrog over less soluble ones: A calcite cement in a leached soil horizon is overlain by a gypsum crust at the depth of wetting. Halite efflorescing at the surface is largely blown away. If seawater at high tide wets an arid soil and then ebbs away, seepage into the ground will form a reverse sequence of halite cement beneath gypsum crusts.

Sebkhas (or sabkhas) are shallow depressions episodically filled by rain, rising groundwater, or storm tides. Diagnostic for their precipitates are lattice imperfections in Sr-enriched anhydrite, replacive or displacive gypsum in diagenetic nodules or enterolithic shapes, a calcite deficiency, and a dominance of detrital fragments.

Paralic sebkhas are prograding peritidal plains subject to storm tides or to seawater interacting with discharging groundwater. Continental sebkhas, also called playas, are periodically flooded by runoff or fed by groundwater; the evaporite minerals form concentric belts with the most soluble minerals closest to the lake shore. The slower the groundwater movement and the more dilute the initial brine, the larger are the crystals (Perthuisot 1975).

Lacustrine evaporites

Lacustrine evaporites accumulate in endorheic basins, i.e., intracontinental basins that do not drain to the outside. They are not easily preserved and are found only in late Mesozoic and Cenozoic sediments. Alkaline lakes initially precipitate Na- and Na-Ca-carbonates. Associated with them are oil shales containing trona [Na₂CO₃·NaHCO₃·H₂O] and thenardite [Na₂SO₄],

such as the Green River shale in Wyoming; any oil extraction requires extensive hydrogenation. All hydrated species of minerals are unstable and redissolve in time or convert to anhydrous forms. Hydrated CaCO₃ varieties normally convert in lakes to calcite. Soda lakes occur over bedrock composed of crystalline rocks or polymictic, feldspathic, or argillaceous sandstones, while Mg-rich brines form where carbonated groundwater leaches basic igneous rocks.

Sulfide oxidation generates sulfate ions. Na-sulfates start forming at four-fold brine concentration. Gypsum [CaSO₄·2H₂O] follows where there is no Na-bicarbonate; otherwise calcite [CaCO₃] precipitates with glauberite [Na₂SO₄·CaSO₄], mirabilite [Na₂SO₄·10H₂O], or thenardite [Na₂SO₄]. Mirabilite occurs wherever the brine approaches freezing temperatures in the winter and dehydrates at 32.4 °C to thenardite.

Bloedite [Na₂SO₄·MgSO₄·4H₂O] forms where some Mg-ions are present; epsomite [MgSO₄·7H₂O] dominates in efflorescences of Mg-rich brines. Lacustrine K-sulfate minerals are extremely rare, because most K⁺ replaces Na⁺ in clays and converts them to illites. K-Mg-solutions can alter precipitated gypsum to polyhalite [K₂SO₄·2CaSO₄·MgSO₄·2H₂O].

Many hypersaline lakes develop an alkalinity and pH high enough to dissolve swept-in silicates. They precipitate as hydrated framework silicates in the zeolite group (e.g., hydrated Na-Al-, Ca-Al-, and Ca-Na-Al-silicates found in several lakes in the sahel in Africa). Complex hydrated minerals are only known from dried-out Neogene lakes, but not from more ancient sediments. They convert in time to euhedral feldspar crystals, or turn into quartz or chert as their cations are leached out.

Igneous and metamorphic rocks contain little chloride. Cl-ions in groundwater come from a discharge of CaCl₂-enriched formation waters or from dissolving ancient marine chloride deposits; salt creeks or salt rivers are common even outside the arid belt. Halite can then precipitate, or below -23 °C hydrohalite [NaCl·2H₂O], which remains stable to about +1.5 °C. Re-precipitation leads to secondary non-marine halite deposits, chemically purer than marine evaporites, with a negligible Br/Cl ratio. Re-precipitated sequences usually do not contain a complete succession of marine evaporites, being either devoid of CaSO₄ or of potash deposits. Great Salt Lake, Utah, derives its salt content from leached Jurassic beds in the Wasatch Range, the Dead Sea from Quaternary salt domes around and under it.

Marine evaporites

Most evaporites are deposited by seawater evaporating in marginal seas in the semiarid belt of subtropical high air pressures. Surrounding them are interstitial precipitates, crusts, crystals or nodules, in coastal sands and silts. The earliest gypsum or anhydrite beds are about 1.7–1.8 Ga old, i.e., bedded precipitates have formed in open lagoonal waters only since the Proterozoic eon (Zharkov 1981). Some speculation can be entertained about available oxygen and bacterial activity levels in a marine environment that produced banded iron formations in one locale, massive gypsum beds in another. Massive chloride (halite and potash) beds are only known since the Infracambrian or Ediacarian (about 700–800 Ma B.P.), better known as the onset of the spread of Metazoa.

Marine halite precipitation appears to have ceased worldwide in several intervals in Phanerozoic earth history. The cause of this unclear; it seems to coincide with bursts in plant development and an apparent breakdown in the protective ozone layer,

in other words, it points towards an atmospheric or radiation cause. Several such interruptions are known, such as the one in the Middle Ordovician, 40 Ma in length (Zharkov 1984), immediately prior to the appearance of land plants. The last one of equal length, at the Cretaceous/Tertiary boundary, extended from Santonian (Upper Cretaceous) to the end of Paleocene. It resulted in the stepwise elimination of all marine and terrestrial animals in excess of 25 kg of weight, while allowing at the same time UV-dependent land plants to thrive and proliferate. It coincided with an increase in the partial pressure of CO₂, indicated by a worldwide spread of marine hardpans (Sonnenfeld 1978).

Currents in the open ocean thoroughly mix the waters and prevent the formation of increasingly saline brines. Even so, individual gypsum or halite crystals occur where concentrated brines discharging into the sea, or into basaltic crevices on the ocean floor.

Precipitation sequence

A cubic meter of seawater of a density of 1.0257 g/cm³ contains 35.77 kg of solute. In marine brines, 40 - 90 cm³ of aragonite [CaCO₃] are the first precipitate, followed by 0 - 675 cm³ of gypsum [CaSO₄·2H₂O] after 81 % of the solvent have been removed, up to 13,000 cm³ of halite [NaCl] at 91 % of the solvent removed, then either 380 cm³ of sylvite [KCl] or 1,750 cm³ of carnallite [KCl·MgCl₂·6H₂O] and finally 0 - 2,435 cm³ of tachyhydrite [CaCl₂·2MgCl₂·12H₂O] (brine-filled pore spaces are not taken into account), leaving 19.3 - 28.5 moles of Mg⁺⁺ and various trace elements in the residual brine. Halite crystallization exhausts the sodium in marine brines, sylvite and carnallite exhaust the potassium, either gypsum or tachyhydrite exhaust the calcium. No other primary Na- or K-minerals are known in a marine sequence (Fig. 1).

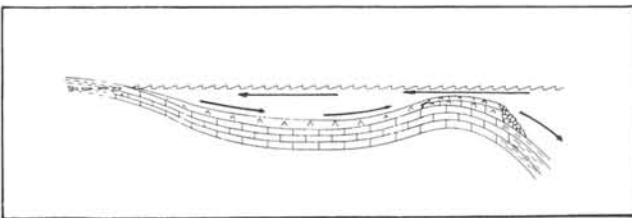


Fig. 1. Marine brine saturation curve.

Rubidium, cesium, thallium, and ammonium do not form independent evaporite minerals, but may substitute for potassium in the crystal lattice. NH₄ may substitute for K, Fe for Mg, and Sr for Ca. Br substitutes for Cl and the amount varies with brine concentration, Mg-availability, distance from shore, brine depth and temperature; degree and frequency of recrystallization of any precipitate, sorption by clays, and scavenging by algae or bacteria. Fluorine, iodine, lithium, and many trace elements remain in the residual brine to be soaked up in interstitial spaces of the precipitates. Poorly soluble barite either occurs in nests in limestones or it replaces gypsum.

Boron comes from volcanic sources or from swept-in muscovite flakes. Borates remain in the terminal brine or form hydrated minerals that precipitate together with gypsum. Authigenic tourmaline slivers form occasionally.

Phosphates are rare in evaporitic environments and are mutually exclusive with sulfates; iodides and chlorates are unknown

in marine evaporites. Nitrates and iodates occur in deserts (< 10 mm annual rainfall); they are unknown as ancient deposits, marine or continental.

The entrance barrier

Marine evaporites precipitate in lagoons of subtropical semi-arid regions with long dry summers, little surface or groundwater runoff, and widely variable seasonal rains. The optimal area lies in either hemisphere on the west side of continents with offshore winds and descending undersaturated air masses of the Horse Latitudes.

Evaporation lowers the sea level in lagoons and surface ocean water drains in by gravity. The Coriolis effect deflects the inflow in the northern hemisphere anticlockwise along the shore, tilts the interface both westward and poleward, and controls the facies distribution. Because of the vertical component of the Coriolis effect, entrance barriers are more effective facing east or equatorward, rather than west or poleward.

The inflow sets up an interface inclined towards the entrance and a bottom outflow. This interface between inflow and outflow, a pycnocline, impedes vertical fluid mixing and prevents convection. Storm energies dissipate along the interface without overturning the density gradient. Its depth is a function of the length of a strait to its total depth, the velocity of the inflow and the density difference; the lower the interface, the less brine can escape.

If the outflow is unhindered (e.g., in the modern Persian Gulf), salinities in the basin equilibrate at values only marginally higher than in the open sea. Open marine shelves, no matter how wide, are unable to concentrate brines by more than about 10 - 12 % before such brines slide along an inclined seafloor into the open sea. Salts dissolved in a marine inflow tend to be balanced by those in the concentrated outflow and no precipitation or further concentration occurs, as an equilibrium establishes itself short of saturation.

Ochsenius (1877) noted that for evaporites to precipitate an entrance sill needs to restrict water circulation in a lagoon and to diminish the solute exchange by frictional drag (e.g., as in the modern Mediterranean Sea). A continuous brine inflow prevents desiccation. Concentration rates are then a function of the degree of restriction, the annual water deficit and the volume of resident brine to be concentrated.

Lagoons do not form a closed system. An isochemical evaporation of seawater should give a ratio of gypsum to halite to K- and K-Mg- salts to Mg- salts as 1 : 19 : 0.6 : 11 (Sonnenfeld 1984), in other words, a volume ratio between CaSO₄ and all other salts of higher solubility of 1 : 30.6. Isochemical ratios have not been observed in any Phanerozoic evaporite basin; instead, there is a substantial deficiency of each salt of progressively higher solubility.

In calculating how much seawater needed to evaporate in order to produce any given evaporite mineral, it was found that volumes of minerals of lower solubility were in surplus, compared to a closed basin situation. The Stassfurt member of Zechstein evaporites displays a six-fold deficiency of halite over gypsum and a three-fold deficiency of potash salts over halite (Krull 1917), while the deficiency of halite over gypsum in the Permian Castile Formation of West Texas and New Mexico is 30-fold (King 1947). The British portion of the Werra anhydrite member in Zechstein evaporites comprises about one sixth of the basin volume or five times as much as theoretically ought to be present. It presupposes over four hundred water exchanges

and an insufficient space would have been left in the basin to accept further seawater because of the volume occupied by the residual brine (Taylor 1980).

A pronounced difference in ratios of compounds dissolved in seawater and present in any evaporite sequence mandates a selective process of eliminating some compounds by seepage or outflow through the entrance. Krull (1917), therefore, augmented Ochsenuis' barred basin model by assuming a continuous inflow/outflow regime, in which the outflow progressively drains increasing fractions of compounds of higher solubility (Fig. 2).

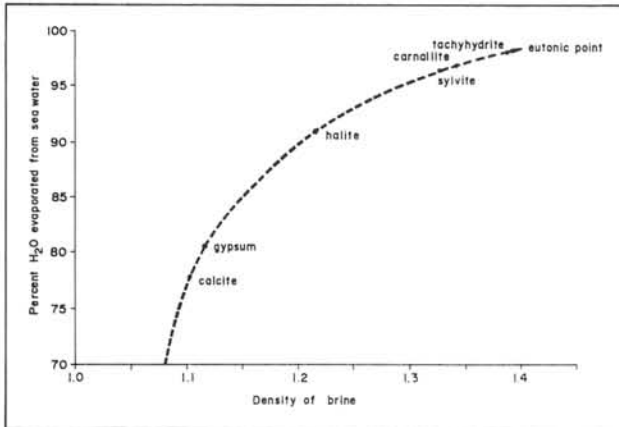


Fig. 2. Inflow/outflow regime in a lagoonal circulation.

The configuration of the entrance strait, its dimensions and its convolutedness constrain a water exchange with the open ocean. An unlimited inflow would prevent its concentration. There are thus severe limits to the size of inflow and outflow in respect to the surface area of the basin and the rates of evaporation.

The ratio between the cross sectional area of the inlet and the surface area of the brine are 6 - 9 orders of magnitude apart (Lucia 1972). To achieve saturation for a given evaporite mineral, the outflow can only be a small fraction of the inflow volume, i.e., less than about 2/9 for gypsum, 2/17 for halite, 1/13 or 1/14 for potash minerals, and 1/16 for tachyhydrite (Sonnenfeld 1984). It makes no difference to the total water exchange whether the dimensions of the entrance strait represent several small inlets or one larger one.

Initial precipitation

Carbon utilization and aragonite precipitation

Seawater initially fills a slowly subsiding shallow depression and algal mats precipitate aragonite on intertidal and offshore shallow sunlit shelves. Hydrous carbonates do not occur in marine evaporites: bacteria and blue-green algae use CO_2 dissolved in seawater for aragonite precipitation, or it escapes when rising salinity or heating decrease its solubility.

Aragonite [CaCO_3] starts precipitating from seawater at a density of about 1.100 g/cm^3 , or three-fold concentration. Rapidly nucleating, it is the preferred form of CaCO_3 once the Mg-concentration exceeds 243 ppm or about 18 % of its concentration in seawater; slowly crystallizing calcites predominate in

lacustrine environments. Fewer Mg-ions are needed in warmer brines to favor aragonite and subdue calcite precipitation; Nations somewhat counteract this effect. However, eventually aragonite converts to calcite; Mesozoic aragonites are very rare, pre-Permian one virtually unknown. Despite the abundance of sodium in seawater, no primary Na-carbonate and -sulfate nests are found in marine evaporites.

Algal reefs

The inflow from the open ocean carries nutrients; it fosters flourishing algal pinnacle reefs at the basin entrance and a prolific planktonic fauna and flora. The bottom outflow depletes the shelf in front of the entrance sill of nutrients by washing them down the continental slope. Bottom dwellers cease to migrate from the open ocean.

Reefs produce more organic material than they consume and their oxygen consumption is high. Salinity increments are deadly to many planktonic organisms. The organic matter and dead plankton eventually sink to the bay floor, but are neither oxidized in the anaerobic environment nor consumed by scavengers. Natural enemies of reefal communities, burrowers or grazers, die out because of a declining oxygen supply and a rising osmotic pressure differential. Bioturbation and scavenging cease and the interface to oxygenated surface waters becomes a barrier to oxygen-consuming marine biota. Only algal mats can survive even in halite saturated brines.

The entrance channel is gradually filled with dead reef trunks and with storm-derived reef debris obstructing the water exchange. The inflow dictated by evaporation losses accelerates, slowing the outflow by increased friction. Thus the reefs promote concentration of the brine. The closing of the Castile reef in West Texas tilted the balance between inflow and outflow of the Delaware Basin and caused the basin to concentrate to saturation first for gypsum, then halite and finally potash deposits of the Castile Formation (Kroenlein 1939).

When sediments block an entrance strait, seawater seepage from outside the basin alone cannot match evaporation losses and drain surplus solutes, unless the land bridge is extremely narrow. The permeability of a broad belt of algal limestones is too small to allow seepage to maintain a water level over wide areas. At least a seasonal open flow must be maintained to prevent a very rapid drying out (Sonnenfeld & Al-Aasm 1991).

Sulfate destruction and gypsum precipitation

The bottom brine inside the lagoon becomes the habitat of anaerobic bacteria, e.g., *Desulfovibrio*, who scavenge incoming SO_4 -ions to obtain their oxygen. They also attack precipitated gypsum, if organic material is available as nourishment. Anaerobes can utilize inorganic carbonate as carbon source, provided there is also a source of hydrogen, such as derived from iron oxidation or clay chloritization. However, they prefer metabolizing organic matter. Macerated organic compounds thus accelerate SO_4 -reduction.

A surplus of hydrogen ions and an excess of cations resulting from hydrogen sulfide removal raise the pH and increase the stability of CaCO_3 . Bicarbonate ions, unstable in hygroscopic brines of high pH, turn into CO_2 . Concentrating marine brines can entrap only minimal quantities of CO_2 , but fluid inclusions in halites, sylvites and carnallites frequently contain some. No bicarbonate ions remain in solution at gypsum saturation and CO_2 -solubility drops below 200 ppm (Sonnenfeld 1984). Carbo-

nate 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, who reoxidize hydrogen sulfide into SO_4^- ions. Reconstituted SO_4^- 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 UV-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 concentrate, 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 1.115 g/cm^3 , or 4.5-fold concentration, at a rate of about $0.5 - 1.0 \text{ mm/yr}$. Hite & 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 (later partially converted to anhydrite [CaSO_4]), e.g., in the Cretaceous Maghreb or the Miocene Po River valley. 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.

Dissolved proteins, resins, sugars, naphthenic and amino acids delay gypsum precipitation or even prevent it; their consumption by anaerobes fosters gypsum precipitation. The higher the pH during gypsum precipitation, the stubbier are the crystals; alkanes, phenols, and fatty acids foster the formation of more tabular, equidimensional, or discoid-lenticular crystals. Gypsum crystals grow in low-pH environments in elongate, prismatic shapes, in high-pH environments only in the presence of dissolved silica.

Bacteria destroying gypsum around lagoon rims produce ^{12}C -enriched low-Mg calcite laminae. Bacterially constituted Nacarbonates are unstable in seawater and react to form either huntite [$\text{CaCO}_3 \cdot 3\text{MgCO}_3$] or hydromagnesite [$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] as possible magnesite [MgCO_3] precursors (Sonnenfeld & Perthuisot 1989). Bacterial sulfate reduction thus leads to calcite precipitation, in some instances to magnesite.

The horizontal Coriolis parameter sweeps the inflowing current along the shores and the sunlit shelves act as preconcentrators, as preferred sites of gypsum precipitation. Stripped of sulfates the brine glides toward deeper, more rapidly subsiding parts of the basin, be they grabens or other depressions. Richter-Bernburg (1957) has aptly named such shelves "saturation shelves". In strict analogy, modern salinas use condenser basins in series before allowing the brine to enter a crystallizer basin.

Ionic imbalance

The density stratification affects a vertical solute transport. The average thickness of the layers decreases with increasing salinity gradients and appears to be independent of the applied heat flux (Huppert & Linden 1979). Several features of shallow stratified waters force the solute into bottom brines, which tend to heat up due to entrapped solar radiation.

The uppermost 10 cm of seawater flowing into subtropical marginal seas absorb about 610 W/m^2 of incoming solar energy,

the next 90 cm about 470 W/m^2 . Much of this used for evaporation. A seawater/brine interface acts as a one-way mirror to entrap in bottom brines of higher refractive index almost all the remaining radiation of about 270 W/m^2 , where it converts to heat, generating a thermocline. Shelves heat up faster than deeper parts of the basin, because less brine needs to be heated per unit area and the interface is shallower. Concentrated brines warm up faster due to reduced evaporation rates and lower specific heat.

Water molecule clusters decrease with rising brine temperature and less hydrogen bonding is available to other cations. Hydrated minerals are not very soluble; higher temperatures of formation lower the number of water molecules attached to crystal lattices and increase the solubility. As the brine salinity increases, so does the hygroscopy and anhydrous minerals precipitate.

The Soret coefficient of thermal diffusivity decreases with concentration but increases more rapidly with temperature; this balances out in warm hypersaline brines (Snowdon & Turner 1960). Thermophile solutes wander towards a heat source where they become more soluble; cryophile solutes do the opposite. Downward ion migration due to thermal diffusion (the Soret effect) fortifies the salinity difference and increases the stability of the density stratification, as most of the major ions in seawater are thermophile. Some solutes change their character, e.g., NaCl becomes cryophile below 12°C . Halite or sylvite precipitation releases heat; gypsum precipitation absorbs heat below 37.5°C and evolves heat above that temperature. The Soret coefficient is very small for dissolved CaCl_2 and MgCl_2 , because the ionization factor compensates here for the Soret effect (Porter 1927).

Both the dynamic and kinematic viscosities increase with concentration, but decrease with temperature. A hydrostatic pressure gradient of overlying brines causes a solute diffusion downward in the direction of increasing salinity, dynamic viscosity, and density. Complexed molecules and other particles larger than water molecules wander into the zone of maximum viscosity (Tollert 1950). In contrast, water molecules in the brine depolymerize because of electrostriction of ions and wander into zones of minimum viscosity. A steep gradient impedes vertical fluid mixing and prevents convection. Large density difference are, however, only possible with a shallow interface between inflow and resident brine; the differences decrease with increasing depth of the inflow.

There is a measured voltage differential of about 400 - 800 mV between readings in surface waters above the pycnocline and in bottom brines (Sonnenfeld 1984). This is interpreted to be caused by a positive redox potential in oxygenated surface waters and a negative one in anaerobic bottom brines. Cations are thus attracted to bottom brines, whereas anions move toward the positive surface layer. The expulsion of CO_3 , HS^- , and possibly even Cl^- is facilitated. Indeed, Kostenko (1982) observed that the heavy metal concentration decreased in surface waters and increased in hypersaline bottom brines in contact with precipitating salts.

Although seawater contains three times as much SO_4 as cations, a sulfur deficiency early in the concentration cycle due to bacterial scavenging, and not all calcium is taken up (Borchert 1969). Halite-saturated brines contain no more SO_4^- ions. Surface runoff and discharging groundwater deliver chemical weathering products mainly as carbonates and bicarbonates; CO_2 , poorly soluble in bottom brines, is expelled.

A cation surplus develops: depending on how much calcium and strontium fail to be precipitated as gypsum and celestite,

about 19.3 - 28.5 moles Mg^{++} per m^3 of seawater influx form hydroxides or metal-organic complexes. This preserves a charge balance while freezing hydrogen atoms for bacterial growth. Any calcium not used for gypsum precipitation eventually precipitates as tachyhydrite or seeps into formation waters as a $CaCl_2$ -brine. All Cl-ions are consumed in halite, carnallite and tachyhydrite precipitation after sulfate and carbonate ions were removed. These figures have to be multiplied by the concentration factor, about 11 for a m^3 of a brine saturated for halite.

The evolving Mg-surplus supplied brucite pillars in mixed-layer clays, and occasionally produced some magnesite where bacteria had access to organic compounds on a gypsum substrate (Perthuisot 1975). Most of the Mg^{++} must have been swept out during the concentration cycle as no significant Mg-concentration have ever been recorded in brines saturated for halite, nor do brucite pillars consume as much as 470 - 695 cm^3 brucite accruing per m^3 of inflow.

Chloride precipitation

Halite saturation

Depressions in the basin floor accumulate the heavier concentrates. Halite saturation is reached at 1.2185 g/cm^3 . Marine halite can precipitate at 36 mm/yr (Täsch 1970), varies between 36 - 140 mm/yr with brine concentration; rates of precipitation in preconcentrated and closed salinas can be even higher. However, much halite is redissolved in the wet season or during storms; halite preservation or net accumulation rates may be as low as 0.1 - 4.0 mm/yr (Barnett & Straw 1983).

Anhydrite coats on halite crystal faces tend to inhibit halite crystal growth; enlarged halite crystals form only with anhydrite absent. Alcohols and other organic compounds decrease halite and sylvite solubility and force both minerals to crystallize as octaheders rather than cubes. Pyrite crystals and hematite needles are very rare in halite.

Depositional fabrics

Hopper crystals form at a becalmed brine surface, if the brine is not density stratified and does not contain soapy surfactants that cut the surface tension.

Current-deposited, cross-bedded gypsum sands (gyparenites) or halite sands (haloarenites or halolites), turbidites, gravity flows, and submarine slides occur in a dense brine over very gentle slopes (for example, in Miocene anhydrites of the northern Apennines in Italy, Permian anhydrites in eastern Germany, Miocene halites from Caltanissetta in Sicily or Verotyshchensk in the Ukrainian Carpathians, and Holocene channels in the southern Dead Sea).

Nodular anhydrite, common in evaporite sequences, has at least four possible modes of origin. It is either a supratidal alteration of a gypsum crust precipitated in the capillary zone of an ancient groundwater table, or an early diagenetic alteration of a semifluid gypsum/brine mush beneath the lagoonal floor, or a compaction texture of soft gypsum, or a recrystallization of gypsum laminations in percolating halite-saturated hygroscopic brines.

Potash saturation

Chlorides of progressively greater hygroscopicity follow upon halite, sylvite in brines covered by inflow, carnallite in those ex-

posed to the atmosphere. Saturation for sylvite occurs at a brine density of 1.3235 g/cm^3 (Strakhov 1962). The amount of water to be extracted from a halite-saturated brine to reach potash saturation is small (less than 5 % of the original amount of water in the brine). Consequently, most major primary salt deposits contain at least one horizon of potash salts, originally encased in halite. Brines saturated for KCl or $MgCl_2$, unlike those for gypsum or halite, are highly temperature-sensitive (Fig. 3). They become lighter upon cooling and can float before deposition (Boeke 1910; Cornec & Krombach 1932), concurrently losing their solubility. Potash salts are always shallow-water deposits in the decimeter-range of brine depths, after halite precipitation has been able to match basin subsidence, and thus display a gentle, near-horizontal dip away from the shore.

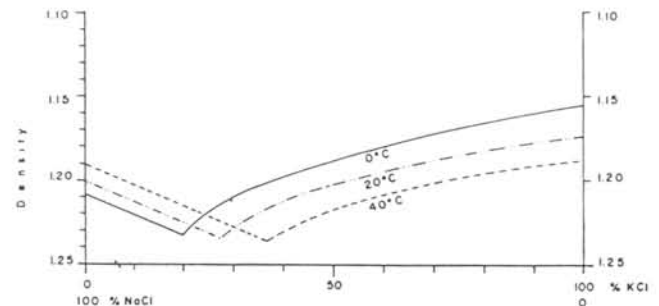


Fig. 3. Decrease in specific gravity of a KCl-NaCl solution by cooling (after Cornec & Kronbach 1932).

Potash beds extend outward from basin shelves, preferentially western ones (in paleoposition), or eastern shelves of islands and shoals within the basin; this could be related to the Coriolis effect moving concentrating currents along the eastern and northern shores or a greater inertia against earth rotation. At times the potash deposit comes within reach of coastal rain wash: within a short distance of gypsum-encrusted red beds in the Upper Kama Basin (Fore-Ural), into marginal interreef in the Michigan Basin. Miocene potash deposits are sandwiched into halites against the ancient Sicilian coast against the north-Carpathian shoreline.

Both carnallites and sylvites alternate with halite beds. Warm brines cooled in contact with rising groundwater can precipitate carnallite (Lowenstein & Spencer 1990) into a halite slush rather than as sharply delineated beds produced in open waters. The carnallite then forms disseminated textures and is called "carnallite"; correspondingly, sylvite in a halite crystal matrix is called "sylvinitite".

Normally, sylvite nucleates more slowly than carnallite. Where inflow or rainwash covers the brine, it prevents the oxidation of dissolved organic compounds, such as alcohols and nitrogen compounds derived from decaying organic matter (Fig. 4). Alcohols greatly reduce the solubility of KCl, while protein derivatives, such as urea, complex cyanides, ammonia and other nitrogen hydrides, raise the $MgCl_2$ -solubility, and so permit a yellowish sylvite to crystallize in preference to carnallite. However, even small amounts of $CaCl_2$, either still in the brine or derived from an influx of formation waters, reduce the solubility of KCl and more so of $MgCl_2$, thus forcing carnallite precipitation or a carnallitization of sylvite.

Carnallite, tachyhydrite and bischofite [$MgCl_2 \cdot 6H_2O$] extract water from the brine, and aid the concentration of the residual liquor. They are hygroscopic that they take on atmospheric

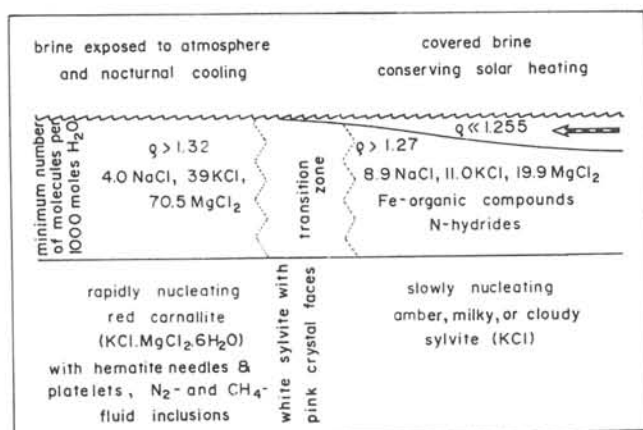


Fig. 4. Lateral distribution of carnallite and sylvite precipitation.

moisture to dissolve in adsorbed and crystal water and are stable only under brine cover. It follows that the basin did not dry out, before halite salted out to cover potash beds. All potash deposits were originally encased in halite, indicating an oscillating concentration of the brine cover.

A carnallite specimen, left exposed to hot humid tropical air in a laboratory, will absorb atmospheric humidity, turn first into a sylvite cube sitting in brine; eventually the sylvite also dissolves. Sylvite and broth revert to a carnallite crystal when both atmospheric humidity and temperature drop slightly; the conversion can repeat several times, e.g., by turning the airconditioning off and on (P. Szatmari, pers. commun.). That makes it impossible to ascertain later which of the two minerals was the original precipitate or how many recrystallization have taken place. Because sylvite cannot be precipitated below 86 °C under isothermal evaporation in sterile laboratory experiments, Holwerda & Hutchinson (1968) interpreted sylvites in the Danakil depression as an alteration of freshly precipitated carnallite by residual bitterns seeping into the ground in each season, a form of preburial leaching.

In an unstratified brine, exposed to the atmosphere, carnallite incorporates tiny hematite [Fe₂O₃] needles and platelets, that are derived from the oxidation of bivalent organic Fe-complexes (from decomposition of chlorophyll and hemoglobin). They often display pseudomorphs after an original goethite [FeO(OH)]. Red carnallite and wine-colored sylvite thus appear to be primary minerals; red sylvite and white carnallite may be secondary, produced respectively by leaching or by the introduction of MgCl₂-solutions. Hematite-bearing carnallite converts into a red sylvite at nearly 80 % loss in volume. Recrystallization of a red hematite-bearing sylvite displaces impurities to crystal boundaries; in carnallite it expels lattice substitutions.

Where several potash seams are separated by halites, frequently only the uppermost is composed of carnallite, brines from the deposition of intervening halites must have percolated down before compaction and converted lower carnallites to red sylvite beds. In turn, sylvite can be carnallitized by percolating MgCl₂-brines at a 475 % volume increase; a secondary carnallite often forms rinds on sylvite cores.

Substitution in carnallite

In the distal parts of a basin both organic compounds and dissolved oxygen reach a minimum; Fe²⁺ may here substitute for Mg²⁺ and NH₄⁺ for K⁺ in the carnallite lattice.

Some carnallite contains up to 6 % kremersite [(NH₄,K)Cl.MgCl₂.6H₂O], in which ammonium replaces some of the potassium; it is more frequent than sal ammoniac [NH₄Cl] substituting for sylvite. Iron may similarly replace the magnesium in a K-Fe-carnallite [KCl.FeCl₂.6H₂O]. Extremely hygroscopic brines can strip 75 % of the crystal water from an iron carnallite to yield douglasite [KCl.FeCl₂.2H₂O]. Rokuehnite [FeCl₂.2H₂O] seems to be its very rare later alterations product.

Rinneite [NaCl.3KCl.FeCl₂] is found in minute quantities, forming nests towards the distal part of a basin in white sylvites, commonly overgrown with sylvite, and containing carnallite, anhydrite, halite, and fluid inclusions. It forms pseudomorphs after, but never accompanies carnallite. This suggests that it is a later recrystallization product in sterile anoxic brines of very low pH < 4.6.

Tachyhydrite

Atmospheric humidity in the Lower Cretaceous of the Angolan Cuanza and Brazilian Sergipe Basins, and of the Sakonnakon and Khorat Basins of Laos and Thailand, must have dropped even further than in most evaporite basins, because here primary tachyhydrite in sandwiched into less soluble carnallite. High Br/Cl and Sr/Ca values mark as source concentrating seawater and not a soaking of carnallites in formation waters in CaCl₂ (Zharkov & Zharkova 1989).

Saturation for tachyhydrite occurs at a brine density of 1.395 g/cm³ (Strakhov 1962), which is only 4.5 kg³ or 3.2 ppt less than the eutonic point of total loss of solvent. It represents the evaporation of about 98 % of the brine at an atmospheric humidity below 35 %, that is reached only in intracontinental surroundings.

Tachyhydrite is a Ca-carnallite in which CaCl₂ substitutes for 2 KCl. For each unit of primary tachyhydrite [CaCl₂(MgCl₂.6H₂O)₂] more than half a unit of carnallite [KCl.MgCl₂.6H₂O] needs to be precipitated to deplete the potassium in the brine; there is always an underlying carnallite bed. One part FeCl₂ replaces MgCl₂ in the crystal lattice for every 10 parts in solution (Kling 1915). In Sergipe, the tachyhydrite also contain antarcticite [CaCl₂.6H₂O]. Carnallite, tachyhydrite and antarcticite use up all the remaining chloride ions, leaving a lot of magnesium unaccounted for (Tab. 1).

Table 1: Mass balance of tachyhydrite formation from seawater completely depleted of sulfate ions. Tachyhydrite formation is prevented if first 1402 g (605 cm³) of gypsum precipitate on shelves.

Brine sp.grav.	Name	Formula	mol/m ³ precip.	Weight kg	Volume cm ³
1.0257	1m ³ seawater	1.257 t/m ³	526.9	35.675	18.013
1.100	aragonite	CaCO ₃	2.2	0.22	75
1.115	gypsum	CaSO ₄ .2H ₂ O	0.0	0.0	0.0
1.212	halite	NaCl	478.2	27.95	13.090
1.3235	carnallite	KMgCl ₃ .6H ₂ O	10.0	2.80	1.745
1.395	tachyhydrite	CaMg ₂ Cl ₆ .12H ₂ O	7.55	3.86	2.315
1.398	antarcticite	CaCl ₂ .6H ₂ O	0.69	0.15	88
<1.3995	[brucite]	Mg(OH) ₂	28.4	1.65	700
escaping	28.6 M SO ₄ , .22 M B ₂ O ₅	.07 M F, .2 M CO ₃	trace elem.	2.78	

Algal photosynthesizers cannot settle and build mats or stromatolites in a basin without shallow shelves and shoals, such as one bordered by steep fault scarps. Primary tachyhydrite occurs only in basins where little or no limestone or anhydrite is present, except as ultimate caprock. Such an extreme sulfate deficiency suggests that bacteria stripped all incoming marine sulfates without any reoxidation by photosynthesizers. It is not necessary to assume a stripping of sulfate ions in some other no longer existing basin, but intercalations of some impermeable rocks had to prevent the escape of a terminal brine into the substrate. Triassic evaporites of Northwest Africa also display a pronounced deficiency of Ca-carbonate and -sulfate similar to the Lower Cretaceous ones; this could also be due to an ancestral absence of sunlit shallow shelves.

Tachyhydrite is highly soluble and unstable in temperature climates, so that extratropical occurrences have long since disintegrated. Yet some tachyhydrite has been found in the Zechstein evaporite, at times intergrown with deliquescent baeumlerite $[KCl \cdot CaCl_2]$, subject to a controversy whether it is secondary of primary.

Upon exposure to air, tachyhydrite deliquesces and leaves behind bischofite crystals. Where bischofite replaces tachyhydrite in Angola, this may be due to groundwater leaching the highly soluble $CaCl_2$. Besides being a decomposition product of tachyhydrite, bischofite has only been found in sulfatized potash deposits, never as a cap on primary potash deposits.

Bischofite can be formed at a density of 1.353 g/cm^3 in artificial pans, where aragonite and gypsum precipitation in preconcentrator pans has depleted available Ca-ions.

Siliciclastic content

Coarse clastics

Lands surrounding an evaporite basin commonly slope gently; a slight oscillation in sea level results in a large change in the water surface. There is a shoreward fining of clastics, with only red clays on the coastal flats, cut by a few wadis, and covered by a sporadic vegetation. Winter rains and storms produce floods, loosen the soil and sweep finer particles towards the coast.

Clastic intercalations in evaporite sequences mark a break in the evaporative brine concentration. They are scarce because of scant runoff in semiarid areas. The amount of swept-in clastics is very subordinate, except close to the shoreline of an abutting hill chain (for example the Miocene Transcarpathian Basin or the Permian Fore-Ural Basins). Without evaporite precipitation such basins would have been "starved basins" (subsiding depressions with meagre sedimentation as, for example, the Quaternary Mediterranean Sea).

Quartz sands and silts are quite commonly embedded in marginal gypsum shelves. They mark a very major freshening. However, discrete quartz sand intercalations, always encased in anhydrite, are extremely rare in halites. No gradation is known from halite through silty or sandy halites to halitic siltstones and sandstones. Quartz sands never occur in sylvites or carnallites, because flash floods tend to dissolve all accessible potash beds, a m^3 of carnallite in $2.5 m^3$ and a m^3 of halite in almost $6 m^3$ of inflow. Even windblown detrital quartz or feldspar grains are absent in halites, sylvites, carnallites, and tachyhydrites. Euhedral quartz and feldspar grains are neoformations due to silica solution.

A few detrital grains of amphibole, epidote, garnet, staurolite,

tourmaline, and zircon in halites and carnallites are the memento of ancient dust- and sandstorms. Modern salt flats always have a layer of dust on their windward crystal faces.

A dissolution of blown-in or washed-in quartz and feldspar and a leaching of some silica from clays attest to a very alkaline pH. Even a few mg/m^3 of ammonia in the brine (derived from protein breakdown) suffice to raise the pH substantially, while dissolved Mg- and Al-ions reduce silica solubility. All the dissolved silica is flushed out; chertified limestones are common on the original down-dip side outside the basin.

Clays

Seawater in surficial ocean currents is virtually free of suspended clay particles. Flash floods supply all clays in evaporites from shore and they spread out along the interface between rainwash and resident brine. They do not signify a total freshening of the brine, but merely a rainstorm in the hinterland. Brackish and freshwater faunas from estuaries can be swept in with the clays and can be dragged along the interface for great distances without showing any abrasion.

The clay floccules settle slowly through the brine; as the solute concentrates, floccules get bigger and retain more brine.

When halite precipitation resumes, the brine entrapped in the floccules keeps the clays permeable. The clay laminae can later act as conduits for brines or meteoric waters entering from basin margins. Percolating hygroscopic brines induce in clays shrinkage cracks, called "syneresis cracks", which are indistinguishable from subaerial desiccation cracks and increase the permeability.

All clays are efficient ion exchangers. A hypersaline brine ultimately transforms them into mixed-layer varieties of the Mg-chlorite family $[Mg_3Si_6O_{15} \cdot 6Mg(OH)_2]$ (with Al substituting both for Mg and for Si) by the insertion of up to 43 weight % of brucite $[Mg(OH)_2]$ pillars. Hydrogen is liberated; some silica, alumina, and various cations are leached out. Dissolution of silica and insertion of brucite pillars is only possible at a very alkaline pH, in excess of 9.

Halloysites kaolinite, Fe-chlorite, muscovite, and montmorillonite are restricted to nearshore sites, attapulgite $[Mg_3Si_6O_{15} \cdot 3Al_2Si_6O_{15} \cdot 3Mg(OH)_2 \cdot 24H_2O]$ or palygorskite $[Mg_3Si_6O_{15} \cdot 3Al_2Si_6O_{15} \cdot 6Mg(OH)_2 \cdot 24H_2O]$ are present offshore, replaced by sepiolite $[Mg_3Si_6O_{15} \cdot Mg(OH)_2 \cdot 6H_2O]$ farther out, indicating a progressive replacement of Al by Mg. Talc $[Mg_3Si_6O_{15} \cdot 1.5Mg(OH)_2]$ is a rarer variety. The Mg-chlorites are thus large magnesium sinks. The Mg-surplus generated by sulfur bacteria in $100 m^3$ of halite-saturated brine can supply enough brucite pillars for 1 - $5 m^3$ of chlorites. Brines rich in potassium can later alter Mg-chlorites to illites (Sonnenfeld 1984).

The general absence of marcasite, pyrite and other sulfides in both gypsum and the chloride facies or associated clays is further evidence of an alkaline medium.

Effluents

Seepage

As the brine increases its density, it eventually displaces underlying formation fluids, giving rise to coastal springs fed by formation waters. At the same time, the inflow/outflow ratio increases with rising drag on the outflow. By the time the basin has reached potash saturation, the bottom outflow through the entrance

strait probably has ceased and further brine escapes only into the subsurface through an as yet unconsolidated bay floor.

The basal cycle of a multicyclic halite sequence commonly contains little bromine, is almost indistinguishable from lacustrine or recycled halites. This is due to Br-leaching by downward percolation of brines from overlying cycles. Red sylvite beds underneath a terminal red carnallite corroborate this percolation.

Disposal of magnesium

A byproduct of the generation of a hypersaline brine is the eventual formation of Mg-rich, sulfate-deficient bitterns, as far as magnesium has not been consumed in altering swept-in continental clays into Mg-chlorites. They seep into the subsurface taking along dissolved or colloidal silica and organic matter. With decaying organic matter present, especially amines, Mg-complexes can turn a CaCO₃-substrate or surrounding limestones into dolomite. All carbonate intercalations, which for the most part extend from marginal reefs and limestone banks, show evidence of extensive secondary dolomitization by a brine that probably carried Mg-complexes (Sonnenfeld 1964).

These dolomites possess a sucrosic texture (i.e., all crystals are nearly euhedral and nearly of equal sizes). The crystals are smallest near the source of Mg-rich brines and become coarser along a paleohydraulic gradient, suggesting a slowing down of the rate of dolomitization with distance from the source of the brine. Dolomites are also found near the interface between groundwater discharge and seawater influx as cryptocrystalline soft paste that eventually hardens into a very fine-grained rock, quite different from sucrosic dolomites. An elimination of CaSO₄ from the brine seems to be an essential step in dolomite formation in either case.

Klement (1895), Van Tuyl (1916) and Linck (1937) have repeatedly shown that limestones are not dolomitized by long-time exposure to seawater or to MgCl₂-solutions, but that the Mg-bond to any anion has first to be broken. However, even after intensive studies of the dolomitization problem, we still have not worked out the details of how it comes about, probably because there are several divergent ways of forming secondary dolomite (Warren 1989).

Fluid inclusions

Fluid inclusions in evaporites fill voids, often negative crystals, filled with gaseous or liquid fluid phases, mainly NaCl-brines, organogenic nitrogen, ammonia, hydrocarbons, and CO₂. Dissolved protein derivatives apparently decompose prior to carnallite precipitation. Fluid inclusions are most frequent in carnallites, less in sylvites, and least in halites. They give rise to the term *řcrackle saltř* or *řpopcorn saltř*.

They migrate, especially under uniaxial stress, because of solubility difference along warmer and colder cavity walls. Those with less than ten volume-percent of gas move toward warmer temperatures, while those with a large gaseous fraction move in the opposite direction. Along the way they may coalesce or be contaminated by intercrystalline moisture. Continued migration is hindered by grain boundaries that can permanently entrap the inclusion. This migration and coalescing of fluid inclusions due to heating affects storage of wasters in evaporitic caverns.

Fate of organic matter

Evaporite basins generate organic matter up to 20 - 30 times

faster than the open ocean (Evans & Kirkland 1988). Lack of oxygen prevents its destruction; anaerobic bacteria contribute to its decomposition. Dissolved organic compounds and even broken up polymers migrate in hypersaline brines as finite globules or as gas. They seep into formation waters through a porous substrate of gypsum or halite slush. In a Na-enriched brine the organic matter goes into solution, or forms chloride-organic complexes with Mg, Fe, and other metals. Colloidal transport of hydrocarbons peaks at 70 °C, above 85 °C the hydrocarbons form an independent phase, a temperature normally reached at a depth of about 1300 - 1,700 m. Such temperatures are common in concentrating brines that captured solar radiation beneath the pycnocline; in seeping into the subsurface the brine is subjected to the geothermal gradient, which is high in chloride sequences. In contrast to hydrocarbon migration through sandstone-shale sequences, temperatures conducive to hydrocarbon maturation are reached at shallow levels in evaporite basins.

The matrix in which the hydrocarbons mature controls the maturation pathway. Ca-sites in gypsum lattices can break up organic chains; clays polymerize them into molecules too large to migrate through available pores. Sodium fosters mobility of liquid hydrocarbons, so NaOH is used as a well stimulant. Because of the catalytic reactions of Ca-, Na-, K-, and Al-sites in crystal lattices of the country rock, different evaporite basins tend to contain different types of hydrocarbons (Sonnenfeld 1985).

Basins in which concentration reached only gypsum saturation produce primarily, but not exclusively, gaseous hydrocarbons and thus gas field. The Neogene fields in the Po Valley of Italy and the Cretaceous fields in Algeria are examples. Basins in which concentration has proceeded to halite saturation produce a mixture of gaseous and liquid hydrocarbons that later migrate into nearby reservoirs of any age. The Mississippian fields of Saskatchewan and Devonian fields of Alberta are examples.

Repositories of organic matter

Reefs, common near the entrance to an evaporite basin, around shoals or islands, can later become important trapping sites for migrating hydrocarbons. The same is true of coarse grained uncemented or partially cemented limestones, be they oolitic, coquinoid, or simply arenites and rudites. Other good exploration targets are secondary idiomorphic (euhedral) and hypidiomorphic (subhedral) dolomites, provided they have been bent into antiformal structures.

Where any argillaceous limestones and uncompacted calcareous shales soaked up migrating immature hydrocarbons, these were trapped and immobilized, resulting in bituminous limestones or shales.

The recrystallization of salt during halokinesis not only squeezes out any dispersed hydrocarbons, but also all other impurities. These then form a veneer of selvage around a rising salt dome. This selvage veneer, mainly composed of anhydrite constitutes an impermeable barrier to hydrocarbons moving through adjacent porous sandstones that are upended by the salt diapirism. The rock salt itself is permeable to non-aqueous fluids. Beds abutting against as well as those draping over salt domes can entrap hydrocarbons, regardless of whether the hydrocarbons were originally squeezed out through the salt sequence or migrated from other sources.

A statistical evaluation of paleolatitudes of hydrocarbon occurrences shows a prevalent correspondence to the latitudinal

belt of marine evaporites, corroborating a postulated genetic relationship.

Release of base metals

Gypsum and halite lattices incorporate base metals that were concentrated in the brine by plankton. Significant amounts of Sr, Zn, Pb, Mn, Fe, and other metals, either built into the crystal lattice or finely disseminated, are released in the conversion of gypsum to anhydrite or the recrystallization of halite before compaction. Pb-Zn-deposits commonly surrounded ancient evaporite beds filling reefs and other porous carbonates or occur in caprock of salt diapirs (Rouvier et al. 1985; Kyle & Price 1986). The organic fraction of metal-organic complexes turns into liquid petroleum that appears in fluid inclusions or in potash mine seeps. The Middle Devonian Pine Point base metal deposit in the Northwest territories of Canada, occurs updip from similar base metal deposits in a reef chain, whose farthest downdip reefs are filled with fluid hydrocarbons (Macqueen & Powell 1983).

Base metals cannot migrate as sulfides and lack the oxygen to move as sulfates. They appear to travel as metal-organic or metal-chloride-organic complexes that are destroyed by reaching the surface or sulfuretted formation waters. In most oil-filled reefs there are minute galena [PbS], sphalerite [ZnS], and pyrite [FeS₂] crystals scattered through pores below the oil/water interface, but they are rare or absent above it.

Basin configuration and facies distribution

Tectonic forces control the shape of evaporite basins, that are frequently outlined by intermittently active normal faults; dissection faults and slumping mark ancient hinge lines of differential subsidence. However, evaporite basins in most cases display an irregular outline. Basic to intermediate volcanic activity is common both during and after evaporite deposition. It is so far only speculation to what extent an increased contemporary volcanic activity might have contributed to the supply of sulfur or chlorine.

A concentric bull's eye distribution of facies, common in lakes, does not occur in marine evaporites. Where a shallow basin is broken up by sills, halites are restricted to the depressions. Even in perfectly round basins (such as the Silurian Michigan Basin) anhydrites surround the halites, but sylvites are on one flank. In elongate basins (for example, the Devonian Elk Point Basin in western Canada) the bottom currents redistribute the sediments into an alignment with the basin axis, yet still displace potash deposits to one margin.

Synsedimentary subsidence

Because inflow and outflow tend to equilibrate and stabilize the salinity in the lagoon, a brine cannot concentrate to halite saturation at deficits in the water budget prevailing over any subtropical sea. Saturation can only be achieved by disturbing the equilibrium through a continued synsedimentary subsidence of the basin floor or a further constriction of the entrance channel (as occurred in the Gulf of Kara Bogaz Gol east of the Caspian Sea, first tectonically in the early part of this century and then artificially in the latter part).

When halite starts precipitating, the brine weight has increased by nearly 1/5 over that of inflowing seawater, and the combined weight of brine and precipitate soon exceeds a corre-

sponding seawater column by 70 %. This must affect the isostatic equilibrium of the earth's crust. Finding several hundred meters of rock salt deposited on top of shallow-water gypsum beds mandates a synsedimentary subsidence.

Flemming (1978) found in the Quaternary Mediterranean region subsidence rates of 2 - 10 m/ka due to tectonic or isostatic causes above Messinian salts, with local extremes up to 15 - 30 m/ka, while Avedik & Hieke (1981) determined an average of 0.5 m/ka for the Plio-Quaternary Ionian Sea. Even intermittent halite precipitation would thus be quite capable of keeping up with rapid subsidence rates.

A basin subsiding at rates of 0.15 - 15 cm/yr, will tend to deepen during the slow precipitation of aragonite and gypsum, but will shallow during the precipitation of halite and other chlorides. A complete cycle of concentration followed by freshening commonly ends with a nearly horizontal surface of a temporarily filled basin. Dolomite, shale or anhydrite beds separating individual halite cycles are usually uniform in thickness, suggesting that they represent a stillstand phase in the differential subsidence once the basin was filled by chloride precipitation. The dolomites often have an algal limestone as precursor, which must have formed within the photic zone.

Synsedimentary subsidence alters thickness ratios between shelf and basin and allows the brine to transgress over its titled shoreline. The ratio in ancient sediments between subsidence rates of gypsum-precipitating shelves and halite-precipitating deeps commonly has been 1 : 5 to 1 : 7. In most evaporite basins, the depocenter migrated somewhat from one cycle to the next. The axis of subsidence shifted NW during sedimentation of Permian evaporites in Germany; the largest expanse of Triassic halite in North Africa is offset against the greatest thickness of the evaporite sequence.

Time is most crucial: more time is needed to concentrate seawater to gypsum saturation than thereafter to the precipitation of any other evaporite mineral. The larger the brine volume in a basin, the longer it takes after a major influx to reach saturation; in turn, the less probable it is that evaporation or subsidence rates remain constant. Saturation of deep, voluminous basins is difficult to achieve. The Red Sea turned into an evaporite basin during the Würm glacial stage (Friedman 1972), mainly on account of a reduction of the cross sectional area of inflow through the Straits of Bab-el-Mandeb during a period of low sea level. However, this glacial stage did not last long enough to bring about a saturation of the Red Sea. The same is true of glacial stages in the Mediterranean Sea.

A shallow basin concentrates its brine faster than a deeper basin, partly because it warms up faster. Most ancient marine evaporite basins have started as shallow basins, progressing from normal salinity through aragonite to gypsum precipitation. The thicker the individual units, the longer was the time interval in which subsidence rates and climatic conditions have remained relatively stable; very thick units may really be multiple cycles.

Area of water surface

A chain of interconnected basins separated by sills encourages brine preconcentration. Halite saturation requires the removal of 91 % of the water, while the evaporation rate of brines drops by about 30 % before halite saturation is reached; for potash deposits the respective figures are 96 % and 50 %. At a water deficit (evaporation losses less rain and drainage) rated at only 1 m/yr, the open water surface of the basin would have to be extensive shelves to achieve an actual evaporation loss of 1 m/yr. To remove 91 % of the solvent and reach halite saturation within

brines descending to the bottom requires a basin configuration, where the area of shelves represents 46.2 % of the water surface to reach halite saturation, and 47.9 % to reach sylvite or carnallite saturation.

Messinian evaporites in the Mediterranean area are composed of three major salt basins, the Balearic, Ionian and Levantine Basins, containing about 870 - 1160 m of salt, separated by subsidiary shallow ridges. Each basin was surrounded by broad gypsum shelves and the water surface covered even further gypsum shelves throughout the Tyrrhenian, Aegean and Adriatic Seas including the Po River Basin, and other smaller embayments (Rouchy 1981, 1982). The Caspian Lowland and Volga Basins were connected to a Permian sea in the north by a series of basins strung all along the Paleo-Ural Mountains (Zharkov 1984). The Zechstein evaporites of Germany and Poland faced foreland basins now buried in the North Sea (Sonnenfeld 1984).

Depth estimates

Basin depth estimates based on studies of halites commonly differ by two orders of magnitude or more from those based on intercalated potash deposits. Equating wave bases in KCl-saturated brines (<5 m) with those in seawater (>30 m) leads to overestimating brine depths. From Br/Cl studies (Tucker & Cann 1986) and from rates of freshening to produce anhydrite intercalations in chloride sequences (Sonnenfeld 1991a), estimates of brine depth in halite basins yielded a maximum of about 100 - 150 m. Holser (1966) and Czapowski et al. (1990) arrived at similar values.

Facies distribution

Marine anhydrites commonly grade abruptly into near-shore limestones in turn into red beds with gypsum crusts in the soil. The thickness of shelf anhydrites varies inversely with halite thicknesses offshore; the thickest halites occupy subsidence centers. Miocene halite precipitated in the Balearic, Ionian and Levantine Seas, but on Tyrrhenian and Aegean gypsum flats only in narrow near-shore grabens, i.e., local sites of more rapid subsidence (Wezel 1985).

Brine concentration is not continuous; it is interrupted by freshenings due to excessive rains, flash floods, or storm tides. Calculated rates of continuous precipitation of any evaporite mineral thus always give too short a time span representing a salt sequence. Basin-wide dissolution and desiccation surfaces signify a temporarily arrested salt accumulation. Redissolutions are common.

A moderate freshening of the brine allows the marginal gypsum platform to expand as a wedge onto precipitated halite. Pronounced freshenings, such as caused by major storms, may even allow marginal algal and reefal limestones to cover the whole basin. They confirm that the bay floor has reached the photic zone. Renewed subsidence eventually leads to more evaporites.

Evaporite sedimentation resumes with a sharp basal contact of an anhydrite bed, giving the sequence a banded character. Each clay lamina, gypsum wafer, or dolomite stringer represents some prior corrosion parallel to bedding planes. The ratio between elapsed periods of deposition and intervals of nondeposition probably exceeds 1 : 10.

Punctuation of subsidence by stillstand periods leads to a reversal of evaporite sequences and frequently to a bank of uniformly thick biostromal limestone or dolomite. Its uniform

thickness suggests a flat bay bottom in the photic zone. Every deposit is ultimately capped by a reverse sequence of precipitates derived from progressively less concentrated brines. This reverse sequence protects the salts from dissolution, unless parts of it later erode. Deposited from a rapidly freshening brine, the sequence is thinner than the one precipitated from a slowly concentrating brine (Fig. 5).

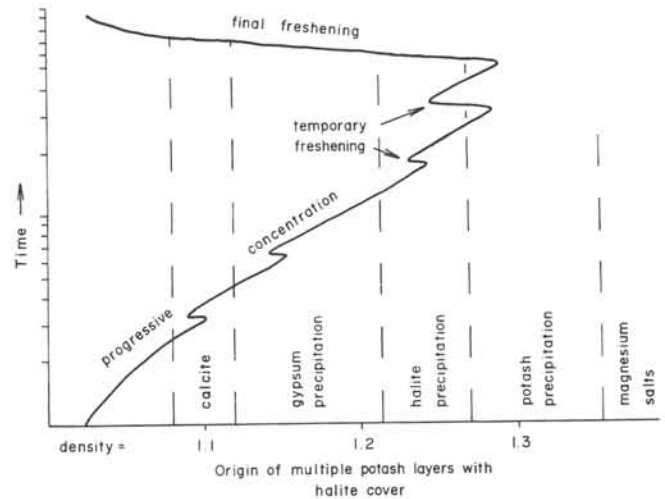


Fig. 5. Concentration and dilution curve of a marine brine.

Cyclic deposition

Cyclic changes of brine concentration or episodic agitation cause varve-type laminations on a millimeter to centimeter scale. Extending over more than 100 km, they mark basin-wide synchronous salinity fluctuations. Laminations form only in perennially submerged shallow parts of the basin, where they are neither destroyed by bioturbation nor by a vertical brine discharge, but they cannot occur in deep brines. Annual, seasonal or daily fluctuations from supersaturation to undersaturation for the more soluble salt are only possible in shallow water.

Alternating calcite/gypsum, gypsum/halite, or halite/sylvite couplets generally have a sharp basal contact of the less soluble member of the pair and an irregular contact on top. Calcite/gypsum couplets can also be attributed to episodic gypsum destruction by anaerobic bacteria. Commonly every eight to tenth couplet is thicker, due to major storms that are possibly related to sunspot cycles. Each storm can remove up to 80 % of varve couplets deposited since the last storm, and their count does not give a realistic estimate of elapsed time.

The Gulf of Kara Bogaz Gol off the Caspian Sea preserved 5 - 6 annual layers in a period of 15 years; 70 years of precipitation in the Dead Sea produced 15 - 20 annual couplets, representing only about 1/4 - 1/3 of the lapsed time (Sonnenfeld 1984). Storms of a periodicity of more than ten years are thereby not taken into account.

Virtually all evaporite deposits contain more than one major cycle of evaporite deposition separated by open marine sediments. The initial basin is often small, containing a very thin cycle, that rarely goes beyond gypsum saturation. Larger cycles of brine concentration and dilution are caused by oscillations of environmental conditions and may even commence before halite saturation is reached, such as for anhydrites and shales underlying the Zechstein chlorides (Peryt 1989).

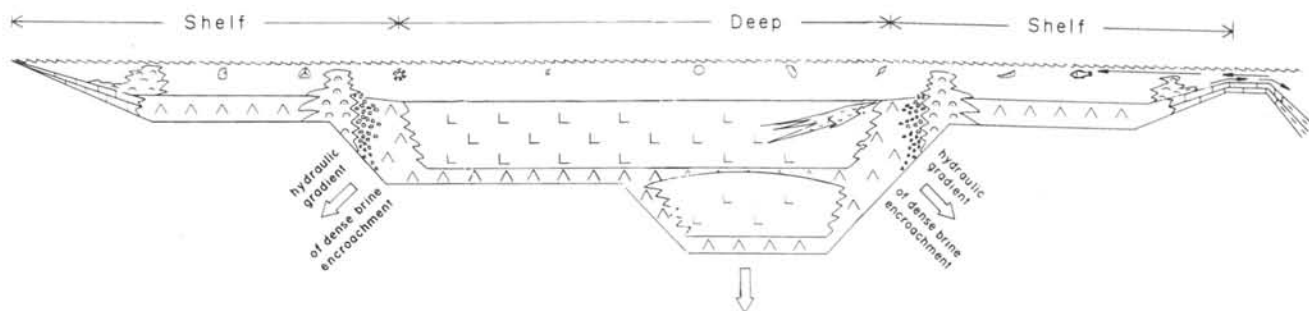


Fig. 6. Multicycle marine evaporite basin expanding over previous shelves

Additional subsiding depressions frequently develop over former shelves in subsequent cycles (in e.g., the Silurian Michigan Basin, the Elk Point Basin in western Canada, the Permian Delaware Basin of West Texas, or the Permian Zechstein Basin of NW Europe). The subsidence spreads from one cycle to the next, as a transgression (Fig. 6). Independently of each other, Matthews (1975) and Jauzein & Hubert (1984) reached the conclusion that chloride precipitation occurs during transgressions of the sea, i.e., an increase in the water surface subject to evaporation. Eventually the basins contract again into smaller areas near the original entrance. The final cycle is then regressive, as subsidence is slowing down and halites no longer precipitate. It is either marked only by anhydrite and open marine limestone beds, or by continental red beds with anhydrite nodules.

Primary marine evaporite deposits display from three or four to a score of such "megacycles" alternating between evaporite precipitation and deposits of normal salinity. A multiplicity of evaporite cycles suggests a repeated renewal of subsidence along rejuvenated faults. Major breaks (cycles) within halite sequences (major freshenings) are common in intervals of 145 or 290 m in the Silurian Michigan Basin, suggesting climatic influences (Sonnenfeld & Al-Aasm 1991); the primary sequences often enclose potash deposits. It is noteworthy that the older halite of the Polish Zechstein has a similar thickness limit (Czapowski et al. 1990). The reported thickness of Messinian salts in the Balearic, Ionian and Levantine Basins of 870, 1020 and 1160 m could well represent 6, 7 and 8 cycles.

Epigenetic alterations

Porosity and permeability

All chloride precipitates are initially slushy with a brine-filled porosity of 10 - 50 %. Compaction by a growing overburden converts the slush into a solid rock, expels interstitial brines and those trapped in clay partings, largely into formation waters.

Horizontal stresses in salt average only 80 % of vertical stresses and facilitate horizontal brine movements. Waters entering laterally eventually rise as artesian brines through cracks and joints to find a hydrostatic equilibrium. Vertical brine movements cause crystal growth at right angles to bedding planes, such as herringbone (chevron) crystals of gypsum, fibrous textures, or halite druses stretched out vertically, separated by individual cylindrical walls. They are also responsible for preserved microfissures filled with salts of greater solubility than the wall rock and by cylindrical vertical voids. Brines percolating before the precipitate has been consolidated lead to recrystallization;

brines percolating later produce pseudomorphs, crystal molds, and casts.

Undersaturated brines dissolve sylvite or carnallite under concurrent salting out of halite. They leave behind a recrystallized barren zone, called a "salt horse". Descending brines produce "roof horses" or "back horses", barren areas along the hanging wall. Ascending brines produce "floor horses", barren areas along the footwall. Waters rising through an evaporite deposit saturate quickly and produce brine chimneys or pipes, salt horses of white halite rimmed at the underside by clays, organic films, and dolomites; all banding is thereby destroyed.

Anhydritization

Chloride-saturated hygroscopic brines lower the temperature range at which anhydrous minerals are stable, so do geostatic temperature increments at depth. Halite-saturated brines extract crystal waters from gypsum at ambient temperatures and convert it to anhydrite, but only if organic decomposition products are present; water salinities as high as 200,000 ppm do not alter gypsum to anhydrite in a sterile environment. About 2 m³ of crystal water are liberated from each m³ of gypsum requiring 230 MJ of energy to be consumed. Admixtures are released during this conversion: strontium reprecipitates as celestine [SrSO₄] nests and other metals migrate with the crystal water.

Dehydration of gypsum increases the pore pressure; the combined volume of anhydrite and released water is more than 10 % greater than that of the original porous, brine-filled gypsum. This pore pressure is the driving force to dissipate the waters and with it trace elements leached out of crystal lattices. Overlying beds commonly show undisturbed laminations; gypsum dehydration has thus occurred before their consolidation. Determinations of transition temperatures from gypsum to anhydrite cover a wide range, with clusters around 38 - 42 °C and 55 - 58 °C, because gypsum from different sources contains different lattice imperfections and varies in content of surface-active organic matter.

While rare at depth, gypsum is common near the surface where anhydrite has been rehydrated by atmospheric humidity or groundwater. Meteoric waters convert anhydrite to selenite, a variety of gypsum. Twinned selenite crystals, with fishtail fins pointing up, are taken to have grown into an open brine column at subaqueous exit points of slowly moving interstitial brines. A porphyroblastic texture seems to denote very early volume-for-volume replacement under near-equilibrium conditions, whereas an alabastine texture seems to form at a later stage. Rehydration generates a large amount of heat that must be rapidly disseminated, lest it would bring the interstitial brine to the boiling point.

K-Mg-Na-sulfatization

Primary K-, Mg-, or Na-sulfates do not occur in marine evaporite sequences. Worldwide, however, Permian and Neogene potash deposits largely have been altered to secondary complex Mg-, KMg-, NaMg- or even KCaMg-sulfate minerals (Sonnenfeld 1992). Evaporite beds of other ages are similarly affected only where they have been tectonically disturbed and opened to meteoric water influx (for example, Cambrian evaporites in the Salt Range, Pakistan, but not undisturbed coeval ones in Siberia). A conversion of basal gypsum beds to anhydrite cannot supply enough sulfate ions (Sonnenfeld 1984). Because of low solubility of gypsum, each meter of a K-Mg-sulfate mineral would have required the conversion of many hundreds of meters of basal gypsum to generate the needed sulfatic waters, and the dissolution of up to 100 m of halite in the undersaturated brine. Such basal gypsum thicknesses or halite caverns cannot be documented. A massive incursion of seawater would have leached some halite and major amounts of the potash deposits, because seawater is undersaturated for these compounds.

However, an early exposure of gypsum shelves to meteoric waters could have supplied the required amounts of Ca^{2+} and SO_4^{2-} . Pre- and post-glacial oscillations in sea level exposed the gypsum shelves. Where the sea level dropped along a shelf of an uncompacted evaporite basin, vast gypsum flats became exposed to atmospheric precipitation and gradually dissolved in the runoff. Only 2.22–2.4 g/l of gypsum are soluble in rainwater, but even a slight dissolution of marginal halites nearly quadrupled the gypsum solubility (Patton 1977). The solubility of gypsum is also dependent on the flow velocity of the runoff (i.e., the slope of the beach), the electric conductivity and the gypsum saturation of the meteoric waters (Navas 1990). Drainage allowed a CaSO_4 -solution containing a little NaCl, to enter any as yet uncompacted clay intercalation extending from the shore, and to obtain easy access to carnallite or sylvite laminae.

Reactions proceeded along a complex path of multiple temperature-dependent alterations (Sonnenfeld 1991b) Either $[\text{4KCl} \cdot \text{4MgSO}_4 \cdot \text{11H}_2\text{O}]$ developed (preferentially as caprock) or in warmed brines langbeinite $[\text{K}_2\text{SO}_4 \cdot \text{2MgSO}_4]$. The latter can locally rehydrate to picromerite $[\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{6H}_2\text{O}]$ or leonite $[\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{4H}_2\text{O}]$ nests. Nests or nodules of aphthi-

talite $[\text{Na}_2\text{SO}_4 \cdot \text{3K}_2\text{SO}_4]$, loeweite $[\text{6Na}_2\text{SO}_4 \cdot \text{7MgSO}_4 \cdot \text{13H}_2\text{O}]$, vanthoffite $[\text{3Na}_2\text{SO}_4 \cdot \text{MgSO}_4]$, d'ansite $[\text{10Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{MgCl}_2]$ and finally, bloedite $[\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{5H}_2\text{O}]$, glauberite $[\text{Na}_2\text{Ca}(\text{SO}_4)_2]$ and thenardite $[\text{Na}_2\text{SO}_4]$ indicate a growing surplus of sodium ions and a further leaching of potassium. Multiple retrograde crystallizations are also known. Nests of Na- or Ca-carbonates or -sulfates in marine series always mark an epigenetic seepage of continental runoff.

Anhydrite beds convert to polyhalite $[\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot \text{2H}_2\text{O}]$ or kieserite $[\text{MgSO}_4 \cdot \text{4H}_2\text{O}]$, if MgCl_2 -solutions are present, to syngenite $[\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{4H}_2\text{O}]$ or much rarer goergeyite $[\text{K}_2\text{SO}_4 \cdot \text{5CaSO}_4 \cdot \text{H}_2\text{O}]$ if not. Both kieserite and polyhalite become more frequent and thicken towards shores, just as their anhydrite precursors. Reduced anhydrite/halite ratios in both Permian and Neogene evaporites mark a loss of anhydrite. Kieserite and polyhalite contain little anhydrite and no clay inclusions even where adjacent to clay-bearing anhydrite. Finally, both minerals fluoresce, a property not shared with other primary evaporite minerals.

Kieserite probably forms either by the intercalation of anhydrite laminae with percolating Mg-Cl_2 -brines, or by magnesite decomposing in hot CaSO_4 -brines. It corrodes anhydrite or forms pseudomorphs after it, and is more common at basin margin sites, which are precisely the sites of gypsum precipitation. In addition to Permian and Neogene sites, minor amounts of kieserite occur also in some Pennsylvanian, Triassic and Eocene evaporite basins. Because of extreme kinetic values (Braitsch 1971), kieserite does not have as precursor a hypothetical primary epsomite $[\text{MgSO}_4 \cdot \text{7H}_2\text{O}]$, although epsomite commonly effloresces on mine walls.

MgCl_2 liberated in carnallite sulfatization and not consumed in the conversion of anhydrite to kieserite precipitates as bischofite, because of its poor solubility in sulfatic brines. Bischofite only occurs in several sulfatized Permian potash horizons (e.g., in Zechstein beds and in the Volga depression), in sulfatized Neogene ones in Sicily, or after disintegration of Cretaceous tachihydrite. It has not been found in any pre-Permian, Triassic, Jurassic, or Paleogene evaporite basin.

When Usiglio (1849) published a now famous and often repeated experiment of evaporating Mediterranean seawater, it was done in the oxygenated conditions of the laboratory, under

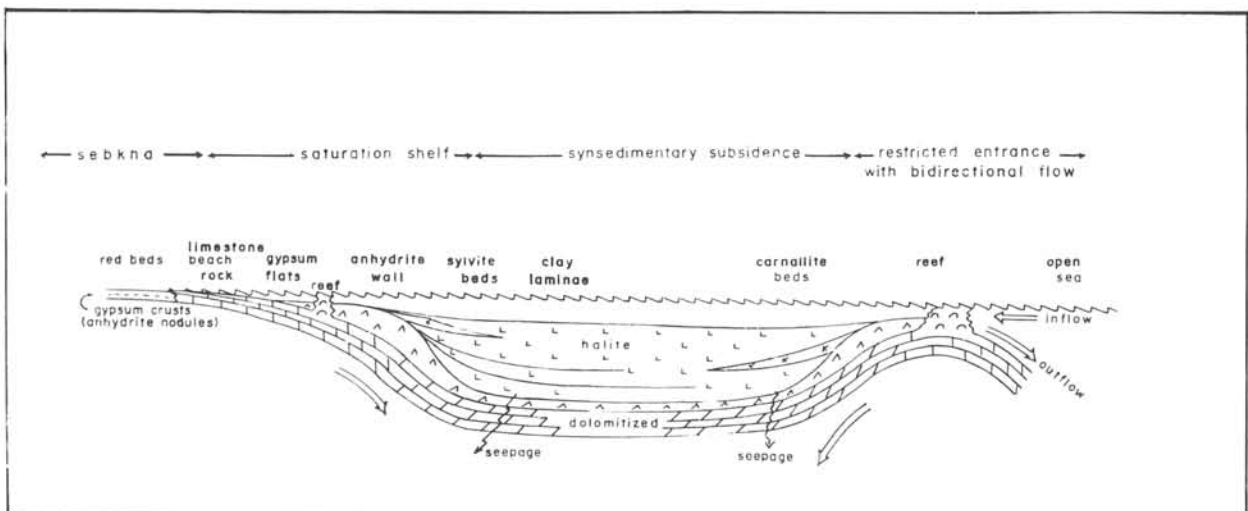


Fig. 7. Model of a marine evaporite basin. Gypsum is restricted to shelves, halites fill deeps, potash deposits rest on flanks, clay and anhydrite markers extend from shores, reefs flourish at the entrance nourished by inflow. The anoxic outflow sweeps the outer slope.

exclusion of the influence of anaerobic bacteria. Consequently, his first precipitate was iron oxide, and then gypsum. Halite and $MgSO_4$ followed, probably as epsomite, because kieserite cannot be produced at temperatures below 110 °C (Braitsch 1971). However, in evaporite basins iron remains dissolved until potash precipitation and marine halite does not normally contain about 5 % $MgSO_4$. A negative redox potential is frequently induced artificially in man-made salinas to prevent the precipitation of red iron-bearing halite.

The volume reduction by sulfatization and by progressive potassium removal leads to very contorted bedding planes and intraformational breccias. $CaCl_2$ -brines derived from formation waters destabilize the secondary minerals and revert them to a new generation of chlorides and salted-out anhydrite.

Salt domes

Salt domes or salt diapirs are stocks or plugs of recrystallized halite, capped by gypsified anhydrites and dolomites. Examples include salt domes along the margin of the Gulf of Mexico, the Arctic Archipelago of Canada, the southeastern margin of the North Sea, offshore Brazil and Angola, eastern Iran and adjacent Pakistan, wherever the crust is stressed.

The weight of overburden plasticizes rock salt, and to a lesser extent, anhydrite. Intercrystalline and intracrystalline brines expelled by compaction recrystallize the precipitates and strongly influence their plasticity; wetting by percolating undersaturated waters increases it (Barnes 1933). At an overburden load of 300 m rock salt begins to expand into voids, potash minerals somewhat earlier. Halite becomes ductile under 12 km of overburden, sylvite under 10 km, but less if exposed to tectonic stresses or to a regional downwarp. A high geothermal gradient lowers the depth of potential mobilization because halite decreases its density with rising temperatures.

In the northwestern Balearic Sea and along the southern slope of the Mediterranean Rise in the Levantine Sea, but not in the deepest parts of either of these salt basins nor in the Ionian Sea a Quaternary downwarp produce diapirs of Miocene salt, originally covered only by a thin veneer of sediments and about 1 - 2 km seawater (equivalent to the load of about 0.4 - 1 km of solid overburden). Salts buried in many tectonically quiet intracratonic basins, e.g., up to 4 - 5 km in the Silurian Michigan and Ohio Basins or the Devonian Elk Point Basin of western Canada, have not yet been mobilized to pierce overlying strata, despite a much larger overburden.

Mobilized salt first produces salt pillows that later grow into swarms of salt domes. Overlying beds are commonly pierced, upended, and cut by normal faults dipping into the salt stocks. Meteoric waters enter along fault planes to produce a salt karst; they deliver bacteria, which scavenge some of the available organic matter, and transform the gypsum in the caprock into native sulfur.

The more competent dolomite, shale, and anhydrite fractions combine in rising salt domes into caprocks thinning away from ancient basin margins, just as the original gypsum, dolomite, and shale intercalations wedged out toward the basin center.

Bedded evaporites are unknown in metamorphic rock suites. Chlorides and sulfates are squeezed out well before pressures and temperatures rise to recrystallize silicates. Only fluid inclusions in the metamorphic rocks then bear witness to the former presence of evaporites. Many tectonic glide planes in both the Alps and the Proterozoic Grenville Province in Canada show evidence of lubrication by traces of anhydrite.

Conclusion

The mineralogy of groundwater-fed endorheic basins differs from that of marine basins because of differing Ca/Na ratios in the water sources. Na- or Na-Ca-carbonates and -sulfates, common in intracontinental basins are unknown as primary deposits of marine basins. In turn, potash deposits, common in basins fed by oceanic waters, are found only in intracratonic basins that are fed by waters dissolving ancient marine deposits.

In marine basins, gypsum is precipitated on shallow shelves and shoals, but ceases to form in depressions, where sunlight no longer penetrates. A differential subsidence drains concentrated brines into deeper parts where they reach halite saturation. Because brines saturated for KCl or $MgCl_2$ are very temperature sensitive both with regard to specific gravity and solubility, they rise upon cooling and precipitate on slopes and even shelves. Close to the shore they are prone to redissolve in rainwash.

The basin configuration is asymmetric in that potash deposits always occur on one flank, halite occupies the depocenter and gypsum/anhydrite the surrounding marginal shelves (Fig. 7). Gypsum is the only primary sulfate deposited in marine basins because of a mounting oxygen deficiency. K-Mg-beds in all Permian and Neogene basins were partially altered to K-Mg-sulfates and Na-Mg-sulfates by meteoric waters carrying dissolved gypsum and halite from shelf margins along clay or anhydrite markers (Tab. 2). Originally, the seawater composition of Permian seas did not materially from modern seawater (Horita et al. 1991).

Table 2: Precipitates of primary brines and their alteration.

Type of brine	Precipitates
continental (meteoric waters)	Na-(Ca)-carbonates Na-(Ca)-sulfates minor gypsum & halite
marine (basin with broad shelves)	aragonite, gypsum; halite with encased sylvite, carnallite
marine (basins with steep flanks)	aragonite, halite carnallite tachyhydrite
marine (altered by lateral meteoric influx)	anhydrite, halite K-Mg-sulfates, bischofite, Na-Mg-sulfates

An inflow/outflow regime is required in an entrance to channel to prevent rapid drying out and to account for deficiencies in precipitates of higher solubility, but the outflow is primarily directed into the subsurface once potash saturation is reached. Periodic freshenings produce a cyclicity of the deposit.

As nekton and benthos die out in concentrating brines of decreasing oxygen content, anaerobes and facultative anaerobes take over. Dissolved organic matter influences both gypsum and halite precipitation, and determines whether sylvite or carnallite becomes the dominant potash mineral; photosynthetic organisms are present for gypsum, absent for tachyhydrite precipitation. Effluents carry with them dissolved silica, magnesium compounds, base metals, and organic matter destined to turn into hydrocarbons. The crystal lattice positions of calcium, so-

dium or aluminium affect the nature of hydrocarbons generated. A detailed analysis of an evaporite basin, its feeder channel location, width of the anhydrite shelf, location of shoals and islands is thus a prerequisite to both oil and base metal exploration. The economic importance of evaporite basins cannot be overestimated.

Acknowledgement: The chemical analysis of tachyhydrites from Sergipe, Brazil, by Prof. Dr. R. Kühn and Mr. M. Gastner of the Sedimentological Institute, University of Heidelberg, Germany, is gratefully acknowledged.

References

- Avedik F. & Hieke W., 1981: Reflection seismic profiles from the central Ionian Sea (Mediterranean) and their geodynamic interpretation. *"Meteor" Forschungsergebnisse*, C, 34, 49 - 64.
- Barnes R. B., 1933: Plasticity of rock salt and its dependence on water. *Phys. Rev.*, 44, 889 - 902.
- Barnett J. M. & Straw W. T., 1983: Sedimentation rate of rock salt determined by micrometeorite analysis. *Geol. Soc. Amer., Abstr. & Progr.*, 15 (6), 521.
- Borchert H., 1969: Principles of oceanic salt deposition and metamorphism. *Geol. Soc. Amer. Bull.*, 80, 821 - 864.
- Boeke H. E., 1910: Ein Schlüssel zur Beurteilung des akristallisationsverlaufes der bei der Kalisalzverarbeitung vorkommenden Lösungen. *Kali*, 4, 271 - 284, 300 - 307.
- Braitsch O., 1971: Salt Deposits, their Origin and Composition. *Springer-Verlag*, Berlin, 297.
- Cornec E. & Krombach H., 1932: Le équilibre de l' eau, chlorure de potassium et chlorure de sodium entre -23 °C et 90 °C. *Ann. Chim.*, 18, 5 - 31.
- Czapowski G., Antonowicz L. & Peryt T. M., 1990: Facies and paleogeography of the Zechstein (Upper Permian) Older halite (Na₂) in Poland. *Polish Acad. Sci. Earth Sci., Bull.*, 38 (1 - 4), 45 - 55.
- Evans R. & Kirkland D. W., 1988: Evaporitic environments as a source of petroleum. In: Schreiber B. C. (Ed.): *Evaporites and Hydrocarbons*. Columbia Press, New York, 256 - 299.
- Flemming N. C., 1978: Holocene eustatic changes and coastal tectonics in the northeastern Mediterranean: implications for models of crustal consumption. *Roy. Soc. London, Philos.*, A, 289 (1362), 405 - 458.
- Friedman G. M., 1972: Significance of Red Sea in problem of evaporites and basinal limestones. *AAPG Bull.*, 56 (6), 1072 - 1086.
- 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, 147 - 159.
- Holland H. D., 1984: Chemical Evolution of the Atmosphere and Oceans. *Princeton Univ. Press*, Princeton, N.J., 582.
- Holser W. T., 1966: Bromide geochemistry of salt rocks. In: Rau J. L. (Ed.): *Second Symposium on Salt*. North Geol. Soc., Cleveland, Ohio, 1, 248 - 275.
- Holwerda J. G. & Hutchinson R. W., 1968: Potash bearing evaporites in the Danakil area, Ethiopia. *Econ. Geol.*, 63 (2), 124 - 150; (5) 572 - 573; (8) 978 - 979.
- Horita J., Friedman T. J., Lazar B. & Holland H. D., 1991: The composition of Permian seawater. *Geochim. Cosmochim. Acta*, 55 (2), 417 - 432.
- Huppert H. E. & Linden P. F., 1979: On heating a stable gradient from bellow. *J. Fluid Mech.*, 95, 431 - 464.
- Jauzein A. & Hubert P., 1984: Les bassins oscillants: un modèle de génèse des séries salines. *Sci. Géol. Bull.*, 37, 267 - 282.
- King R. H., 1947: Sedimentation in Permian Castile Sea. *AAPG Bull.*, 31, (3), 470 - 477.
- Kinsman D. J. J., Boardman M. & Borcsik M., 1974: An experimental determination of the solubility of oxygen in marine brines. In: Coogan A. H. (Ed.): *Fourth Symposium on Salt*. North Ohio Geol. Soc., Cleveland, Ohio, 1, 325 - 327.
- Klement C., 1895: Über die Bildung des Dolomits. *Tschermak's Mineral.-Petrogr. Mitteil.*, N.F., 14, 526 - 544.
- Kling P., 1915: Tachyhydritvorkommen in den Kalisalzagerstätten der Mansfelder Mulde. *Centralbl. Mineral. Geol. Paläont.*, 11 - 17, 44 - 50.
- Kostenko I. F., 1982: Hydration ions as an index halogenesis. *Geol. Zhurnal*, 42, (1), 21 - 28.
- Kroenlein G. A., 1939: Salt, potash and anhydrite in the Castile Formation of southeastern New Mexico. *AAPG Bull.*, 23, 1682 - 1693.
- Krull O., 1917: Beiträge zur Geologie der Kalisalzlager. *Kali*, 11 (14), 227 - 231.
- Kyle J. R. & Price P. E., 1986: Metallic sulphide mineralization in salt dome caprocks, Gulf Coast, U.S.A. *Inst. Mining Metall., Trans.*, B, 95, 6 - 16.
- Linck G., 1937: Bildung des Dolomites und Dolomitisierung. *Chemie der Erde*, 11, 278 - 286.
- Lowenstein T. K. & Spencer R. J., 1990: Syndepositional origin of potash evaporites: petrographic and fluid inclusion evidence. *Amer. J. Sci.*, 290 (1), 1 - 42.
- Lucia F. J., 1972: Recognition of evaporite-carbonate shoreline sediments. In: Rigby J. K. & Hamblin W. K. (Eds.): *Recognition of Ancient Sedimentary Environments*. Soc. Econ. Paleont. Mineral. Spec. Publ., 16, 160 - 191.
- Macqueen R. W. & Powell T. G., 1983: Organic geochemistry of the Pine lead-zinc ore field and region, Northeast Territories, Canada. *Econ. Geol.*, 78 (1), 1 - 16.
- Matthews R. D., 1975: Evaporite cycles in the Devonian of Michigan. *Ontario Petroleum Institute, 14th. Ann. Conf. Paper*, 11, 13.
- Navas A., 1990: The effect of hydrochemical factors on the dissolution rate of gypsiferous in flowing water. *Earth Surf. Processes and Landforms*, 15 (8), 709 - 715.
- Ochsenius C., 1877: Die Bildung der Steinsalzlager und ihrer Mutterlaugensalze unter spezieller Berücksichtigung der Flöze von Douglasshall in der Egel'n'schen Mulde. *C.E.M. Pfeffer Verlag*, Halle, 172.
- Patton C., 1977: Oil Water Systems. *Cambell Petroleum Ser.*, Norman, O.K., 252.
- Perthuisot J. P., 1975: La sebkhia El Melah de Zarzis. Génèse et évolution d' un basin paraliq. *Ecole Normale Supér., Labor. de Géol., Trav.*, Paris, 9, 252.
- Peryt T. M., 1989: Basal Zechstein in southwestern Poland: Sedimentation, diagenesis and gas accumulations. In: Boyle R. W., Brown A. C., Jefferson C. W., Jowett E. C. & Kirkham R. V. (Eds.): *Sediment-hosted stratiform copper deposits*. *Geol. Assoc. Canada, Spec. Paper*, 36, 601 - 625.
- Porter A. W., 1927: Note on the Soret effect. *Trans. Faraday Soc.*, 23, 314 - 316.
- Richter-Bernburg G., 1957: Zur Palaeogeographie des Zechsteins. *Accad. Naz. Lincei Ente Naz. Idrocarburi, Atti*, 1, 87 - 99.
- Rouchy J. M., 1981: La génèse des évaporites de Méditerranée. *Museum Nat. de l' Hist. Nat.*, Paris, 295.
- Rouchy J. M., 1982: La crise évaporitique messinienne de Méditerranée: nouvelles propositions pour une interprétation génétique. *Museum Nat. de l' Hist. Nat., Bull.*, C, 4, (3 - 4), 107 - 136.
- Rouvier H., Perthuisot V. & Mansouri A., 1985: Pb-Zn deposits and salt-bearing diapirs in southern Europe and North Africa. *Econ. Geol.*, 80, 666 - 687.
- Snowdon P. N. & Turner J. C. R., 1960: Concentration dependence of the Soret effect. *Trans. Faraday Soc.*, 56, 1812 - 1819.
- Sonnenfeld P., 1964: Dolomites and dolomitization - a review. *Bull. Canad. Petrol. Geol.*, 12, (1), 101 - 132.
- Sonnenfeld P., 1978: Effects of a variable sun at the beginning of the Cenozoic era. *Climatic Change*, 1, 355 - 382.
- Sonnenfeld P., 1984: Brines and Evaporites. *Academic Press*, Orlando, Fla., 61.
- Sonnenfeld P., 1985: Evaporites as oil and gas source rocks. *J. Petrol. Geol.*, 8, (3), 253 - 271.
- Sonnenfeld P., 1987: Evaporites. In: *Encyclopedia of Physical Sci. and Technol.*, 5, 273 - 293.
- Sonnenfeld P., 1991a: On depth of ancient marine evaporite basins. *Zentralbl. Geol. Paläont.*, Pt. I (4), 1137 - 1147.

- Sonnenfeld P., 1991b: Marine evaporite facies. *Zentralbl. Geol. Paläont.*, Pt. I (4), 1107 - 1136.
- Sonnenfeld P., 1992: Chemical facies of marine evaporites. *Geol. Carpathica* (Bratislava), 43, 1, 3 - 14.
- Sonnenfeld P. & Perthuisot J. P., 1989: Brines and Evaporites. *28th Internat. Geol. Congress, Short Course Notes, Amer. Geophys. Union*, Washington, D.C., 3, 128.
- Sonnenfeld P. & Al-Aasm I., 1991: The salina evaporites in the Michigan Basin. In: Catacosinos P. A. & Daniels P. A. Jr. (Eds.): Early Sedimentary Evolution of the Michigan Basin. *Geol. Soc. Amer., Spec. Paper*, 256, 139 - 153.
- Strakhov N. M., 1962: Principles of lithogenesis. *Izd. Akad. Nauk SSSR* (Moscow), transl. New York, N.Y., Consultants Bureau, 3 vols., 1967 - 1970.
- Tasch P., 1970: Biochemical and geochemical aspects of the White Salt Pan - Bonaire, N. A. In: Berticker A. C., Hoekstra K. E. & Hall J. F. (Eds.): *Symposium on Salt*, Ohio Geol. Soc., Cleveland, Ohio, N., 1, 204 - 210.
- Taylor J. C. M., 1980: Origin of the Werraanhydrit in the U. K. Southern North Sea, a reappraisal. *Contrib. Sedimentol.*, 9, 91 - 113.
- Tollert H., 1950: Über die Verteilung der temperatur, der Konzentration und der Strömungsgeschwindigkeit in dynamischpolythermen Systems. *Z. Phys. Chem.*, 195, 281 - 294.
- Tuckner R. M. & Cann J. R., 1986: A model to estimate the depositional brine depths of ancient halite rock: implications for ancient subaqueous evaporite depositional environments. *Sedimentology*, 33 (3), 401 - 412.
- Usiglio J., 1849: Analyse de l' eau de la Méditerranée sur les cotes de France. *Ann. Chim. Phys.*, C, 27 (2), 92 - 107 and 27 (3), 177 - 191.
- Van Tuyl F. M., 1916: The origin of dolomite. *Iowa Geol. Survey, Reports*, 25, 251 - 422.
- Warren J. K., 1989: Evaporite Sedimentology. Importance in Hydrocarbon Accumulation. *Prentice Hall*, Engelwood Cliffs, 285.
- Wezel F. C., 1981: Sedimentary basins of Mediterranean margins. *Terra Cognita*, 1 (2), 99 - 104.
- Wezel F. C., 1985: Structural features and basin tectonics of the Tyrhenian Sea. In: Stanley D. J. (Ed.): Geological Evolution of the Mediterranean Basins. *Springer-Verlag*, New York, 153 - 194.
- Zharkov M. A., 1981: History of Paleozoic Salt Accumulation. *Springer-Verlag*, New York, 308.
- Zharkov M. A., 1984: Paleozoic Salt Bearing Formations of the World. *Springer-Verlag*, New York, 427.
- Zharkov M. A. & Zharkova T. M., 1989: Cretaceous tachyhydrite containing evaporite formations. In: Borisenkov V. I.: Geochemistry of Halogenesis. *Moscow University Press*, Moscow, 20 - 49 (in Russian).