

## CHEMICAL FACIES OF MARINE EVAPORITES

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**Abstract:** Evaporite basins equilibrate inflow and outflow in the gypsum saturation field, unless synsedimentary subsidence destroys the equilibrium. Anaerobic bacteria destroy sulfate ions, thiobacteria and cyanophyta reconstitute them on sun-lit shelves; protein-, alcohol- and chlorophyll derivatives extensively control the sequence of primary precipitates and their alterations. The brine concentrates to chloride precipitation, depleting first sodium, then potassium ions, and dissolves all blown-in quartz and feldspar grains. Permian and Neogene potash deposits were secondarily sulfatized worldwide. This is deemed to have happened by meteoric waters dissolving gypsum beds on marginal shelves dried out during low sea level positions or in evaporites accessed by deformation. A lateral influx of calcium and sulfate ions, that dissolve more easily in an Na-Cl-enriched brine, can explain all products of K-Mg-sulfatization.

**Key words:** primary marine evaporite sequence, clay interbeds, ionic substitution, secondary sulfatization, K-Mg-sulfates, Na-Mg-sulfates, desulfatization.

### Introduction

All Phanerozoic marine evaporites show a sequence of precipitates derived from a concentrating brine, which progress from anhydrites to halite, hence to sylvite or carnallite, and in rare cases to tachyhydrite, before a reverse sequence indicates a progressive dilution of the solution. Permian and Neogene evaporite sequences have worldwide been subjected to sulfatization and a resulting incomplete alteration of potash seams to contain a diversified mineralogy of bedded K-Mg-sulfates. All the alterations observed in potash deposits of these two periods can, however, be explained by assuming that a gypsum-saturated runoff was able to enter the evaporite sequence, facilitated by sea level oscillations shortly after deposition and desiccation of newly exposed near-shore shelf deposits.

### Primary marine evaporites

#### *Initial gypsum precipitation*

Evaporite concentration of marine brines occurs in semi-arid regions within marginal bays or seas with a narrow entrance channel. A long dry summer, little surface or groundwater runoff, and winter rains of wide variability are characteristic for such areas. The evaporative deficit in the water budget causes an ever so slight slope in sea level and ocean waters flow down the gradient into such a bay to counteract the water loss, creating a bottom outflow along a bay bottom sloping outwards. Continuous inflow prevents the basin from drying out, the outflow drains concentrated brines. The quantities of dissolved salts in normal marine inflow have a tendency to become balanced by those in the concentrated outflow. Wherever a sill, shoal, or reef chain, constricts the entrance, the bottom outflow is partially curtailed and the resident brine progressively concentrates.

The volume of the basin is decisive: a shallow basin concentrates its brine faster than a deeper basin. Most ancient marine evaporite basins have started as rapidly subsiding shallow basins. Solubilities of oxygen (4 ppm), carbonate (200 ppm) and bicarbonate (0 ppm) ions decrease to negligible values well before the onset of gypsum saturation (Kinsman et al. 1974; Sonnenfeld 1984). The dissolved oxygen is thus insufficient to account for gypsum precipitation.

Bedded gypsum appears to be produced at water depths within the photic zone, where oxygen is supplied by photosynthesizers concentrated in a bacterial immediately beneath the interface to inflowing waters. Anaerobic sulfur bacteria break down incoming seawater sulfate; the resulting hydrogen sulfide is reoxidized and attacks precipitated algal carbonates. Completely gypsified stromatolites are common in this environment. Gypsum crusts are transparent to ultraviolet radiation and always contain several levels of bluegreen algae and red bacterial photosynthesizers.

If the inflow and outflow equilibrate within the calcium sulfate saturation field, gypsum will be the only precipitated evaporite mineral (Fig. 1). Concentrated, oxygen-deficient and heavy bottom brines that drain back into the open ocean cause an anoxic environment in the open ocean. Busson (1984) referred to a basin arrested in such a position as an "aborted evaporite basin" and cited the Upper Cretaceous gypsum flats of the Maghreb in Northwest Africa as an example, coeval with an anoxic event in the ancestral tropical Atlantic Ocean.

Seawater delivers three times as many sulfate as calcium ions, mainly as magnesium sulfate, yet terminal brines in salt basins contain some calcium as calcium chloride. This suggests that more than two thirds of the sulfate ions are lost, decomposed by anaerobic bacteria feeding on organic matter. A sulfate deficiency in the concentrating brine is an early consequence and develops even before halite crystallization (D'Ans & Kühn 1960).

Some brines are able to percolate through the still permeable substrate. A transition to anhydrite in NaCl-saturated solution occurs at 18 °C, in a solution concentrated to precipitate gypsum

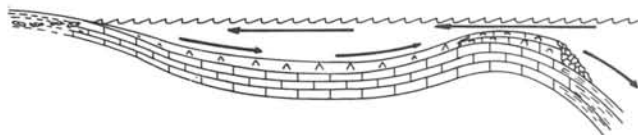
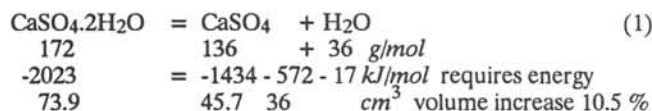


Fig. 1. Synsedimentary subsidence in evaporite basins I: An initial stage of gypsum precipitation without synsedimentary subsidence leads to an "aborted basin".

at 27 °C, but at 10 °C in the presence of 30 mol MgCl<sub>2</sub>/1000 mol H<sub>2</sub>O (Borchert 1959). The transition temperature is lowered in concentrated brines, in the presence of dissolved magnesium, and is also affected by dissolved organic matter. Even brines saturated only for halite are thus hygroscopic enough to turn underlying and laterally contiguous gypsum into anhydrite before overlying beds are hardened.



The total absence of disturbed bedding due to a volume loss proves anhydritization prior to compaction of overlying halites. Once they have become impermeable, additional dewatering of any residual gypsum can occur only laterally.

Strontium replaced calcium in the crystal lattice of gypsum preferentially near basin margins (Braitsch 1963) where brine temperatures were higher; celestite [SrSO<sub>4</sub>] crystallizes during the anhydritization.

#### Ca- or Mg-carbonates after gypsum

Where organic matter is present, anaerobic bacteria decompose some of the precipitated gypsum into calcite and hydrogen sulfide. Modern gypsum crusts in coastal lagoons sometimes are underlain by thick layers of calcite grains; at other times there is a rim of magnesite around the area of gypsum precipitation (Perthuisot 1975). Indeed, an inflow of calcium and bicarbonate ions from

groundwater or runoff into a marine brine ought to produce gypsum and magnesite (Braitsch 1962). In ancient evaporites magnesite can occur in small nests in juxtaposition to anhydrite laminae, especially those close to potash horizons. With sulfate and carbonate ions effectively removed, further precipitation is then restricted to chlorides, unless the brine is diluted.

#### Primary halite precipitation

A basin cannot reach saturation for halite over its whole area at prevailing rates of evaporation, unless the entrance has an unreasonably small cross section. However, the brine concentrates further, if the inflow/outflow ratio does not equilibrate in the gypsum saturation field. When a part of the depression starts subsiding at an accelerated rate compared to its shelves, possibly along normal faults, the increments in bay volume allow denser brines to accumulate in the deeper part, while gypsum continues to precipitate on shelves and shoals (Fig. 2). Richter-Bernburg (1957) has aptly named them "saturation shelves". It is no accident that the occurrence of halites on Miocene Tyrrhenian and Aegean gypsum flats is restricted to local graben structures. Anhydrite beds beneath halites are always much thinner than those on the basin flanks. Once the brine has concentrated beyond halite saturation, there is no other primary sulfate precipitation and the brine continues to produce only chloride minerals.

Differential synsedimentary subsidence is thus an essential component of basins precipitating chlorides (Sonnenfeld 1984). With progressive deepening of the rapidly subsiding depression, the margins are bent towards the deep (Rouchy 1982), at times even more than 45°. They are frequently involved in synsedimentary slumping and cut by distension faults. This gives rise to an "anhydrite wall" on the margins of the halite territory.

The total water surface subject to evaporation losses thus exceeds the area of halite precipitation, depending on prevailing evaporation rates, about 3 - 4 times. Sparse runoff in a semi-arid terrain yields a dearth of siliciclastics, turning the subsiding depression into "starved basins", were it not for the equally rapid filling of such throughs by the precipitation of chloride minerals.

Halite precipitation rates easily exceed even very high rates of subsidence, but periodic redissolutions produce a net accumulation rate of halite equivalent to a small fraction of the optimum precipitation rate. Halite crystallization completely strips the brine of all sodium ions. No further primary sodium compounds crystallize out even to the eutonic point of total solvent removal.

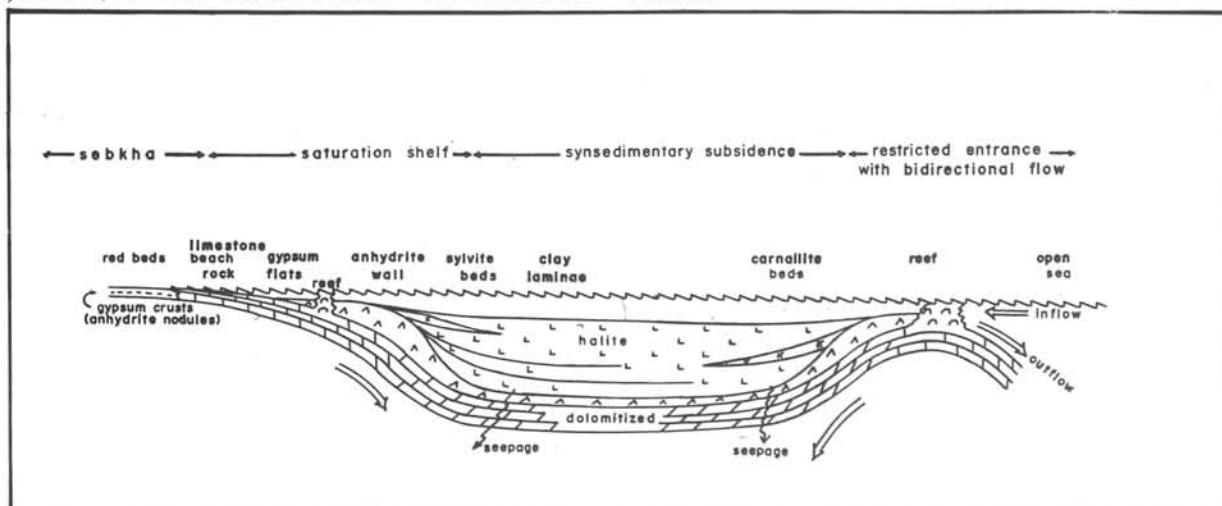


Fig. 2. Synsedimentary subsidence in evaporite basins II: Gypsum precipitation retreats from the basin floor onto the shelves. Halite precipitates in deeps generated by accelerated subsidence. A gradual downwarp of margins creates a wall with beds dipping into the depression. Potash beds extend from basin slope onto the shelves and so do clay laminae delivered by flash floods.

### Flash floods

Heavy downpours and resulting flash floods are not uncommon in semi-arid regions. Flash floods not only deposit a layer of fresh water onto the brine, they also mobilize large amounts of loose soil. Sands and coarse silts are dropped at the shores and often form gypsiferous sandstones. Clays and some finer silt float towards the basin center along the interface between flood waters and resident brine. They eventually settle as a thin blanket on the deeper basin floor, retaining their brine-filled porosity and permeability (Sonnenfeld & Hudec 1985). As such, clay laminae act as conduits for epigenetic waters. Near shoals they can form chaotic mud-halite mixtures above the storm-wave base (Sonnenfeld 1984).

Detrital tourmaline, zircon, staurolite, epidote and other blown-in grains are occasionally found, but wind-blown quartz grains are not preserved in precipitating halite or other chlorides, suggesting dissolution. Siliciclastic sand-halite mixtures are only known as superposition of two environments, e.g., the deposition of sands, eolian or fluvial, into an exposed, eroding older halite (such as in Iran or along the Dead Sea). Discrete sandstone intercalations extend into the basin only where flash floods are on rare occasions large enough to dilute the whole brine column; such sandstones are then sheathed in a thin layer of anhydrite as evidence that the brine has dropped out of the saturation field for halite.

The pH of fluid inclusions and of interstitial waters in marine evaporite sequences is at about 7.5 to 8.5 or higher. In a concentrated brine of elevated temperature this suffices to dissolve silica out of mud flows or out of blown in clastics. A fraction of the silicate lattice is leached out of entering kaolinites, halloysites and other clays and brucite  $[Mg(OH)_2]$  pillars are installed, altering them to members of the Mg-chlorite family. This process is a major sink for magnesium ions that have lost their corresponding anion by sulfate reduction. Potassium-rich percolating brines can convert the chlorites to illites.

The silica, derived from detrital quartz and feldspar dissolution, and from clay leaching, either percolates in solution into the substrate or produces occasional euhedral quartz and feldspar crystals. Chertification of surrounding limestone beds commonly accompanies evaporite basins.

### Alternating precipitation

Dilution of the brine by seasonal (but not necessarily annual) rains takes it out of the saturation field of one mineral into that of the one with the next lower solubility; dry seasons return the brine to greater concentration. This leads to couplets of calcite/gypsum or gypsum/halite. Potash intercalations in halite may be merely expressions of alternating cooling and solar heating of the brine.

Major flash floods or increased seawater influx can lead to a reverse sequence of minerals. Unless concentration resumes, the dilution proceeds from halite to gypsum precipitation, before ultimately reaching open marine salinities. Much less time is usually required for the terminal freshening than for the initial concentration to saturation; consequently, the reverse sequence above the bed of maximum solubility is always less thick than the sequence below that bed (Fig. 3). Potash beds or of halites covered by terrigenous material or by carbonates always indicate an unconformity, a hiatus.

Evaporite cycles range from seasonal couplets of two minerals to multiple phases of evaporite precipitation punctuated by normal marine limestone or dolomite intercalations. No evaporite basin is without these minor and major cycles.

### Primary potash precipitation

Brines saturated for K-Mg-salts become less dense when cooling (Boeke 1910; Cornec & Krombach 1932) and concurrently become less soluble. They then precipitate on the slopes of the basin and on the shelf margin. Such a slope can be extremely gentle, as

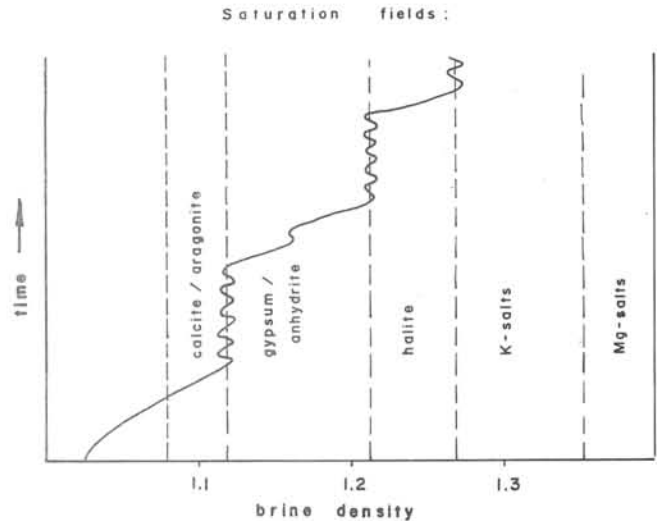


Fig. 3. Saturation curve of a concentrating basin that experiences several temporary freshenings. Salinity oscillations around saturation field boundaries produce couplets.

is suggested by rhythmic halite-sylvite bedding in the Upper Rhine Valley, or by the very gradual coalescence of such rhythms into one sylvite bed thickening upon approach to a marginal reef chain in the Michigan Basin. Beyond this reef chain the sylvite bed ends abruptly, probably because of redissolution by runoff and ancient minor flash floods that entered episodically from nearby shores. The location of the potash seams with respect to the basin intake, in the Devonian Elk Point and Pripyat Basins against a distal shelf, in the Fars Basin near the proximal end, in the Delaware and Michigan Basins against the port side, in all instances against the paleo-western margin. This may be due to a retardation of heavy brines against the earth rotation and thus a Coriolis effect.

Potash beds are always sandwiched into halite beds and are either primary light yellowish sylvite  $[KCl]$  or red carnallite  $[KCl \cdot MgCl_2 \cdot 6H_2O]$ . The precipitation is either due to nocturnal or seasonal cooling, or as brines soak into the substrate, such as a halite slush, where they come in contact with much cooler groundwater (Lowenstein & Spencer 1990).

The slowly nucleating sylvite precipitates wherever a density stratified brine prevents contact with the atmosphere; dissolved organic nitrogen compounds, sheltered from decomposition, prevent  $MgCl_2$  precipitation.

Both nitrogen hydrides (e.g., urea and ammonia from protein decomposition) and Fe-organic complexes (from chlorophyll and hemoglobin decomposition) disintegrate in brines exposed to the atmosphere. Nitrogen hydride destruction lowers the solubility of  $MgCl_2$  and the more rapidly nucleating carnallite precipitates with abundant fluid inclusions, giving it the nickname "crackle salt" or "popcorn salt". The fluid inclusions are mainly organic nitrogen gas, ammonia and invariably some hydrocarbons (methane and ethane) from decomposed organic matter. Presence or absence of macerated organic matter, such as protein derivatives, thus controls the type of primary potash mineral crystallization.

A break-up of the Fe-organic complexes, largely derived from a breakdown of chlorophyll and hemoglobin, leads to the precipitation of various iron chloride minerals in the very concentrated brine, provided there is no oxygen available. Oxidation of Fe-organic complexes and of iron chlorides imparts the red color to carnallite. Iron is liberated that initially forms finely disseminated goethite  $[FeO(OH)]$  needles, platelets or smudges. The hygroscopic brine then promptly dehydrates them to hematite  $[Fe_2O_3]$ . Seasonal drying out of the pool, often marked by a more tabular

habit of hematite, causes some carnallite to dissolve in its own crystal water, absorb atmospheric moisture and then recrystallize at night as sylvite. A further source of iron lies in the conversion of various clays to Mg-chlorites; halite vein fillings in clays are often stained red.

Anoxic formation waters (of Ca-Na-Cl composition) leave sylvites unaffected. A partial carnallitization of sylvite crystals (Wardlaw 1968) can be due to the destruction of nitrogen hydrides. However, if carnallite is exposed to waters undersaturated in respect to  $MgCl_2$ , it will decompose to sylvite (Dana 1951). The occurrence of sylvite after carnallite by  $MgCl_2$ -leaching is common, such as in the Upper Eocene Navarra Basin, Spain (Rosell Ortiz & Pueyo Mur 1984) or in the Stassfurt cycle of Zechstein evaporites (Braitsch 1960). Wherever there are several potash horizons present, one frequently finds all but the uppermost altered to sylvite.

Where sylvite precipitates after carnallite dissolution the red hematite color is not incorporated into the crystals, but remains restricted to the crystal boundaries of sylvite cubes and octaheders, whose inside cores are milky white with few inclusions. In transition to carnallite the sylvite is coarse, pale red, with blue rock salt. Big nests of sylvite occur along fractures and near barren zones (Braitsch 1960).

#### *Residual primary precipitation*

Where steep coasts without shelves prevent algal mats and photosynthetic bacteria to settle, neither aragonite nor gypsum precipitation can occur to deplete the calcium content of the brine. In that case the brines eventually precipitate tachyhydrite [ $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ ] sandwiched into bedded carnallites. Tachyhydrite is thus generated only because of the failure of calcium ions to precipitate earlier. However, for every unit of volume of tachyhydrite, a preceding precipitation of half a unit carnallite [ $KCl \cdot MgCl_2 \cdot 6H_2O$ ] is necessary in order to eliminate the dissolved potassium.

The tachyhydrite can be seen as a Ca-carnallite [ $CaCl_2 (MgCl_2 \cdot 6H_2O)_2$ ], in which calcium substitutes for the potassium. Tachyhydrite is stable only in environments continuously above 23 °C and is thus rare in ancient evaporite sequences that have not remained in a subtropical geothermal gradient. It is found in the Lower Cretaceous Cuanza Basin of Angola and the Sergipe Basin of Brazil (in Aptian time one joint basin), and the coeval Sannakot and Khorat basins of Laos and Thailand. In all these cases there are no aragonite, calcite, gypsum or anhydrite beds associated with the evaporites, except for a thin roof anhydrite terminating the sequence.

Since neither the Br nor the Sr contents are reduced, they are primary precipitates (Zharkov & Zharkova 1989). Although Braitsch (1971) considered a sylvite-tachyhydrite paragenesis unstable at any temperature, even such a combination is found in Brazil (Wardlaw 1972). Overlying carnallites indicate that additional brines were able to enter and to slightly dilute the brine.

Water accounts for more than half the crystal volume of carnallite and tachyhydrite (and also bischofite). Their crystallization further depletes the solvent availability; if exposed to air and its humidity, they dissolve in their crystal water. Neither one can, therefore, be the product of a complete drying out of the basin, as each would decompose as soon as the brine cover evaporates.

#### *Ionic substitution*

Towards the distal part of an evaporite basin the partial pressure of oxygen becomes negligible. Here iron can partially replace magnesium, giving an Fe-carnallite [ $KCl \cdot FeCl_2 \cdot 6H_2O$ ], or a Fe-tachyhydrite [ $CaCl_2 \cdot 2(Mg, Fe)Cl_2 \cdot 12H_2O$ ], which turn red upon exposure to the atmosphere. The iron chlorides indicate not only a lack of oxygen availability and the prior destruction of all inco-

ming sulfate ions, but also the complete release of hydrogen sulfide. Strontium can replace calcium in the tachyhydrite lattice as Sr-tachyhydrite [ $SrCl_2 \cdot 2MgCl_2 \cdot 12H_2O$ ]. Both the Br/Cl and the Sr/Ca ratios in tachyhydrites support their origin as primary precipitate and not as a soaking of bischofites [ $MgCl_2 \cdot 6H_2O$ ] in  $CaCl_2$ -rich formation waters.

Derivatives of organic compounds, essentially nitrogen hydrides, can replace potassium ions to form ammonium sylvite (sal ammoniac,  $[NH_4Cl]$ ), or somewhat more commonly kremersite  $[(NH_4, K)Cl \cdot MgCl_2 \cdot 6H_2O]$ .

#### *Secondary iron chlorides*

The hygroscopic brine strips Fe-carnallite of some of its water molecules douglasite [ $KCl \cdot FeCl_2 \cdot 2H_2O$ ], which contains only about 3/10 of the water volume in carnallite of 20.5 % by weight.

Rinneite [ $3KCl \cdot FeCl_2 \cdot NaCl$ ] appears to be secondary, indicated by its low bromine content (Borchert 1959) and because its precipitation requires a pH below 4.6 (Marr 1957) that would be common only in epigenetic brine movements. It occurs after carnallite in juxtaposition to sylvite (Stewart 1956), with carnallite inclusions (Siemens 1961) or in nests or small intercalations along joints (Kühn 1966), in the Permian Zechstein, the Pennsylvanian Paradox Basin, the Devonian Tuva Basin north of Mongolia, the lower Cambrian of eastern Siberia, the Jurassic of Uzbekistan, and together with douglasite in Morocco and Tunisia (Hite 1961; Sonnenfeld 1984; Popov et al. 1985). Decomposition of these Fe-containing minerals leads to rokuehnite [ $FeCl_2 \cdot 2H_2O$ ].

Even a small increase in the partial pressure of oxygen would produce hematite needles and destroy the iron chloride minerals. A minute presence of  $H_2S$  would yield pyrite [ $FeS_2$ ]. Pyrite is very rarely found in halites, but never in K-Mg-salts.

## Sulfatization

#### *Meteoric water seepage*

Sulfatization of potash horizons required the entry of oxygenated brines. Once brines have saturated for halite, they are anoxic and the primary precipitation sequence is sulfate-free in all Phanerozoic marine evaporite basins. Inflowing sulfate ions are consumed either by anaerobic bacteria or in gypsum precipitation (Borchert 1959). Pore waters are only oxygenated near the surface where meteoric waters have contaminated formation waters. Waters in deeper horizons are without exception anaerobic. Sulfatization has thus to be caused by meteoric waters (rain and runoff) entering potash beds, the only waters that carry a sufficient amount of oxygen.

#### *Extent sulfatization*

Some evaporite basins were subjected to tectonic deformation and meteoric waters could gain access. For each occurrence of bedded K-Mg-sulfates a local explanation can be found for the mode of entry of oxygenated brines. Both the Neogene deposits in Transcarpathia and the Permian evaporites in Austria are considerably disturbed by tectonic movements and the infusion of a tectonic breccia. There were ample opportunities for meteoric waters to enter, not only in Quaternary times. Neogene deposits in Sicily are in an area of intense post-Miocene tectonic activity and much evidence has been produced on later isotopic alteration of both limestones and anhydrites by meteoric waters entering on basin margins (Sonnenfeld 1986). Zechstein evaporites contain broad anticlines with zones of dilation, fissuring and shearing, where foreign solutions had a chance to enter (Borchert 1969). Permian deposits along the paleo-Ural Mountains or in the Delaware Basins of New Mexico and West Texas experienced

other potential ways of exposure to later infusion of oxygenated brines. However, any of the individual local explanations could apply also to some of the evaporites of other ages that have not been sulfatized.

Scattered minor sulfate mineralization occurs in several other horizons. Polyhalite [ $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ ] has been reported as an alteration product of Eocene anhydrites in Spain, associated with minor kieserite [ $MgSO_4 \cdot H_2O$ ] (Orti Cabo 1985), or related to dissolution surfaces near the top of a Keuper salt sequence in eastern France (Marchal 1985). Glauberite [ $Na_2SO_4 \cdot CaSO_4$ ] is present in Triassic salts of both the Lorraine and southern Germany, where it replaces halite or polyhalite (Dana 1951).

Small amounts of kieserite are found in carnallite horizons of the Pennsylvanian Paradox in Utah together with traces of polyhalite and rinneite (Hite 1961). The kieserite can here be ascribed either to an influx of meteoric waters along the many paper-thin clay partings or to a percolation of excess  $MgCl_2$ -brines (left over after carnallite precipitation) through a still permeable, banded halite containing multiple anhydrite laminae. However, the illitization of the clay waters suggests mobilization of potassium ions and thus redissolution of some carnallite, a process unlikely to occur in a brine residual to carnallite precipitation. The impact of percolating brines on evaporites in the Paradox Basin could have been only very limited, because (1) Br/Cl ratios do not indicate any massive redissolution of either carnallite or halite, (2) both rinneite and magnesite are only preserved in an environment totally free of both sulfate and sulfide ions (both underneath and above the evaporite series the waters presently display an alkaline pH, rather than an acid pH required for rinneite formation).

Traces of polyhalitization of individual gypsum crystals occurred on the very margin of the Silurian Salina Basin in Michigan (Dellwig 1955). Of all the evaporite cycles in that basin (Sonnenfeld & Al-Aasm 1991), they occur only in the one that elsewhere contains sylvinite intercalations. These sylvinite laminae coalesce and thicken towards a marginal reef chain, but are abruptly absent between reefs and ancient shores. The alteration of gypsum crystals is here a product of a local remobilization of potassium-bearing solutions, possibly where sylvinite was redissolved in meteoric waters close to the ancient shores.

Along fractures in the Cambrian evaporite sequence of the Punjab Salt Range occurs a lens of langbeinite [ $K_2SO_4 \cdot 2MgSO_4$ ] with kainite [ $4KCl \cdot 4MgSO_4 \cdot 11H_2O$ ] and picromerite [ $K_2Mg(SO_4)_2 \cdot 6H_2O$ ], and with a growth of bloedite [ $Na_2Mg(SO_4)_2 \cdot 4H_2O$ ] and glauberite druses. Kieserite occurs here in ferruginous clays that act as caprock (Mallet 1897, 1900; Christie 1914; Alam & Asrarullah 1972) and in the past may have served as a brine conduit. It should be noted that no sulfatization has as yet been found in time-equivalent evaporites in eastern Siberia.

Major worldwide sulfatization of potash deposits occurred only in Permian and Neogene evaporite basins. Without exception, all potash horizons have been at least partially sulfatized. They are most intense sulfatized near an ancient shore and laterally grade toward the center of the basin into their unaltered chloride precursors. In each seam, sulfatization decreases in intensity away from shore, shoal, or island and extends a different distance. A worldwide phenomenon specific to those periods delivered sulfatic brines to the evaporite deposits. Permian and again Neogene evaporites had no chance to compact completely before the world sea level underwent extensive fluctuations before, during and after ice ages. A temporary lowering of sea level exposed great expanses of shelf areas with freshly deposited gypsum and probably even exposed the rim of the halite precipitate (Sonnenfeld 1985a). Post-glacial crustal rebound near some evaporite basin shores

furthered the shelf exposure. The runoff flowing over desiccated gypsum flats saturated in time with dissolved calcium and sulfate ions despite the low solubility of gypsum.

Rains dissolve about  $1 \text{ cm}^3$  of gypsum per liter of runoff, producing a brine with an ionic sulfate/calcium ratio of about 1, and a weight ratio of about 7.2 : 1. Where halite also becomes exposed, up to  $146 \text{ cm}^3/\text{l}$  of it can dissolve. This adds not only sodium and chloride ions in equal proportions, but also increases gypsum solubility about four times (Fig. 4).

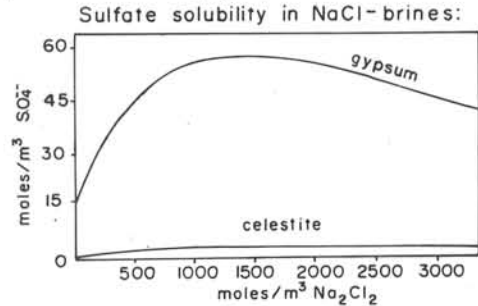


Fig. 4. Gypsum and celestite solubility in NaCl-brines (after Patton 1977).

Other sources of sulfate ions can be eliminated. Basal gypsum beds were in all cases at least an order of magnitude too thin to provide the sulfate ions required (Sonnenfeld 1984). The Phanerozoic sulfur isotope curve attains a minimum value in the Permian, suggesting a drastic drop in bacterial sulfate consumption at that time. There is, however, no such anomaly associated with Neogene deposits.

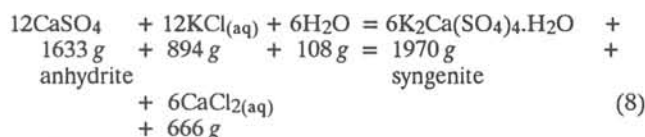
During stages of low sea level runoff draining into a basin of lowered water surface was charged with calcium and sulfate, but also contained progressively more sodium and chloride ions. Some such waters mixed into the residual open brine, but a significant fraction was also able to seep into the as yet uncompacted precipitates along brine-logged clay laminations. Such meteoric waters were able to react with the potash horizons or with anhydrite laminae in contact with them. The path of the brines through fissures can sometimes be observed by following the trace of salted out halite and anhydrite (Borchert 1969). In compacted porous strata, the advance of a diffusion front is slow. Sonnenfeld (1964) found that a younger diffusion front in Devonian carbonates of western Canada had progressed at a rate as low as 10 – 20 km per million years.

Salting out of halite under concurrent sylvite or carnallite dissolution increased the Ca/Na ratio in the brine, but left the  $SO_4/Cl_2$  ratio largely unaffected. Döhner and Elert (1975) suggested that hard salt (langbeinite-sylvite-halite or kieserite-sylvite-halite mixtures) was formed by brines of a Ca- $SO_4$ -composition; the kieseritic hard salt is thus, indeed, a very early diagenetic feature (Schulze 1960). This is not to say, that the present mineral distribution may not be a function of multiple entries of oxygenated brines.

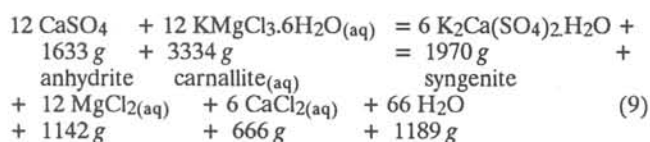
On the way into the evaporite basin, sulfatic brines not only dissolved halite, but initially also a part of the potash horizons creating a barren zone filled with salted out halite. A liberation of the significant ammonia content in fluid inclusions in carnallite reduces the solubility of any alkali- or alkali earth sulfates being formed (Suttle 1957, p. 159) while promoting the leaching of  $MgCl_2$  by increasing its solubility. Brines percolating from above were relatively cool and created barren zones, called roof or back horses. Brines entering in artesian form from below leached out barren zones called floor horses after first warming up due to the high geothermal gradient in salt sequences. The temperature of percolating brines becomes a major factor in determining the resulting mineral species.



Less common is a lack of magnesium ions, which produces either syngenite  $[K_2SO_4 \cdot CaSO_4 \cdot H_2O]$  or goergeyite  $[K_2SO_4 \cdot 5CaSO_4 \cdot H_2O]$ , both of which entail a volume increase. Dissolving KCl can turn anhydrite laminae into syngenite, especially at low temperatures:

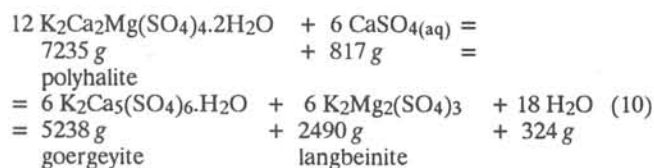


Dissolving carnallite could produce syngenite with a strong evolution of heat:



Syngenite crystallization involves a 38% increase in volume and its generation decreases with a rising temperature and if excess sodium or magnesium ions are present. It occurs much more rarely than polyhalite, because its stability field is relatively small.

A hot brine can decompose polyhalite endothermally to goergeyite and secondary langbeinite under a 15% volume increase, although goergeyite is more likely a direct alternation product of anhydrite by KCl-bearing brines:



Both polyhalite and syngenite can be derived from red carnallites or sylvites and are frequently stained by hematite, but goergeyite is not.

Kalistrontite  $[K_2SO_4 \cdot SrSO_4]$  is rare replacement mineral of celestite liberated in the anhydritization of Sr-bearing gypsum.

### Kieserite

$MgSO_4$  coprecipitates with NaCl from the onset of rock salt crystallization in lacustrine but never in marine environments, contrary to the findings of Usiglio (1849) in his laboratory experiments.

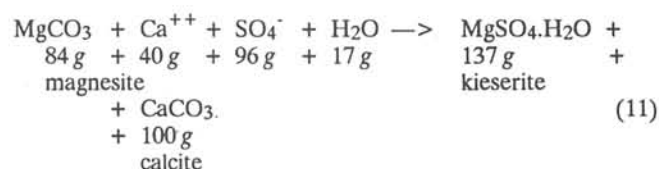
Epsomite  $[MgSO_4 \cdot 7H_2O]$  occurs in surface exposures as weathering product, or in lacustrine efflorescences, and so do  $MgSO_4$ -minerals with lesser amounts of crystal water. Kieserite  $[MgSO_4 \cdot H_2O]$ , however, is a  $MgSO_4$ -mineral found only in the subsurface, although it remains stable down to 18 °C (Hintze 1915).

If it had been a primary deposit of a brine containing magnesium sulfates, kieserite should have coprecipitated with halite and should not have formed distinct beds; epsomite would have formed at normal halite precipitation temperatures. Nowhere have unequivocal pseudomorphs been found of monoclinic kieserite after rhombic (pseudotetragonal) epsomite. It has not been possible to synthesize kieserite at temperatures below 110 °C; consequently, it cannot be justified to assume the formation of kieserite by direct precipitation from a solution (Borchert 1959, 1969; Braitsch 1964). It might be mentioned that the sulfates being precipitated around the Great Salt Lake of Utah or in the Gulf of Kara Bogaz Gol do not contain any kieserite, but only epsomite (Neitzel 1971; Fedin & Medvedev 1989), nor does

kieserite occur in any modern salinas driven to precipitation of magnesium salts.

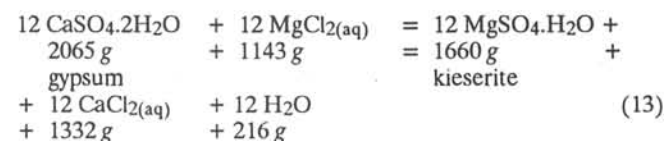
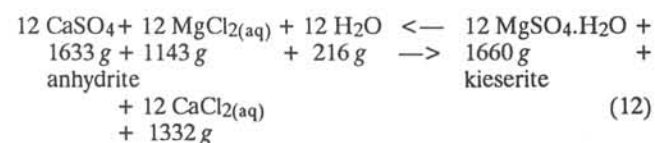
Kieserite is more abundant at the basin margin, the site of increased gypsum precipitation, where percolating warm magnesium chloride brines could interact with anhydrite laminae (Kling 1913; Weber 1931) or with as yet unaltered gypsum. It occurs preferentially on steeper slopes (Seidel 1966). Kieserite pseudomorphs after cubic sylvite, langbeinite, or halite, and even rhombic anhydrite occur in Zechstein evaporites in both the Leine and Stassfurt horizons (Weber 1931; Dana 1951; Braitsch 1960; Schulze 1960), but anhydrite is either absent or only a small component in samples rich in kieserite (Braitsch 1971). Clay inclusions are also absent (Braitsch 1960), having been expelled in recrystallization. Kieserite extends tongues into sylvite or corrodes it on the rims, but itself contains very little sylvite (D'Ans 1969); in halite it usually shows rounded corners and corroded anhedral or subhedral surfaces. In contrast, it may harbor rhombic (pseudo-hexagonal) carnallite inclusions, called "flame carnallite" (Löffler 1960; Meyer 1969).

Magnesite  $[MgCO_3]$ , derived from a bacterial decomposition of gypsum in the presence of organic matter, is decomposed by gypsum dissolved in hot brines and yields calcite and kieserite (Bolley 1841):



Magnesite can develop in modern lagoons (Sonnenfeld & Perthuisot 1988); in ancient marine evaporites it can occur in small quantities in juxtaposition to anhydrite laminae, especially those close to potash horizons; however, it has not yet been documented as an intermediary to kieserite stringers.

Anhydrite or gypsum are evidently the precursors of kieserite:



The reactions consume heat and lead to a 18% volume increase if anhydrite is involved; a further 25 J/mol are consumed and the volume is reduced by 27% if gypsum is the precursor. Kieserite, like anhydrite, is never stained by hematite and thus cannot be the direct decomposition product of a red carnallite. Both kieserite and polyhalite fluoresce, a property not shared with primary salt minerals (Weber 1931).

Even though kieserite does not occur as a basin-wide primary precipitate, it is common decomposition product of other sulfated potash minerals in hot brines, especially near the basin margin, near shoals, or near islands. Extending the opinion of Borchert & Muir (1964), it is, therefore, concluded that all kieserite and polyhalite occurrences are secondary with their origin often obscured through complete recrystallization. In any case, their appearance can be explained satisfactorily by the introduction of a warm brine saturated for gypsum into a potash horizon.





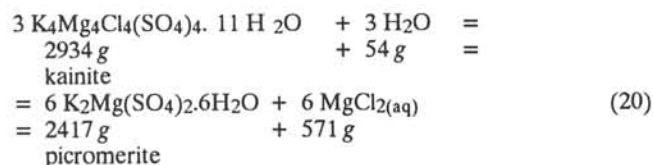
[Na<sub>2</sub>SO<sub>4</sub>] in sulfatized potash beds. Both are produced in the presence of anhydrite [CaSO<sub>4</sub>], provided that there are no more chloride minerals in the vicinity. Glauberite is stable to 18 °C, thenardite to 13.5 °C.

Sodium sulfate minerals are rare in marine evaporites but common in lacustrine ones. Thenardite, glauberite, bloedite and apthitalite are the preferred species in continental brines, where the Na/Ca ratio is usually very large. Especially thenardite and glauberite are then the normal sulfate minerals, dominating over the Ca-sulfates gypsum and anhydrite. Mirabilite [Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O] is a frequent weathering product at a temperature below 32.38 °C.

#### Further alterations

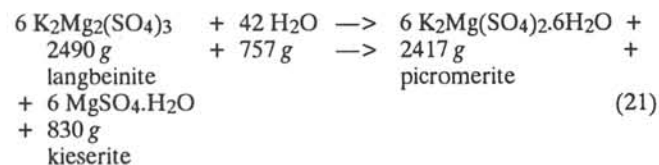
As a brine temperature is a deciding factor in selecting the appropriate secondary precipitate, both positive and negative post-depositional temperature changes yield a host of further alterations of any of these precipitates.

In circulating waters of less than 26 °C kainite can convert to picromerite at a 16 % loss in volume:

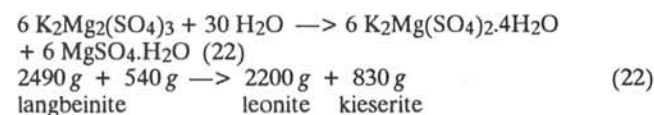


In the Great Salt Lake of Utah, kainite forms in the daytime and picromerite at night, but in NaCl-saturated brines the latter is not stable below 26 °C (Neitzel 1971).

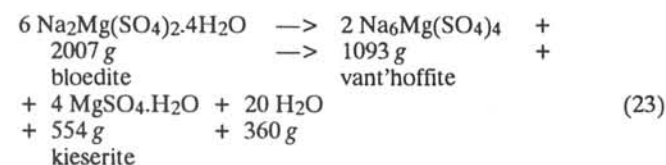
Langbeinite exposed to cool brines (under 26 °C) can hydrate to picromerite under a volume increase, and a new generation of kieserite precipitates:



Continuous contact with warming up hygroscopic brines (to 61.5 °C) can produce leonite together with kieserite. Leonite frequently appears as a secondary decomposition product of langbeinite or above 27.5 °C also of picromerite:

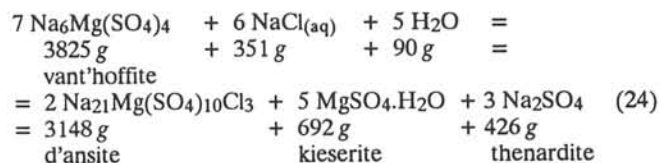


Exposed to atmospheric humidity leonite reverts to picromerite, increasing its volume by 12 %. The much rarer bloedite yields in hot hygroscopic brines at temperatures in excess of 46 °C kieserite and nodules of vant'hoffite [3Na<sub>2</sub>SO<sub>4</sub>·MgSO<sub>4</sub>]:



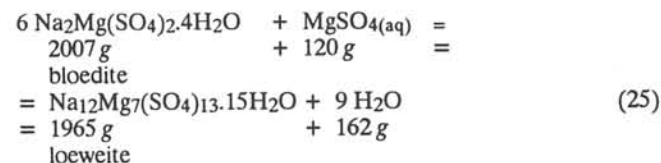
Picromerite occurring in caprocks underneath kainite is indicative either of a watery decomposition of underlying langbeinite in a cooler brine, or of a two-stage decomposition of kainite. In both

cases kieserite is also produced. In a NaCl-saturated solution, that no longer contains any potassium, the rarer vant'hoffite yields kieserite, d'ansite [10Na<sub>2</sub>SO<sub>4</sub>·MgCl<sub>2</sub>·NaCl] and some thenardite.

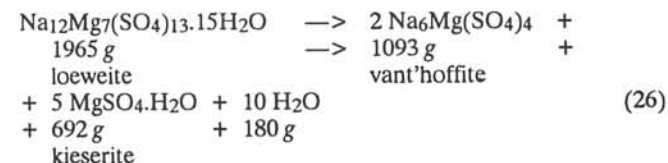


Where carnallite is still present, the dissolved thenardite (stable above 13.5 °C) does not precipitate, but causes further sulfatization of carnallites under concurrent salting out of halite. D'ansite, vant'hoffite and thenardite represent a substantial increase in sodium availability.

Where Mg-content of the brine is very low, any small quantity of dissolved MgSO<sub>4</sub> would convert bloedite to loeweite [6Na<sub>2</sub>SO<sub>4</sub>·7MgSO<sub>4</sub>·15H<sub>2</sub>O] at temperatures above 39 °C (rising with Mg-content of the brine), especially along polyhalitized anhydrite laminae or along kieserite stringers, at a volume loss of about 8 %.



Above 61.4 °C loeweite decomposes to vant'hoffite (Braitsch 1971):



Loeweite may also represent a retrograde diagenesis of langbeinite at its base (Harville & Fritz 1986). It then occurs together with vant'hoffite and langbeinite. That neither loeweite nor vant'hoffite possess a direct carnallite precursor is indicated by the observation that neither is ever stained by hematite.

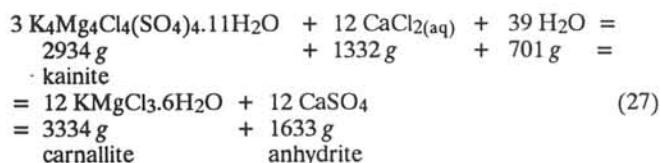
#### Desulfatization

Desulfatization is brought about by CaCl<sub>2</sub>-brines. CaCl<sub>2</sub> is more than twice as soluble as MgCl<sub>2</sub> or MgSO<sub>4</sub>. Such brines can be derived from large-scale kainitization or langbeinitization of carnallites or the decomposition of tachyhydrite, precipitated as end member of a primary sequence and then cooled or exposed. After the exhaustion of the sulfate ion content through extensive sulfatization of primary potash beds, even diffusing meteoric waters are converted to a brine that largely contains only CaCl<sub>2</sub>. To derive desulfatized minerals in deeper formations from a later soaking in CaCl<sub>2</sub>-rich formation waters meets with the difficulty to find a passage through which these waters would have percolated into compacted salt beds that are otherwise impermeable to aqueous fluids.

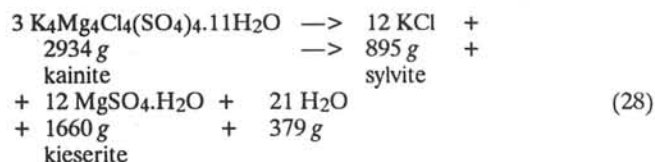
Reactions of a CaCl<sub>2</sub>-rich brine with sulfatized minerals are able to initiate a partial retrograde decomposition of all sulfatized minerals; all the reactions are endothermic and cause large increases in volume of daughter minerals and thus a convolute bedding. They result in a secondary generation of anhydrites, polyhalites, sylvites, carnallites, or even kieserite. Such sylvites and carnallites are whitish, resembling primary precipitation in

a covered brine. They are not stained by hematite needles, because the recrystallization expels foreign inclusions.

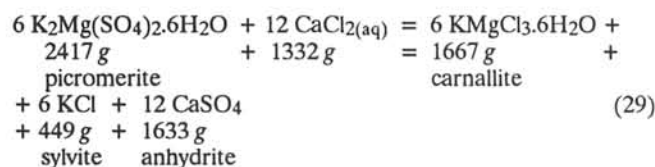
Kainite produces a second generation of carnallite and anhydrite:



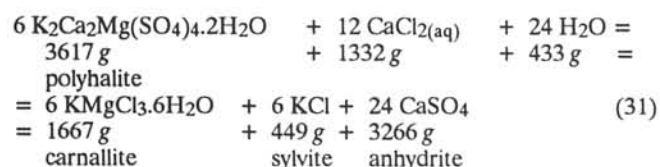
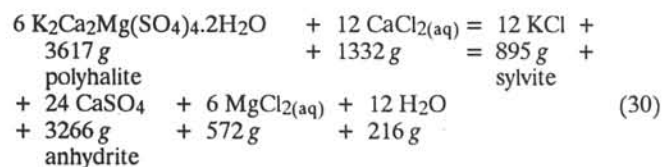
At temperatures above 72.5 °C kainite can yield a second generation of sylvites:



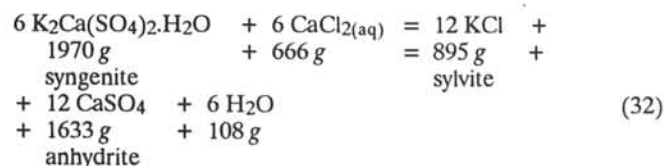
Picromerite can decompose to carnallite, sylvite and anhydrite:



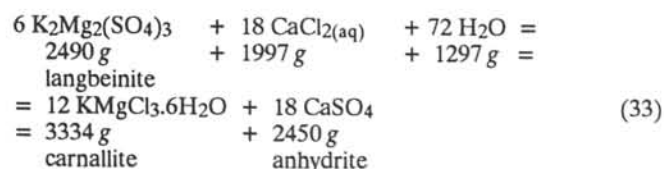
Polyhalite can decompose either to sylvite and anhydrite or carnallite, sylvite and anhydrite in strongly endothermic reactions:



Syngenite can produce sylvite and anhydrite:



Langbeinite decomposition results in carnallite and anhydrite precipitation and is rare because of a required 230 % volume increase:



Only kieserite remains untouched as confirmed by numerous kieserite stringers emanating from basin margins in lieu of anhydrite stringers; exposure to warm and strong enough  $\text{CaCl}_2$ -brines would liberate  $\text{MgCl}_2$  (Döhner & Elert 1975), a temperature-controlled reversible reaction.

The primary Br/Cl ratio has likewise been affected by the circulating meteoric waters, both in the partially altered potash beds and in adjacent apparently unaltered halites. Substantial amounts of bromine are released to formation waters during recrystallization and all chloridic daughter minerals offer a drastically reduced Br/Cl ratio.

## Conclusion

The syndimentary and epigenetic history dictates the mineral facies distribution in evaporite basins. Without accelerated subsidence in a portion of a basin, the depression becomes an "aborted" basin containing only gypsum precipitation. Where such accelerated syndimentary subsidence occurs, the gypsum continues to precipitate on extensive shelves due to the interplay between anaerobic sulfur bacteria and photosynthetic thiobacteria and cyanophyta.

Gypsum ceases to precipitate as soon as the sea floor drops beneath the photic zone and becomes covered by halite in the deeper parts of the depression where it readily converts to anhydrite in the presence of NaCl-saturated hygroscopic brines. On western slopes and outer shelves sylvite or carnallite are usually sandwiched into the halite. Urea, ammonia or cyanides dissolved in the brine can play a decisive role in determining the type of potash precipitation; destruction of chlorophyll derivatives imparts a red coloration. With continuing water extraction, tachyhydrite or baemlerite will form; they are preserved only if the temperature of the deposit remains a tropical one. Dilution of the brine by increasing water influx leads to a retrograde sequence that usually is several times less thick than the initial sequence derived from a progressive brine concentration. The precipitates of lesser solubility then cover and protect those of greater solubility.

In Permian and Neogene evaporite basins sea level fluctuated and the gypsum shelves became exposed before being covered by further marine sedimentation. Their erosion supplied sulfatic brines that seeped into uncompacted potash beds. It is evident from the reaction series given above that the progressive sulfatization of potash beds can be explained simply in terms of a gradually increasing availability of dissolution of gypsum or anhydrite due to exposure of marginal shelves, and of progressively more halite added near the shelf margin. Enough  $\text{CaCl}_2$ -brine was generated to desulfatize a portion of the bed, limited by the drastic volume increases that this alteration calls for. No other post-depositional brine movements are required to be adduced to explain the mineral associations, although such movements have, no doubt, occurred. Sulfatization and desulfatization thus entirely represent a continental influence on marine precipitates.

Meteoric waters entered an evaporitic sequence only as long as the clay laminae were insufficiently compacted and still contained enough interstitial brine; these laminae were then able to act as conduits.

Once the brine was squeezed out under the weight of growing overburden, the potash beds became inaccessible to migrating brines. From this follows that the sulfatization of Permian and Neogene potash deposits has occurred in each case within a very short period after primary deposition. A later exposure of gypsum shelves has not affected the potash beds, once compaction had eliminated the accessibility.

In other periods of earth history, the sea level oscillations were either not sufficient to expose large areas of marginal shelves with their gypsum flats to meteoric waters and dissolution, or they did

not take place not soon enough. Occasional nests of sulfated minerals occur where meteoric waters were able to gain local access. The mobilization of interstitial waters and of fluid inclusions through the introduction of a heat source, such as, e.g., a volcanic pipe, has not been able to alter mineralogical assemblages or fluid inclusion characteristics on any but a local scale. Occurrences of carnallite in contact with basalt pipes in the Zechstein indicate that the crystal water liberated by volcanic heat rehydrated the cooled dehydrated carnallite and did not escape with the rising lava.

It must be stressed that thiobacteria and bluegreen algae foster gypsum precipitation, proteins and alcohols delay it. Cyanides and alcohols reduce the solubility of chlorides (Sonnenfeld 1984, 1985b); a presence or absence of protein derivatives controls the primary potash mineral crystallization. Protein derivatives and other nitrogen compounds liberated in the dissolution of carnallite also lower the solubility of kieserite and all other sulfates common in evaporite basins. Not only bacteria and bluegreen algae, but also organic maceration products thus control the primary and in part the secondary evaporite mineral formation.

The history of alterations is difficult to unravel because the present evaporite mineralogy depicts for the most part the effects of only the last of several brines of different concentration and composition that percolated past and induced recrystallization.

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