

The evolution of marine evaporite deposition

Peter Sonnenfeld

Professor Emeritus, University of Windsor, Windsor, ON, N9B 3P4, Canada.*

*Present address: 280 Simcoe Street, Toronto, ON, M5T 2Y5, Canada

Abstract

Rock salt depositions have evolved during the earth history. Until about 1700 Ga B.P. there was only a type of precipitation in arid or semiarid soils and no bedded evaporite deposits are known. Around volcanic deposits occurred bedded barites and borates. The first bedded gypsum deposits formed after 1700 Ga B.P. and remained the only bedded evaporite deposit until about 700 Ma, when Na- and KMg-chlorides started to precipitate, protected by surrounding rock salt. At specific time intervals the KMg-chlorides were turned into a variety of sulfates by terrestrial runoff entering bedded deposits.

Introduction

Evaporite deposition has evolved during the earth history, starting in the early days with gypsum crystals in arid soils, and bedded barites and borates around volcanic deposits. No bedded marine evaporites are known from the Archean.

Evaporite deposition has evolved slowly during the earth history. The precipitation of marine evaporites is due to evaporation of seawater and a consequent progressive concentration of a brine, whose outflow is retarded behind an entrance bar^{1,2}. Because of the vertical Coriolis effect, the bar is more effective, if in the northern hemisphere the entrance faces east or south, than if it faces west or north. That oriented most evaporite basins in the past.

The luminosity of the sun was originally 0.72 of the present one. The temperature was $238^\circ\text{K} = -3.5^\circ\text{C}$, i.e., below freezing, for the first 2 Ga. Stromatolites, that are 3.5 Ga old, prove the existence of liquid water^{3,4}, but the evaporation of brines was avoided. Crystals of evaporite minerals occur to this day in dry lands: Only individual crystals and druses of evaporite minerals occurred in Archean arid or semi-arid soils and small bedded barite deposits in lakes. However, Archean marine evaporites are unknown.

After 1700 Ga B.P. bedded gypsum deposits appeared as the results of chemical weathering of igneous and metamorphic rocks and are known from many places in the Proterozoic of the Yukon, Australia, southern Africa, and Siberia. They required the generation of extensive quantities of water, largely sweated out of igneous rocks in aerobic weathering.

Photosynthesizers regenerated oxygen scavenged by anaerobic bacteria in a water depth within the photic zone of shelves. Gypsum deposition depletes a water body of its Ca-ions; it requires a water depth in which organic debris is decomposed.

Gypsum remained the only bedded evaporite deposit until about the late Ediacaran (Vendian) when Na- and KMg-chlorides started to coprecipitate with rock salt. An exposure to hygroscopic brines of chloride saturation converts gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ to anhydrite $[\text{CaSO}_4]$. Celestite $[\text{SrSO}_4]$ and kalistrontite $[\text{K}_2\text{Sr}(\text{SO}_4)_2]$ are occasional admixtures to anhydrite.

Thereafter evaporite deposition occurred in closed marine basins in the subtropics.

The first Vendian (Ediacaran) rock salt and KMg-chloride protected by surrounding rock salt started to precipitate in marine embayments with restricted water circulation. Greater brine concentration led to either sylvite under cover of a wedged inflow, where nitrogen compounds derived from a breakdown of proteins rendered MgCl_2 highly soluble. Carnallite precipitated beyond the inflow, where nitrogen compounds broke down in sun light. This carnallite always contains organic nitrogen bubbles. In each instance, Br substitution for Cl increases, as the brine concentrates.

The sequence terminated with sylvite or carnallite that redissolve in a new brine entry, unless a basin had steep margins with no gypsum shelves. With the calcium retained in the brine, the precipitation then ends with tachyhydrite, also called Ca-carnallite, with streaks of hydrated calcium chloride. This primary sequence has not changed throughout the Phanerozoic.

Meteoric water entering evaporite sequences in tectonically active belts alter KMg-chlorides into sulfates. Worldwide, all Permian and all Neogene KMg-salts were altered to sulfates in their shoreward facies, under progressive leaching of potassium and magnesium, until only sodium sulfates were left. This was due to a lowering of sea level that exposed gypsum shelves to rain and runoff even before the onset of continental glaciation. KMg-chlorides intercalations abutting against such a shelf margin were accessible to that runoff. Their distal beds often remained as chlorides.

There are only two periods in the Phanerozoic, when marine evaporite precipitation ceased worldwide: (1) in a part of the Ordovician⁵, and 2) between the Upper Cretaceous Coniacian stage and the end of the Paleocene, right across the K/T boundary⁶. Each of these periods lasted about 40 Ma. The cause of this cessation of evaporite deposition might be a temporary change in the mix of solar radiation. Early Cambrian and Middle Devonian evaporite thicknesses are two orders of magnitude greater than Ordovician and Silurian ones. The same can be observed for Permian against Triassic evaporites. The present low stand of the oceans minimizes evaporite deposition and probably causes an ongoing accumulation of sulfates and other species in the ocean⁷.

Evaporation lowers the water level in the embayment away from the entrance bar and ocean water enters as surface inflow. Some resident brine is pushed out as bottom outflow, again driven by gravity. As a brine concentrates, the solubility of oxygen diminishes. When the difference in density between the inflow and the resident brine rises above 0.05, an interface forms and microbial activity causes an oxygen loss in the resident brine. At the point of gypsum saturation oxygen in solution is less than 4 ppm and thus insufficient to generate a chemical precipitation of gypsum even from supersaturation in calcium⁸.

A growing scarcity of oxygen in the brine allows anaerobic sulfur bacteria to enter the brine from the subsoil and attack inflowing sulfate ions. They strip sulfates of oxygen and release H₂S, which becomes less soluble in brines of rising concentration⁹. Later they can even attack precipitated gypsum and release calcium chloride¹⁰.

Reefs as entrance barriers

Reefs flourish at the entrance, nourished by inflow.

An anoxic outflow sweeps the outer slope free of biota and thus fosters endemism inside the basin¹¹. Reef chains near the entrance strait, often with stromatolitic growths, constrain a free water exchange and are almost always accompanied by anhydrite in their backreef area. Storm-derived reef debris and reef trunks curtail the outflow further. Associated shales and micritic limestones are often bituminous, because an increasing salinity plays havoc with the osmotic pressure of any biota that accidentally enter increasingly concentrating brines.

The organic content of an anaerobic marine brine is three orders of magnitude greater than that of the open ocean and explains the association of crude oils with reefs and other porous beds on the margins of evaporite basins. A frequently observed relationship to Pb-Zn sulfide deposits mobilized in the anhydritization of gypsum or the dolomitization of limestones along porous conduits are corollaries.

Gypsum deposition

Because the brine is practically anaerobic at brine concentrations reaching gypsum saturation, another source of oxygen is needed. The sunlight reflected from shallow bottoms is reflected again at the interface to surface inflow and is absorbed; the water heats up. Photosynthetic bacteria and bluegreen algae settle here below the interface between inflow and resident water. These archaeobacteria supply new oxygen to convert released hydrogen sulfide to sulfate ions and then precipitate available calcium ions as gypsum.

The rate of gypsum precipitation is faster in the wet season, when algae are thriving, or at the peak of algal activity during the daytime. Where the coastlines have been steep without any shelves, no reflection from a shallow bottom occurred and no energy maximum formed under the interface. No gypsum precipitated as photosynthetic bacteria have not been able to settle and calcium remains in solution into the terminal brine.

As the supply of new oxygen is a function of photosynthesis, gypsum continues to precipitate only where the basin does not subside below the penetration of sunlight. Vast gypsum platforms formed, such as the Cretaceous one of the Maghreb¹² in North Africa or the Miocene ones in Hungary and in the Adriatic and Aegean seas.

Gypsum exposed to the atmosphere turns into bassanite [(CaSO₄)₂·H₂O] that reverts to gypsum when again covered by brine. Excess brine is dumped into the open ocean and may there cause an anoxic event¹³.

Gypsum nucleation is inhibited in NaCl-brines¹⁴ or in the presence of proteins, but even traces of NH_4 -chloride will increase the solubility of gypsum. Resins, sugars and other vegetable compounds stabilise calcium sulfate solutions. A maximum gypsum solubility is reached at 37.5°C, it initially increases as the brine concentrates, but decreases in the presence of calcium or sulfate ions.

When the brine reaches saturation for chlorides, the hygroscopicity of the brine converts gypsum to anhydrite. This occurs in semi-arid regions at ambient summer temperatures, i.e., at any water temperature >18°C¹⁵. The conversion to anhydrite is thus not a function of burial, but of exposure to more concentrated brines. Celestite [SrSO_4] is expelled in the anhydritization and then forms independent nodules.

Rock salt deposition

Brines stripped of calcium accumulate in differentially subsiding areas and eventually precipitated halite [NaCl]. The precipitation occurs in the dry season, when evaporative concentration is at a maximum, or in the early morning hours, at the peak of diurnal water loss¹⁶. Organic compounds that retard gypsum precipitation, accelerate halite precipitation.

Narrow grabens in gypsum platforms contain halite, such as on the Miocene margins of the Tyrrhenian and Aegean Seas. Otherwise it is the deeper offshore part of the basin where halite saturated brines can accumulate. In contrast to older estimates¹⁷, thought of halite precipitation in the range of a few meters of water depth on the basis of halite textures. This requires a syndimentary subsidence to accumulate substantial thicknesses of halite. Depths of brines in halite basins have commonly been over-, and in potash deposits underestimated¹⁸.

Potash deposition

Most marine evaporite basins that reached halite saturation also produced intercalated potash horizons, either as sylvite [KCl] or as carnallite [$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$], even though the precipitation of K-phases requires a more than 90-fold concentration of the brine¹⁹. KMg-brines are highly sensitive to brine temperatures, once they reach saturation. KCl-brines²⁰ and even more so MgCl-brines rise and are less solubility upon cooling. Consequently, there are two sites where KMg-chlorides accumulate: firstly, in discrete beds abutting against the shelf margin as sylvite or farther out as carnallite, secondly, on the

basin floor in an intimate mixture with precipitating halite, called **sylvinite** and **carnallite**. The carnallite often acts thereby as a cement of the original halite slush²¹.

NaCl reaches a minimum solubility in saturated KCl-solutions at 105°C. In a cooling brine, the solubility of KCl decreases while that of NaCl increases and the brine precipitates sylvite. A NaCl-solution saturated at 50°C will reach critical supersaturation at 50.1°C, a KCl-solution at 35.1°C and a KBr-solution at 42°C. The presence of MgCl_2 in the brine decreases the solubility of NaCl and more rapidly that of KCl.

Where the inflowing brine covers the resident one and prevents its oxygenation, both N-hydrides (derived from a decomposition of proteins) and $\text{Fe}(\text{OH})_2$ (derived from the decomposition of chlorophyll and hemoglobin) remain in solution. Beneath the cover of the inflow, the N-hydrides (e.g., urea, NH_4Cl) increase the pH, decrease the solubility of KCl and raise that of MgCl_2 ^{22,23}. N-hydrides thus foster the precipitation of the slowly nucleating sylvite.

KCl-solubility decreases with rising content of ammonium chloride in the brine and vanishes at 273.5 g/L NH_4Cl ²⁴. Once the surface waters are burnt off, the N-hydrides convert into pure organic nitrogen that is then retained in bubbles in rapidly nucleating carnallite, giving it the name **crackle salt**. Organic matter is frequently present in fluid inclusions as members of the alkane family.

When the brine is exposed to air, the $\text{Fe}(\text{OH})_2$ is precipitated as brown goethite [$\text{FeO} \cdot \text{Fe}(\text{OH})$] and then oxidized to red hematite [Fe_2O_3] in the fiercely hygroscopic brine. Thus primary carnallite is red, while primary sylvite is ivory colored or off-white. Secondary sylvite (after the leaching of MgCl_2) is red, while secondary carnallite is white, a reversal of colors. A presence of tertiary sylvites and carnallites complicates the analysis.

CaMg-deposition

If the basin had steep margins with no gypsum shelves, the calcium was not depleted and stayed retained in the brine. A further concentration of the brine led to the precipitation of tachyhydrite or Ca-carnallite [$\text{CaCl}_2 \cdot (\text{MgCl}_2 \cdot 6\text{H}_2\text{O})_2$]²⁴. Eventually, antarcticite [$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$] formed at temperatures to 29.8°C or at higher rock temperature sergipite [$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$] (at 29.8°C - 45.3°C) and sinjarite [$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$] (above 45.3°C)²⁵. Because of the high

solubility of CaCl_2 , they dissolve easily in formation waters and when exposed, absorb humidity from the air. They are rare²⁶ and only preserved in Early Cretaceous evaporite sequences of Brazil and Laos, where the rock temperature has never dropped below 23°C.

FeKNa-deposition

Rinneite ($\text{FeK}_3\text{NaCl}_6$ or $\text{FeCl}_2 \cdot 3\text{KCl} \cdot \text{NaCl}$) occurs in distal parts of a basin, where it crystallizes only above 26.4°C, often covered by sylvite as a replacement in carnallite. It has a narrow stability field even at 55°C, little altered by increasing MgCl_2 -concentrations that raise its solubility. It is unstable in the presence of oxygen, has not been exposed to the atmosphere or to oxygenated (sulfatic) brines and never contains organic compounds.

Bromine in the crystal lattice

Bromine is incorporated into halite and sylvite lattices, substituting for chlorine. In carnallites it substitutes preferentially in Mg-chlorides and this depletes surrounding halite. The amount of substitution increases with concentration of the brine.

Once NaCl-saturation is reached, rock salt starts coprecipitating with a small amount of NaBr. As the brine concentration increases, more and more Br^- substitutes for Cl^- . Where some brines are able to percolate later down and come in contact with higher values of NaBr just above a sylvite layer, they will leach Br^- , since they have become saturated for Na^+ and Cl^- , but not for Br^- . The result is a series of blue halite nodules containing platelets of metallic sodium and an increased porosity. They never occur underneath potash beds.

Blue halite does not occur above carnallite beds, because the MgCl_2 sweeps up all available Br^- into $\text{Mg}(\text{Cl},\text{Br})_2$ ²⁷. The leaching of Br^- from sylvite produces a violet colour in the sylvite. The amount of available bromine increases whenever the basin is inundated with clays²⁸. At points of previously particularly high bromine contents the number of lattice defects is unduly high because of the different size of Br^- and Cl^- -atoms.

Several evaporite basins show an absence of bromine in their lowermost halite cycle, proving the leaching by circulating brines from above. This is the case for the Delaware Basin of West Texas, the evaporites beneath the Zechstein horizons of W. Europe, or the lower Elk Point salts in Saskatchewan¹⁶. A downward percolation

of brines is also indicated by the leaching of bromine from $\text{Na}(\text{Cl},\text{Br})$ precipitates above a sylvite horizon, leaving metallic platelets of native sodium²⁹. The downward percolation of brines is, however, still not understood: the diagenesis of halite is virtually completed within 45 m of burial and a tightly crystallized halite impedes the downward percolation of brines, having reduced porosity from a halite slush to less than 10%³⁰.

Dearth of clastics

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

Because of the sparse rainfall in semiarid regions, there are few rivers, limiting the delivery of siliciclastics. Saltwater encroaches onto groundwater which overrides it and surfaces in a series of springs that are apt to dry out before reaching a shore.

A subsiding depression would become a "starved basin," if it were not for the eventual precipitation of evaporites.³¹ found Quaternary evaporites to be restricted to shallow coastal embayments of the Red Sea, lacking in the deeper parts of it, even though it had been a barred basin during various stages of the Quaternary. The period of restriction by the entrance sill at the Strait of Aden evidently lasted not long enough during glacial stages to lead to saturation of the brine in the Red Sea.

Meteoric waters enter mainly as flash floods and float on the resident brine. Unabraded brackishwater fossils can then occur far offshore in an evaporite basin. Such occasional flash floods pick up loose earth and may deposit a coarse fraction in the proximity of the shore, as gypsiferous sandstones or sandy gypsum. In that respect they differ from the prograding coast of sabkha environments in the Persian Gulf, where siliciclastics often comprise more than 50% of the sediment¹⁰. Where gypsum flats are set into a carbonate platform, they lack a siliciclastic admixture.

A sandy fraction extends extremely rarely into halite sequences and always marks an instant of extensive freshening and redissolution. In contrast, clays swept into the basin spread along the interface to surface waters³² and may be correlatable over several

hundred kms.

When descending through a brine saturated at least for halite, the clays convert to members of the Mg-chlorite family of mixed-layer clays. This is a sink for some magnesium ions liberated in the destruction of Mg-sulfates in the brine by anaerobic bacteria. In older evaporites the Mg-chlorites are often converted to illites. Clays settling on near-shore gypsum surfaces are not so altered. Blown in detrital quartz and feldspars dissolve in a brine of high pH and yield euhedral neoformations. Chaotic deposits of salt and siliciclastics, such as found at the north rim of the Carpathian Mountains, are invariably a mixture of silty clays and halite.

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Sulfatization

KMg-chlorides are sulfatized by meteoric waters that gain access to an evaporite deposit in tectonically active areas, or through a temporary lowering of sea level and exposing of the gypsum shelves. In the former case, only those beds are affected that have been raised locally to levels where groundwater can obtain access. An example is the presence of KMg-sulfate minerals in the Salt Range of Pakistan and the absence of such minerals in the coeval evaporites on the Angara Shield in Siberia.

Worldwide, all Permian and all Neogene KMg-salts are represented at least in their shoreward facies by sulfates. The lowering of sea level before the onset of wide-spread continental glaciation exposed the gypsum shelves to rain and runoff.

Bedded KMg-chlorides abut against the shelf margin and thus are easily accessible to runoff flowing over the shelf. The gypsum solubility in fresh water is rather small (2.1 kg/t or up to 901 cm³/m³ water). However, as soon as the runoff starts dissolving NaCl at the shelf margin, the solubility of gypsum rises drastically to over fourfold; proteins dissolved in the runoff can raise the solubility even further¹⁶. That the KMg-sulfate minerals are secondary is shown by the preservation of KMg-intercalations in the German Zechstein-3 salts (Ronnenberg seam) as chlorides at a

distance from the shelf margin.

Initially, the carnallite converts to kainite [4KCl₄·MgSO₄·11H₂O] in a "kainite hat" on top of the potash seam, while warmer waters entering from the base of the deposit form langbeinite [K₂Mg₂(SO₄)₃]. The langbeinite can partially turn into kainite and sylvite in a retrograde conversion³². Picromerite [K₂Mg(SO₄)₂·6H₂O] and leonite [K₂Mg(SO₄)₂·4H₂O] are further alterations. Some celestite nodules in anhydrite convert to kalistrontite [K₂Sr(SO₄)₂].

More dissolved halite in the brine leads to bloedite [Na₂Mg(SO₄)₂·4H₂O], loewite [Na₁₂Mg₇(SO₄)₁₃·15H₂O], vanthoffite [Na₆Mg(SO₄)₄], and dansite [Na₂₁Mg(SO₄)₁₀·Cl₃], ending in glauberite [Na₂Ca(SO₄)₂] or apthitalite [K₆Ca(SO₄)₄] and thenardite [Na₂SO₄]^{33,34}.

Bischofite [MgCl₂·6H₂O] settles out in sulfatized beds on account of a low solubility of MgCl₂ in sulfatic brines. In addition, it is found where tachyhydrite [CaCl₂·(MgCl₂·6H₂O)₂] has been partially decomposed in humid air, or in manmade evaporator pans where sulfur bacteria were unable to digest all the sulfate ions. However, it is not known from any natural evaporite basin as a primary deposit. An almost ubiquitous bischofite in Permian KMg-sulfate layers is a secondary byproduct of sulfatization that decomposes at 116°C.

A reaction of gypsum intercalations in halite with percolating warm potash brines yields polyhalite [K₂Ca₂Mg₂(SO₄)₄·2H₂O], with cooler ones syngenite [K₂Ca(SO₄)₂·H₂O], very rarely goergeyite [K₂Ca₃(SO₄)₄·6H₂O], with MgCl₂-brines kieserite [MgSO₄·H₂O].

Kieserite [MgSO₄·H₂O] is only formed above 110°C and is often found in a reciprocal relationship with gypsum intercalations. Epsomite [MgSO₄·7H₂O] is a surficial weathering product. It occurs in lakes, but does not occur in the subsurface.

There are no bedded KMg-sulfate minerals known from any undisturbed evaporite sequence other than Permian and Neogene ones. The formation waters of Silurian salts in the Michigan Basin do not appear to have been diluted by meteoric waters³⁵ even though the brine concentration exceeds in places 643 g/L³⁶, and neither have those of other horizons that contain only chlorides.

Conclusion

Evaporite deposition started in the early days of earth history with crystals in arid soils or lakes; no

bedded marine evaporites are known from the Archean. Proterozoic bedded marine gypsum is found in many places, bedded chlorides from the late Ven dian (Ediacaran) onwards. An exception is the lack of evaporites at the Cretaceous/Tertiary (K/T) boundary.

Gypsum precipitates in a water depth within the photic zone of shelves. Chloride brines accumulated in deeper, differentially subsiding areas, where anaerobic bacteria scavenged sulfate. The deposition terminated with potash beds, unless the basin had steep sides that prevented the early precipitation of gypsum and led to terminal tachyhydrites covering carnallites.

Meteoric waters in tectonically active belts altered KMg-chlorides to sulfates. Permian and Neogene KMg-chlorides worldwide were likewise altered to sulfates under progressive leaching of the cations by meteoric waters.

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