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Sulfatization and Desulfatization of Marine Evaporite Facies

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ABSTRACT

All Permian and Neogene evaporites, and some tectonically disturbed ones of other ages contain K-Mg-sulfate minerals that have replaced K-Mg-chlorides. The sulfatization was caused by oxygenated brines infiltrating via brine-logged clay laminations. It is suggested that a drop in sea level exposed gypsum shelves to meteoric waters, halite dissolution quadrupled the gypsum solubility, and brine-logged clay laminations acted as conduits to move the runoff towards the near-shore potash horizons. A rising Na-content of the brine eventually fostered secondary alterations, excessive $CaCl_2$-generation induced desulfatization. The reactions probably occurred at about 45–85°C.

Carnallite converted to kainite as caprock or to langbeinite along floor horses. Dissolving carnallites altered gypsum or anhydrite interbeds to polyhalite, as betrayed by pseudomorphs. As indicated by pseudomorphs and inclusions, kieserite formed either where warm $MgCl_2$-brines affected anhydrite or gypsum stringers near basin margins, or where warm $CaSO_4$-brines decomposed magnesite, or where langbeinite was altered further. Unlike primary salt minerals, both kieserite and polyhalite fluoresce. Other byproducts of sulfatization are rare. Mg-free brines produce syngenite or goergeyite. Kainite or langbeinite can locally hydrate to picromerite or leonite nests. A growing Na-enrichment in the brine generates nests of bloedite in the kainite caprock, then decomposes bloedite to loeweite, vanthoffite, and dansite. Thenardite and glauberite form where Mg-chlorides have become exhausted.

Kainitization at times yields a secondary tachyhydrite with kieserite inclusions and a reduced Br/Cl ratio. Subaerially exposed, tachyhydrite turns into bischofite, which also forms in polyhalitization or carnallite decomposition; bischofite converts sylvite into carnallite. Being poorly soluble in sulfatic brines, it occurs primarily in sulfatized potash beds or where Aptian primary tachyhydrites have become exposed, but it is absent in evaporites of other ages. $CaCl_2$-brines promote desulfatization, a retrograde alteration to K-Mg-chlorides. Only kieserite stringers in halite remain unaffected.

Sulfatization of marine potash beds into a complex and diverse mineralogy can be explained by an early meteoric runoff dissolving gypsum on shelves and progressively more halite before accessing sylvites and carnallites in undercompacted marine evaporites. No other source of sulfates needs to be invoked.

INTRODUCTION

A conversion of basal gypsum beds to anhydrite provides grossly insufficient amounts of sulfate ions to sulfatize potash horizons and would have led to major leaching of halite (Sonnenfeld, 1984). Each meter of K-Mg-sulfate would have required the dehydration of many hundred meters of basal gypsum to generate the needed sulfatic waters; such thicknesses have not been available. A massive incursion of seawater would have leached not only some halite, but almost all of the potash deposits, because seawater is undersaturated for these compounds.

Once brines have saturated for halite, they become 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, 1969). Formation waters in deeper horizons are without exception anaerobic, while near-surface pore waters are oxygenated where contaminated with meteoric waters. Sulfatization of potash horizons thus requires the entry of oxygenated brines, that is, meteoric waters (rain and runoff), the only waters that carry a sufficient amount of oxygen.

K-Mg-SULFATE DISTRIBUTION

Primary K-, Mg-, or Na-sulfates do not occur in marine evaporite sequences. Worldwide, however, all Permian and Neogene potash deposits have largely been altered to secondary complex K-, Mg-, or even Na-sulfate minerals. They are most intensely sulfatized near an ancient shore and grade laterally 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 (Sonnenfeld, 1991).

Evaporite beds of other ages are similarly affected only wherever they have been tectonically disturbed and opened to meteoric water influx. Cambrian evaporites in the Salt Range, Pakistan, contain K-Mg-sulfate minerals, but not undisturbed coeval ones in Siberia. Both the Neogene deposits in Transcarpathia and the Permian evaporites in Austria are disturbed by tectonism and the infusion of a tectonic breccia. 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 have had a chance to enter (Borchert, 1969).

Source of diffusing brine

Marine evaporite basins are rimmed by shelves covered with gypsum and contain chlorides only in deeper parts. As such shelves become exposed to rain and runoff, the gypsum gradually dissolves in meteoric waters. Such happened worldwide in the Permian and Neogene, possibly because of a temporary drop in sea level during pre- and post-glacial oscillations, or in other instances due to local tectonic events.

Rains dissolve about 1 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. The solubility of gypsum depends 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). Where halite also becomes exposed, up to 146 cm^3/l of it can dissolve. This adds not only sodium and chloride ions in equal proportions, but increases gypsum solubility about four times (Patton, 1977) (Fig. 1).

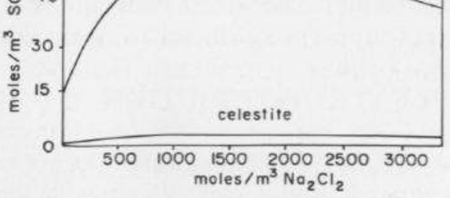

Fig. 1. Gypsum and celestite solubility in NaCl brines. (After Patton, 1977).

Döhner and Elert (1975) have previously suggested that brines of a Ca-SO_4-composition have had caused all alterations observed in Zechstein potash beds. Because of the surface origin of the waters, the temperatures involved have been either close to ambient or modified by a high geothermal gradient typical of salt sequences. All reactions have probably occurred in the range of about 45–85°C.

Access of brine

Both K- and Mg-chlorides become lighter upon cooling and tend to rise toward the brine surface and spread towards the flanks of the basin. Flash floods deliver coarse siliciclastics to near shore environments, while clays float out along the interface between runoff and resident brine. Upon settling they retain their brine-filled porosity until the growing overburden of new halite precipitation squeezes out interstitial brines (Sonnenfeld, 1984). Consequently they are ideal conduits for a diffusion of meteoric waters. The path of the brines through fissures can sometimes be observed by following the trace of salted out halite and anhydrite (Borchert, 1969).

SULFATIZATION OF CARNALLITES

All K-Mg-sulfate minerals require the entry of an external influx of a Ca-SO_4-brine. Such brines reacting with carnallites produce $CaCl_2$-brines and K-Mg-sulfate minerals. Mg-chlorides also accrue in the brine and cause further reactions with anhydrite laminae. Potash beds, sulfatized near ancient shores, along basin margins or island flanks, tend to grade basinward into unaltered chloride precursors.

Kainitization or langbeinitization

In descending brines of at least 35°C carnallite [$KCl\cdot MgCl_2\cdot 6H_2O$] converts to kainite [$4KCl\cdot 4MgSO_4\cdot 11H_2O$] at a potential loss of volume of about 35% and an evolution of heat. The kainite forms a caprock, called a "kainite hat" (Fig. 2) and always occurs where brines have soaked into the potash seam (Bessert, 1933). It is often found at the base of kieserite-rich beds, sometimes associated with back horses of barren zones. A kainitization together with carnallite displacement by sylvite suggests a decreasing $MgCl_2$- and increasing SO_4-content (Siemeister, 1961).

Langbeinite [$K_2SO_4\cdot 2MgSO_4$] forms from slightly warmer, more hygroscopic brines, preferentially along floor horses of concurrently salting out halite, at a loss of 58 vol.%. It contains sylvite, halite and kieserite inclusions (Borchert, 1969). Langbeinite pseudomorphing after sylvite separates Zechstein salt horses from carnallite; the langbeinite eventually disappears in favor of kieserite and halite (Middendorf, 1930). Sylvite is also common in langbeinite areas of the Delaware Basin (Harville and Fritz, 1986); sylvitization of carnallite thus seems to precede langbeinitization. The ammonia liberated from fluid inclusions in carnallite reduces the solubility of K-Mg-sulfates (Suttle, 1957, p. 159) but raises that of $MgCl_2$.

While kainite is commonly stained red by hematite derived from the carnallite precursor, langbeinite very rarely accepts red hematite staining; instead the hematite is lodged in halites recrystallized underneath leached zones.

Under concurrent kieserite precipitation kainite and langbeinite can convert in cold brines to picromerite [$K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$], in warmer brines to leonite [$K_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$] nests. Leonite turns to picromerite when exposed. Ca-Mg-sulfates are unknown in marine evaporites.

Alteration of anhydrite

Brines dissolving carnallites have altered gypsum or anhydrite to polyhalite as indicated by pseudomorphs (Schaller and Henderson, 1932; Schulze, 1960; D'Ans and Kühn, 1960) or in the absence of dissolved potassium to kieserite (Table 1).

Kieserite forms pseudomorphs after anhydrite, sylvite [KCl], langbeinite and halite (Weber, 1931; Schulze, 1960), but anhydrite is either absent or only a small component in samples rich in kieserite (Braitsch, 1971). Kieserite harbors carnallite inclusions ("flame carnallite") (Löffler, 1960), corrodes sylvite rims, but itself contains little sylvite (d'Ans, 1969) and occurs preferentially on steeper slopes (Seidel, 1966). Kieserite, like anhydrite, is never stained by hematite.

A saturated NaCl-$CaSO_4$ solution converts carnallite to kieserite, sylvite and halite; anhydrite salts out due to a low $CaSO_4$-solubility in $MgCl_2$-solutions (Weber, 1961). Hot Ca-SO_4-brines also decompose magnesites [$MgCO_3$], which have been produced by bacteria from gypsum in the presence of organic matter (Sonnenfeld and Perthuisot, 1989), and yield kieserite and calcite [$CaCO_3$] (Bolley, 1841).

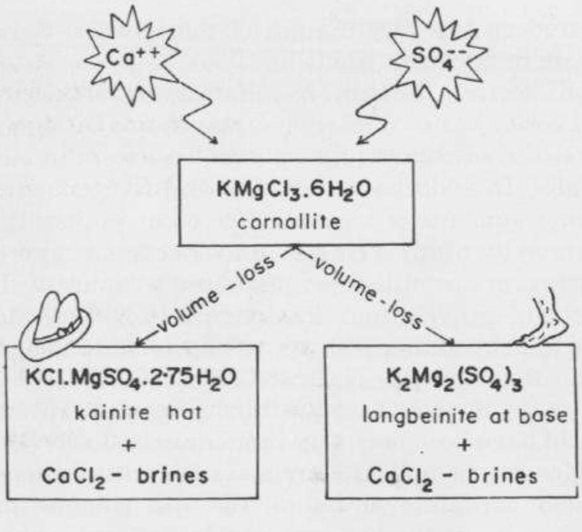

Fig. 2. First-order sulfatization.

Neither polyhalite nor kieserite form basin-wide beds, but occur where warm $MgCl_2$-brines soaked into anhydrites near basin margins (Kling, 1915; Weber, 1931). Both become more frequent and thicken towards shores, just as their anhydrite or gypsum precursors, and both contain little anhydrite and no clay inclusions even where adjacent to clay-bearing anhydrite. Reduced anhydrite/halite ratios in Permian and Neogene evaporites compared to those of other ages, confirm a loss of anhydrite.

Mg-free brines, in turn, can produce syngenite nests, or convert polyhalite to a secondary langbeinite together with a little goergeyite; the generated heat has to be dispersed quickly. Syngenite and goergeyite cause volume increases, have a small stability field, and are rare. Both polyhalite and syngenite are frequently stained by hematite, but goergeyite is not.

Polyhalite has been reported as an alteration product of Eocene anhydrites in Spain, associated with minor kieserite (Orti Cabo et al., 1985), or related to dissolution surfaces near the top of a Keuper salt sequence in eastern France (Marchal, 1985). Traces of polyhalitization of individual gypsum crystals oc-

TABLE 1

Alterations of gypsum or anhydrite

From:		Gypsum $CaSO_4{\cdot}2H_2O$		Anhydrite $CaSO_4$
To:	polyhalite	$K_2SO_4{\cdot}2CaSO_4{\cdot}MgSO_4.2H_2O$	syngenite	$K_2SO_4{\cdot}CaSO_4{\cdot}H_2O$
or to:	kieserite	$MgSO_4{\cdot}H_2O$	goergeyite	$K_2SO_4{\cdot}5CaSO_4{\cdot}H_2O$

curred on the very margin of the Silurian Salina Basin in Michigan (Dellwig, 1955).

Kieserite is the only Mg-sulfate mineral in ancient evaporite basins. Other hydrated forms of Mg-sulfates do not occur in the subsurface, except in mine shafts. In addition to Permian and Neogene sites, minor amounts of kieserite also occur in disturbed Pennsylvanian, Triassic and Eocene evaporite basins. In carnallite horizons of the tectonically disturbed Pennsylvanian Paradox Basin in Utah they are found together with traces of polyhalite, magnesite and rinneite [$NaCl{\cdot}3KCl{\cdot}FeCl_2$] (Hite, 1961). Here the impact of percolating brines on evaporites 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).

Usiglio published in 1849 a now famous and often repeated experiment of evaporating Mediterranean seawater, which was often quoted as evidence for primary Mg-sulfate precipitation from evaporating seawater. The experiment was carried out in the oxygenated conditions of the laboratory, under exclusion of the influence of anaerobic sulfur bacteria. Consequently, his first precipitate was iron oxide [Fe_2O_3], and then gypsum. In anaerobic marine brines, iron remains dissolved until potash precipitation. Indeed, a negative redox potential is frequently induced artificially in man-made salinas to prevent the precipitation of red iron-bearing halite (Herrmann et al., 1973).

Halite followed upon gypsum in Usiglio's experiment and with it about 5% $MgSO_4$, probably as epsomite. Marine halite beds normally do not contain 5% $MgSO_4$ in whatever degree of hydration.

Both kieserite and polyhalite fluoresce, a property not shared with other primary evaporite minerals (Weber, 1931). Nowhere have unequivocal pseudomorphs been found of monoclinic kieserite after rhombic (pseudotetragonal) epsomite, nor does kieserite precipitate in any natural or man-made evaporite basin today. It is, indeed, a very early diagenetic mineral (Schulze, 1960), that cannot be produced at temperatures below 110°C (Braitsch, 1964), which is outside the stability field of many other K-Mg-sulfates present in evaporite basins. Because of extreme kinetic values (Braitsch, 1964), kieserite must be regarded as a decomposition product of other minerals and does not have as precursor a hypothetical primary epsomite [$MgSO_4{\cdot}7H_2O$], even though epsomite commonly effloresces on mine walls.

Byproducts of sulfatization

A secondary tachyhydrite [$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O$], formed during kainitization, contains kieserite inclusions and displays a reduced Br/Cl ratio (Kühn, 1969). Exposed tachyhydrite turns into bischofite [$MgCl_2{\cdot}6H_2O$], which also forms in carnallite decomposition, polyhalitization, or around bloedite [$Na_2Mg(SO_4)_2{\cdot}4H_2O$] nests.

Bischofite is not known as a primary marine deposit from any pre-Permian, Triassic, Jurassic, or Paleogene chloridic evaporite sequence. It is unlikely that brine concentration in a multiple set of sylvite beds always stopped short of bischofite saturation; Kühn (1952) found that sylvite will turn into carnallite in the presence of bischofite at any temperature between −21°C and +152.5°C. $MgCl_2$ liberated in carnallite sulfatization and not consumed in a conversion of anhydrite precipitates as bischofite, because of its poor solubility in sulfatic brines. It occurs in many Permian potash beds (containing inclusions of anhydrite and kieserite) in the Zechstein and the Volga depression, in Neogene ones in Sicily (Yarzhemskiy, 1967; Ramberti, 1980), otherwise only where a primary Aptian tachyhydrite has decomposed. As it decomposes at 116°C, it provides an upper limit to temperatures in Permian evaporite basins. Braitsch (1971) considered it to be mainly of secondary origin. However, in artificial pans, bischofite forms at a density of 1.353 g/cm^3 (Bhat et al., 1979), where aragonite and gypsum precipitation in preconcentrator pans has been permitted to deplete available calcium and most sulfate ions.

GROWING SODIUM SUPPLY

By dissolving some halite, the brine changes from an initial Ca-SO_4- to a $CaCl_2$-Na-SO_4-composition and that leads to further alterations in form of nests and nodules of Na-Mg-sulfate minerals of progressively greater rarity. The growing Na-enrichment (Table 2) first generates bloedite nests in the kainite caprock (d'Ans and Kühn, 1960; Borisenkov, 1968). Aphthitalite, the only K-Na-sulfate mineral, forms nests where ammonia is present; it occurs in Transcarpathian Neogene evaporites either in picromerite or with syngenite and is usually stained red.

Warm brines convert bloedite or langbeinite at their base to loeweite as a retrograde diagenesis (Harville and Fritz, 1986), the temperature increasing with Mg-content of the brine. Loeweite decomposes at higher temperatures to vanthoffite nodules (Braitsch, 1971). Neither loeweite nor vanthoffite are ever stained red. A NaCl-saturated solution free of potassium alters vanthoffite to dansite. Both loew-

TABLE 2

Na-enrichment during sulfatization

Mineral:	Aphthitalite	Bloedite	Loeweite	Vanthoffite	Dansite	Thenardite	Glauberite
Formula:	$Na_2SO_4\cdot$ $3K_2SO_4$	$Na_2SO_4\cdot$ $MgSO_4\cdot 4H_2O$	$6Na_2SO_4\cdot$ $7MgSO_4\cdot 15H_2O$	$3Na_2SO_4\cdot$ $MgSO_4$	$3NaCl\cdot$ $9Na_2SO_4\cdot MgSO_4$	Na_2SO_4	$Na_2SO_4\cdot$ $CaSO_4$
Na wt.%	9.73	13.75	14.04	25.24	30.67	32.37	16.53

eite and vanthoffite decomposition generates more kieserite precipitation.

Thenardite and glauberite nests indicate that chlorides have become exhausted. Glauberite is present in Triassic salts of both the Lorraine and southern Germany, where it replaces halite or polyhalite (Dana, 1951).

DESULFATIZATION

Desulfatization is brought about by $CaCl_2$-brines. $CaCl_2$ is more than twice as soluble as either $MgCl_2$ or $MgSO_4$. $CaCl_2$-brines are derived from kainitization or langbeinitization of carnallites, from the decomposition of tachyhydrite, or as seepage from surrounding formation waters.

After extensive sulfatization of primary potash beds exhausts the sulfate ion content, the diffusing meteoric waters are converted to a brine that largely contains only $CaCl_2$, as the chloride liberated in carnallite decomposition entraps inflowing calcium ions. Compacted salt beds are impermeable to aqueous fluids; a later soaking of sulfatized potash beds in $CaCl_2$-rich formation waters meets with the difficulty of finding a passage through which these waters could have percolated.

Reactions of a $CaCl_2$-rich brine with sulfatized minerals are able to initiate a retrograde decomposition, converting the K-Mg-sulfate minerals to a second generation of chloride minerals. All the reactions are endothermal and cause large increases in volume of daughter minerals and thus a convolute bedding. They result in secondary anhydrites, polyhalites, sylvites, carnallites, or even kieserites. The sylvites and carnallites are whitish, resembling primary precipitation in a covered brine. The minerals are not stained by hematite needles, because the recrystallization expels foreign inclusions.

Kainite yields a second generation of carnallite and anhydrite, at temperatures above 72.5°C a second generation of sylvites. Picromerite decomposes to carnallite, sylvite and anhydrite, polyhalite either to sylvite and anhydrite or carnallite, sylvite and anhydrite. Syngenite can produce sylvite and anhydrite. Langbeinite decomposition to carnallite and anhydrite is rare because it requires a 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 $CaCl_2$-brines would liberate $MgCl_2$ (Döhner and 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.

CONCLUSIONS

Only Permian and Neogene potash beds are massively sulfatized. A fluctuating sea level can be deemed to have briefly exposing the gypsum shelves. Their erosion supplied sulfatic brines that seeped through uncompacted clay laminae into potash beds. A progressive sulfatization of potash beds can be explained in terms of a gradually increasing dissolution of gypsum or anhydrite on marginal shelves, and the progressive addition of more halite near the shelf margin. The brine changed from a Ca-SO_4- to a $CaCl_2$-Na-SO_4-composition. Enough $CaCl_2$-brine was eventually generated to desulfatize portions of the deposit, limited by the drastic volume increases that such an alteration requires. It follows that the sulfatization of Permian and Neogene potash deposits has occurred in each case within a very short period after primary deposition. No alteration resulted from an exposure of portions of the gypsum shelves after compaction had eliminated the accessibility of the potash beds. In other periods of earth history, occasional nests of sulfatized minerals formed where meteoric waters were able to gain local access to carnallite beds.

The history of alterations is difficult to unravel because the present mineralogy depicts effects of only the last brine that percolated by. However, the sulfatization of marine potash seams is probably due to meteoric runoff dissolving gypsum and halite on basin margins before accessing potash beds. Sulfatization and desulfatization thus entirely represent a continental influence on marine precipitates.

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