Salty Matters

John Warren - Monday August 10, 2015

Potash bitterns and Phanerozoic marine brine evolution (1 of 2)

Introduction

The significance of evaporites as indicators of the chemical evolution of seawater across time and in relation to potash bitterns is considered in the next two Salty Matters articles. This article focuses on Phanerozoic seawater chemistry, where actual salts are widespread and the proportions of potash bittern salts are a useful pointer to the chemical makeup of the mother brine. Throughout both articles, the term "lower salinity" refers to marine brines with salinities between one and ten times that of ambient seawater. The second article considers seawater chemistry based on Precambrian evaporites, where much of the evidence of mother brine composition comes from salt pseudomorphs, rather than remnants of actual salts. In the second article we shall see that atmospheric conditions in the Early Precambrian were reducing and hotter than today, so that seawater was more saline, warmer, anoxic, with higher levels of calcium and bicarbonate compared to Phanerozoic seawater. Gypsum (CaSO4.2H2O), which requires free sulphate, was a rare precipitate during concentration of Archean seawater. Changing atmospheric proportions of CO2, CH4 and O2 meant sodium carbonate salts were significant lower-salinity early Archean marine-brine precipitates. Yet today, sodium carbonate salts, such as trona (NaHCO3.Na2CO3), nahcolite (NaHCO3) and shortite (2CaCO3.Na2CO3) cannot precipitate from a brine with the ionic proportions of modern seawater. The presence of sodium carbonate salts in any evaporite succession across the Phanerozoic is a reliable indicator of a nonmarine mother brine (Figure 1).

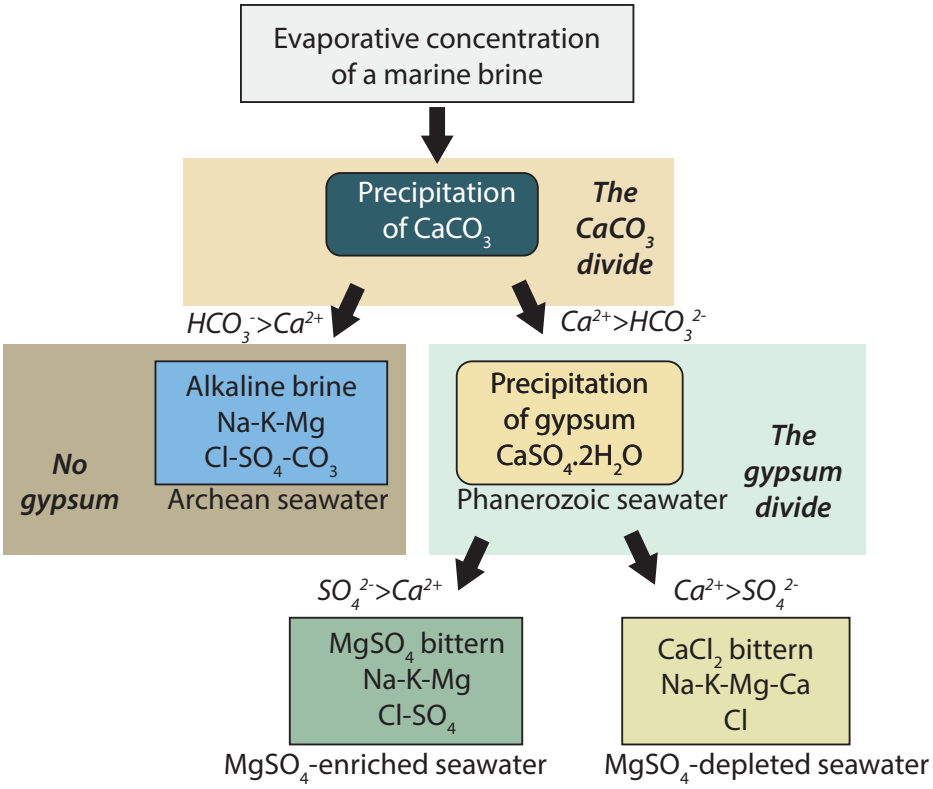

Figure 1. Chemical divides and the evolution of three major marine brine types across deep time.

A Phanerozoic dichotomy: evolving marine potash bitterns

Consistently across the last 550 million years, halite and gypsum (mostly converted to anhydrite in the subsurface) are the dominant lower-salinity marine salts. But potash-bittern evaporite associations plotted across the same time framework define two end-members (Figure 1):

1) Sulphate-enriched potash deposits, with ores typically composed of halite (NaCl) with carnallite (MgCl2.KCl.6H2O) and lesser sylvite (KCl), along with varying combinations of MgSO4 salts, such as polyhalite (2CaSO4.MgSO4.K2SO4.H2O), kieserite (MgSO4.H2O) kainite (4MgSO4.4KCl.11H2O) and langbeinite (2MgSO4. K2SO4); and

Phanerozoic seawater fluctuates between waters enriched in MgSO4 and waters depleted in MgSO4

2) Sulphate-depleted potash deposits are composed of halite with sylvite and carnallite, and entirely free or very poor in the magnesium-sulphate salts. The sulphate-depleted association typifies more than 65% of the world's exploited Phanerozoic potash deposits. Sylvite ores with this association have properties that are easier to process cheaply (Warren 2016; see also blog 4 of 4 in the Salty Matters Danakhil articles).

The sulphate-enriched group of ancient potash salts contains a bittern mineral suite predicted by the evaporation and backreaction of seawater with proportions similar to modern marine brine. In contrast, the sulphate-depleted group of bittern salts must have precipitated from Na-Ca-Mg-K-Cl brines with ionic proportions quite different from that of concentrated modern seawater. The separation between the two bittern associations is defined by brine evolution across the gypsum divide. That is, once gypsum (CaSO4.2H2O) and halite (NaCl) have precipitated in the lower salinity spectrum, are the remaining brines enriched in sulphate or calcium (Figure 1)? The greater suitability for potash utilisation of the sulphate depleted bitterns makes understanding and hence predicting occurrences of the sulphate-depleted association in time and space a useful first-order potash exploration tool.

Why the dichotomy?

In the older literature dealing with Phanerozoic salt chemistry, MgSO4-depleted potash evaporites were often explained as diagenetically-modified marine evaporite brines, thought to result from backreactions during burial diagenesis of normal marine waters (Borchert, 1977; Dean, 1978; Wilson and Long, 1993). If so, then the mother seawater source across the Phanerozoic had ionic proportions like those of today, but diagenetically altered via; a) dolomitisation, b) sulphate-reducing bacterial action, c) mixing of brines with calcium bicarbonate-rich river water, or d) rock-fluid interaction during deep burial diagenesis. As another option, Hardie (1990) suggested MgSO4-depleted potash bitterns formed by the evaporative concentration of sulphate-depleted nonmarine inflow waters seeping into an evaporite basin via springs and faults. Such springs were sourced either from CaCl2-rich hot hydrothermal brines or via cooling of deep basinal brines. Such fault-fed deeply-circulating CaCl2 brines source the various springs feeding the Dead Sea, the Qaidam Basin, the Salton Sea and the Danakil Depression. In all these cases, the elevated salinities of inflow waters are related, at least in part, to the dissolution of buried evaporites. Upwelling of brines in these regions is driven either by thermally-induced density instabilities, related to magma emplacement, or by the creation of tectonically-induced topographic gradients that force deeply-circulated basinal brines to the surface. Ayora et al. (1994) demonstrated that such a deeply-circulating continental Ca–Cl brine system operated during deposition of sylvite and carnallite in the upper Eocene basin of Navarra, southern Pyrenees, Spain.

Today, a more widely accepted explanation for SO4-enriched versus SO4-depleted Phanerozoic potash bitterns, is that seawater chemistry has evolved across deep time. Background chemistry of the marine potash dichotomy is simple and can be related to brine evolution models published by Hardie more than 30 years ago (Hardie, 1984). He found that the constituent chemical proportions in the early stages of concentration of any marine brine largely controls the chemical makeup of the subsequent bittern stages. These ionic proportions control how a brine passes through the lower salinity CaCO3 and gypsum divides (Figure 1). That is, a marine brine's bittern make-up is determined by the ionic proportions in the ambient seawater source. It determines the carbonate mineralogy during the precipitation of relatively insoluble evaporitic carbonates (aragonite, high-magnesium calcite, or low-magnesium calcite) which in turn controls its constituent chemistry as it attains gypsum saturation. These two stages are called the CaCO3 and gypsum divides. Hence, the chemical passage of a bittern is controlled by the ionic proportions in the original ambient seawater. The CaCO3 divide kicks in when a concentrating seawater brine attains a salinity around twice that of normal seawater (60‰). The gypsum divide occurs when brine concentrations are around 4-5 times that of normal seawater (140-160‰). Normal seawater has a salinity around 35-35‰ and the various potash bittern salts precipitate when concentrations are around 40-60 times that of the original seawater (Figure 2 – lower part).

As seawater concentrates and calcium carbonate mineral(s) begin to precipitate at the CaCO3 divided then, depending on the relative proportions of Ca and HCO_3 in the mother seawater, either Ca is used up, or the HCO3 is used up. If the Ca is used up first, an alkaline brine (pH>10) forms, with residual CO3, along with Na, K, SO4 and Cl, but no remaining Ca (Figure 1). With ongoing concentration this brine chemistry will then form sodium bicarbonate minerals, it cannot form gypsum as all the Ca is already used

MgSO4 salts in a marine potash ore means increased processing costs

Current seawater is enriched in MgSO4 and there are no economically significant marine potash deposits known anywhere in Quaternary-age sediments

up. Such an ionic proportion chemistry likely defined oceanic waters in the early Archaean but is not relevant to seawater evolution in the Proterozoic and Phanerozoic, as evidenced by widespread gypsum (anhydrite) or pseudomorphs in numerous post-Archean marine-evaporite basins. At higher concentrations, early Archean marine brines would have produced halite and sylvite bittern suites, but with no gypsum or anhydrite (Figure 1).

If, instead, HCO3 is used up during initial evaporitic carbonate precipitation, as is the case for all Phanerozoic seawaters, the concentrating brine becomes enriched in Ca and Mg, and a neutral brine, depleted in carbonate, is formed. Then the ambient Mg/Ca ratio in a concentrating Phanerozoic seawater will control whether the first-formed carbonate at the CaCO3 divide is aragonite (Mg/Ca>5) or high-magnesium calcite (2>Mg/Ca>5), or low-Mg calcite(Mg/Ca>2). The latter Mg/Ca ratio is so low it is only relevant to concentrating Cretaceous seawaters. Elevated Mg/Ca ratios favouring the precipitation of aragonite over high Mg-calcite typify modern marine seawater brines, which have Mg/Ca ratios that are always >5 (Figure 2). At lower salinities, modern marine brines are Na-Cl waters that with further concentration and removal of Na as halite evolve in Mg-SO4-Cl bitterns (Figure 2)

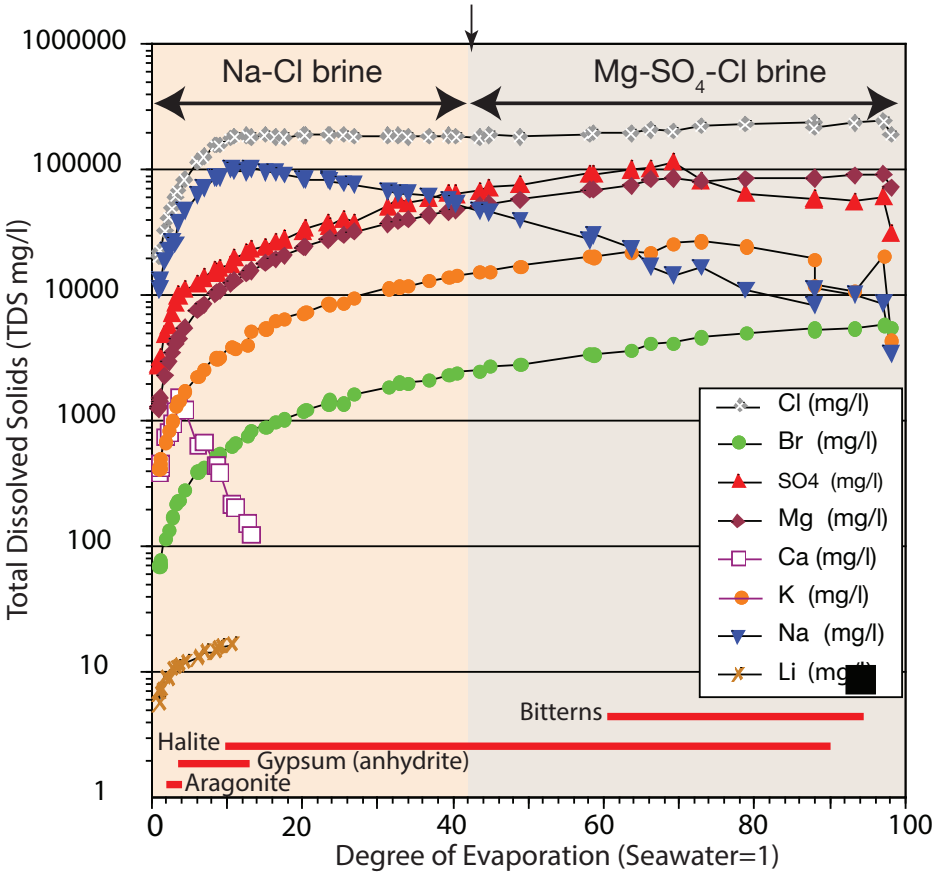

Figure 2. Changes in ionic proportions due to sequential precipitation of aragonite, gypsum, halite and bittern salts as modern seawater is evaporated to 100 times its original concentration (in part after McCaffrey et al. 1987)

The next chemical divide reached by concentrating marine Phanerozoic brines (always depleted in HCO3 at the carbonate divide) occurs when gypsum precipitates at around 4-5 times the concentration of the original seawater (Gypsum divide in Figure 1). As gypsum continues to precipitate, either the Ca in the brine is used up, or the SO4 in the brine is used up. If the Ca is depleted, a calcium-free brine rich in Na, K, Mg, Cl, and SO4 will be the final product and the diagnostic bittern minerals will include magnesium sulphate minerals. This is the pathway followed by modern seawater bitterns. If, however, the sulphate is used up via gypsum precipitation, the final brine will be rich in Na, K, Mg, Ca, and Cl. Such a sulphate-depleted brine precipitates diagnostic potassium and magnesium chloride minerals such as sylvite and carnallite. If calcium-chloride levels are very high, then diagnostic (but uncommon) minerals such as tachyhydrite (CaCl2.2MgCl2.12H2O), and antarcticite (CaCl2.6H2O) can precipitate from this brine. But both these assemblages contain no sulphate bittern minerals, making potash processing relatively straightforward (Warren, 2016). In Phanerozoic marine salt assemblages, tachyhydrite, which is highly hygroscopic, is present in moderate quantities only in Cretaceous (Aptian) marine sylvite-carnallite associations in the circum-Atlantic potash basins and the Cretaceous (Albian) Maha Sarakham salts of Thailand, along with its equivalents in Laos and western China. The CaCl2-entraining bittern mineral assemblages of these deposits imply ionic proportions of Cretaceous seawater differ from those of today.

At lower salinities a hypersaline marine brine is dominated by Na and Cl

At higher salinities modern marine-derived brines evolve into high-density fluids dominated by Mg, SO4 and Cl.

Time	Age (Ma)	*m* (Na)	*m* (K)	*m* (Ca)	*m* (Mg)	*m* (Cl)	*m* (SO4)	*m*(Mg)/*m*(Ca)	Reference
Modern seawater	0	485	11	11	55	565	29	5.2	
Albian-Cenomanian	112 - 93.5	462	11	26 (20-28)	34	565	14 (8-16)	1.3 (1.2-1.7)	Timofeeff et al., 2006
Aptian	121 - 112	416	11	35.5 (32-39)	42	565	8.5 (5-12)	1.2 (1.1-1.3)	"
Pennsylvanian (Desmoinain)	309-305	427	3	24 (20-28)	55	565	12 (8-6)	2.3 (2.0-2.8)	Holt et al., 2014
Mississipian (Asbian-Pendleian)	335-330	436	3	22 (17-26)	55	565	14 (9-17)	2.5 (2.1-3.2)	"
Silurian	445-423	445	11	35 (27-55)	48	565	11 (5-29)	1.4 (1.0- 1.6)	

Table 1. Chemical proportions of selected ancient seawaters based on brine inclusions preserved in halite chevron structures.

Inclusion evidence

Based on a study of brine inclusion chemistry preserved in halite chevrons, from the Early Cretaceous (Aptian, 121.0–112.2 Ma) of the Sergipe Basin, Brazil, the Congo Basin, Republic of the Congo, and the Early to Late Cretaceous (Albian to Cenomanian, 112.2–93.5 Ma) of the Khorat Plateau, Laos and Thailand, Timofeeff et al. (2006) defined a very different chemical makeup for Cretaceous seawater, compared to that of today. Brine proportions in the fluid inclusions in these halites indicate that Cretaceous seawaters were enriched several fold in Ca, depleted in Na and Mg, and had lower Na/Cl, Mg/Ca, and Mg/K ratios compared to modern seawater (Table 1).

Elevated Ca concentrations, with Ca>SO4 at the gypsum divide, allowed Cretaceous seawater to evolve into Mg–Ca–Na–K–Cl brines lacking measurable sulphate. Aptian seawater was extreme in its Ca enrichment, more than three times higher than present day seawater, with a Mg/Ca ratio of 1.1–1.3. Younger, Albian-Cenomanian seawater had lower Ca concentrations, and a higher Mg/Ca ratio of 1.2–1.7. Cretaceous (Aptian) seawater has the lowest Mg/Ca ratios so far documented in any Phanerozoic seawater from fluid inclusions in halite, and lies well within the range chemically favourable for precipitation of low-Mg calcite ooids and cements in the marine realm.

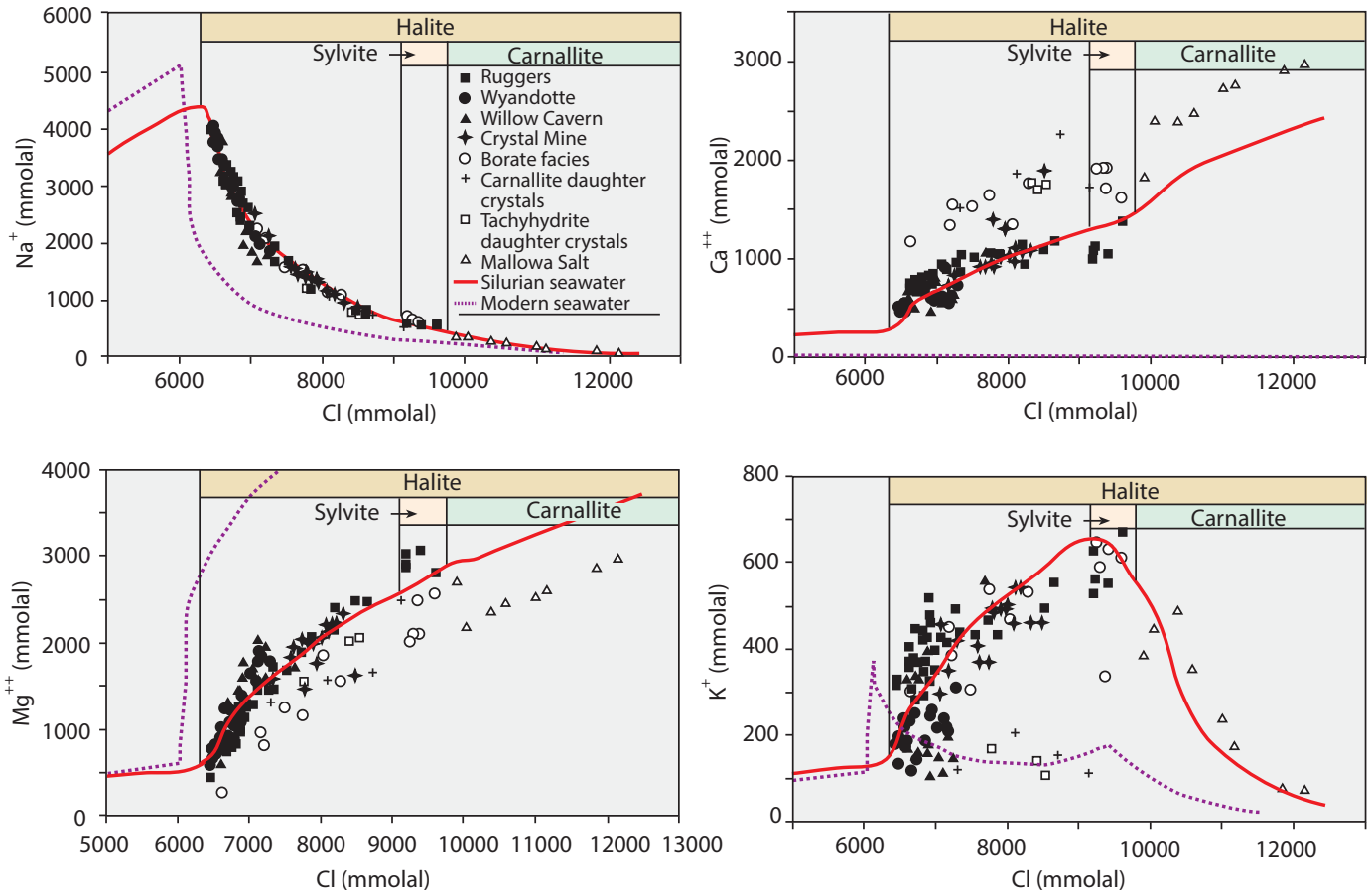

Figure 3. Plots of the major-ion concentrations of the fluid inclusions versus chloride concentrations in Silurian salt with preserved primary structures (after Brennan and Lowenstein, 2002). Closed symbols represent fluid inclusions from pristine marine halites, open symbols represent suspect fluid inclusions from halites associated with potash mineralization or high degrees of evaporation. Only the closed symbols were considered for determining Silurian seawater. The evaporation pathway of modern seawater is shown with a dashed line, and the best-fit evaporation pathway for the Silurian data is shown with a solid line. All the plots show that the evaporation pathways defined by Silurian fluid inclusions are different from the modern seawater pathways. The Silurian fluid inclusions all have an excess of calcium, and no measurable sulphate. Modern seawater evaporated to halite saturation has abundant sulphate, and negligible amounts of calcium. Salts expected to precipitate at given Cl concentrations in evaporated "best-fit" Silurian seawater are indicated along the top of each plot. Sylvite is a primary precipitate from concentrated seawater with these ionic proportions.

Likewise, a detailed analysis of the ionic make-up of Silurian seawater using micro-inclusion analysis of more than 100 samples of chevron halite from various Silurian deposits around the world was published by Brennan and Lowenstein (2002), clearly supports the notion that ionic proportions in the world's Silurian oceans were different from those of today (Figure 3). Samples were from three formations in the Late Silurian Michigan Basin, the A-1, A-2, and B Evaporites of the Salina Group, and the Early Silurian in the Canning Basin (Australia) in the Mallowa Salt of the Carribuddy Group. The Silurian ocean had lower concentrations of Mg, Na, and SO4, and much higher concentrations of Ca relative to the ocean's present-day composition (Table 1). Furthermore, Silurian seawater had Ca in excess of SO4. Bittern stage evaporation of Silurian seawater produced KCl-type potash minerals that lack the MgSO4-type late stage salts formed during the evaporation of present-day seawater and allowed sylvite as a primary precipitate. In a similar fashion, work by Kovalevych et al. (1998) on inclusions in primary-bedded halite from many evaporite formations of Northern Pangaea, and subsequent work using micro-analyses of fluid inclusions in numerous chevron halites (Lowenstein et al., 2001, 2003), shows that during the Phanerozoic the chemical composition of marine brines has oscillated between Na-K-Mg-Ca-Cl and Na-K-Mg-Cl-SO4 types. The former does not precipitate MgSO4 salts when concentrated, the latter does (Figure 3). A recent paper by Holt et al. (2014), focusing on chevron halite inclusions from various Carboniferous evaporite basins, further refined the transition from the Palaeozoic CaCl2 high Mg-calcite sea into a MgSO4-enriched aragonite ocean of the Permo-Carboniferous, so showing CaCl2 oceanic chemistry (and sylvite-dominant bitterns) extend somewhat further across the Palaeozoic than previously thought (Figure 4).

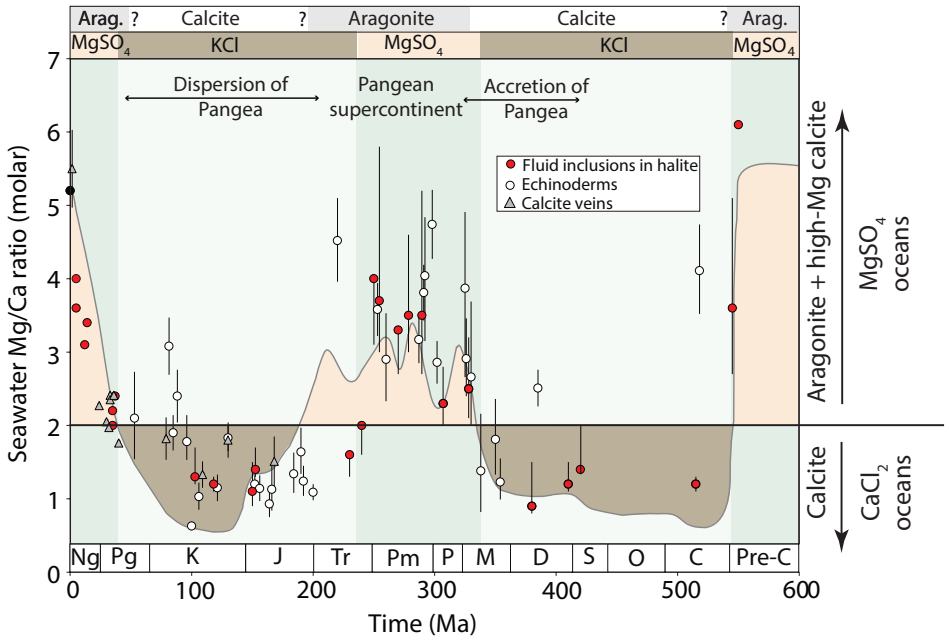

Figure 4. Secular variation in the Mg/Ca ratio of seawater during the Phanerozoic. Red points are Mg/Ca ratios from inclusions in chevron halite, open circles from marine echinoid skeltons and triangles from vein calcites. Horizontal line at Mg/Ca = 2 represents the approximate divide between aragonite + high-Mg calcite (Mg/Ca > 2) and calcite (Mg/Ca < 2) nucleation fields in seawater at 25°C. (after Holt et al., 2014 and references in text).

Phanerozoic ocean sulphate rather than Mg/Ca variations are perhaps more significant in controlling aragonite versus calcite at the CaCO3 divide and the associated evolution of MgSO4-enriched versus MgSO4-depleted bittern suites in ancient evaporitic seaways than previously thought. Bots et al. (2011) found experimentally that an increase in dissolved SO4 decreases the Mg/Ca ratio at which calcite is destabilized and aragonite becomes the dominant CaCO3 polymorph in an ancient seaway (Figure 5). This suggests that the Mg/Ca and SO4 thresholds for the onset of ancient calcite seas are significantly lower than previous estimates and that Mg/Ca levels and SO4 levels in ancient seas are mutually dependent. Rather than variations in Mg/Ca ratio in seawater being the prime driver of the aragonite versus calcite ocean chemistries across the Phanerozoic, they conclude sulphate levels are an equally important control.

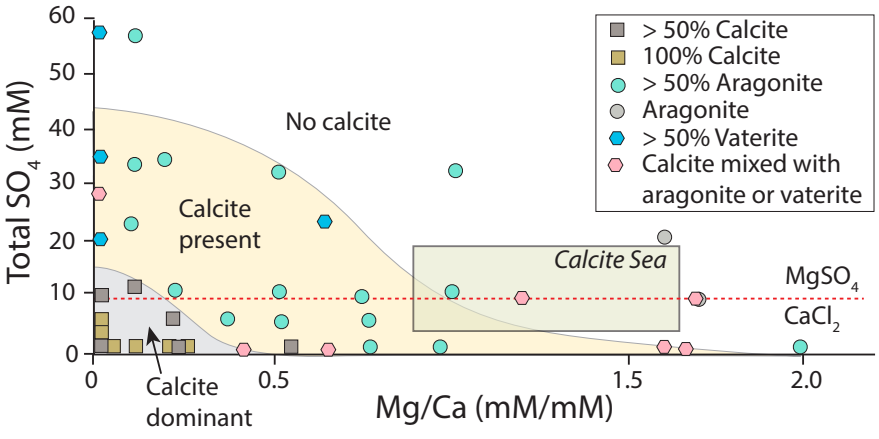

Figure 5. Polymorph distribution as a function of solution chemistry; closed symbols represent dominant CaCO3 polymorph. Yellow shaded area highlights Mg/Ca and SO4 field where calcite was present in solid phase after 48 h between 0% and 50%; green shaded area represents proposed calcite sea concentrations and dashed horizontal line represents switch from KCl to MgSO4 evaporites (after Bot et al., 2011 and contained references).

Cretaceous seawaters are unusual in their elevated CaCl2 contents and low Mg/Ca ratios

Tachyhydrite is a significant secondary component of a number of marine-derived Cretaceous potash deposits

Mechanisms

There is now convincing inclusion-based evidence that the chemistry of seawater has varied across the Phanerozoic from sulphate-depleted to sulphate-enriched, what is not so well understood are the various worldscale processes driving the change (Figure 4). Spencer and Hardie (1990) and Hardie (1996) argued that the level of Mg in the Phanerozoic oceans has been relatively constant across time, but changes in the rate of seafloor spreading have changed the levels of Ca in seawater. This postulate is also supported in publications by Lowenstein et al. (2001, 2003). Timing of the increase of Ca in the world's oceans was likely synchronous with a decrease in the SO4 ion concentration, which at times was as much as three times lower than the present.

Simple mixing models show that changes in the flux rate of mid-oceanic hydrothermal brines can generate significant changes in the Mg/Ca, Na/K and SO4/Cl ratios in seawater. For example, Spencer and Hardie's (1990) model predicts that an increase of only 10% in the flux of mid-ocean ridge hydrothermal brine over today's value would create a marine bittern that precipitates sylvite and calcium-chloride salts, as occurred in the Cretaceous, instead of the Mg-sulphate minerals expected during bittern evaporation of modern seawater. Such Ca-Cl potash marine bitterns correspond to times of "calcite oceans" and contrast with the lower calcium, higher magnesium, higher sulphate "aragonite oceans" of the Permo-Triassic and the Neogene (Figure 3; Hardie, 1996; Demicco et al., 2005).

Ocean crust, through its interaction with hydrothermally circulated seawater, is a sink for Mg and a source of Ca, predominantly via the formation of smectite, chlorite, and saponite via alteration of pillow basalts, sheeted dykes, and gabbros (Müller et al., 2013). Additional removal of Mg and Ca occurs during the formation of vein and vesicle-filling carbonate and carbonate-cemented breccias in basalts via interaction with low-temperature hydrothermal fluids. Hence, changing rates of seafloor spreading and ridge length likely influenced ionic proportions in the Phanerozoic ocean and this in turn controlled marine bittern proportions.

According to Müller et al., 2013, hydrothermal ocean inputs are and the relevant ionic proportions in seawater are driven by supercontinent cycles and the associated gradual growth and destruction of mid-ocean ridges and their relatively cool flanks during long-term tectonic cycles, thus linking ocean chemistry to off-ridge low-temperature hydrothermal exchange. Early Jurassic aragonite seas were a consequence of supercontinent stability and a minimum in mid-ocean ridge length and global basalt alteration. The breakup of Pangea resulted in a gradual doubling in ridge length and a 50% increase in the ridge flank area, leading to an enhanced volume of basalt to be altered. The associated increase in the total global hydrothermal fluid flux by as much as 65%, peaking at 120 Ma, led to lowered seawater Mg/Ca ratios and marine hypercalcification from 140 to 35 Ma. A return to aragonite seas with preferential aragonite and high-Mg calcite precipitation was driven by pronounced continental dispersal, leading to

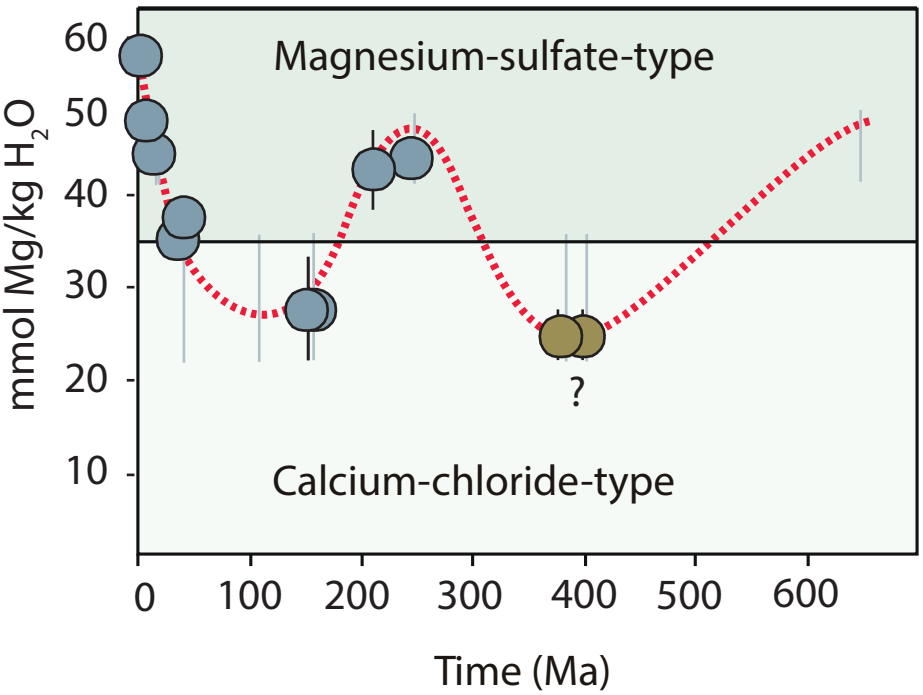

Figure 6. Secular changes in seawater chemistry based on micro-analysis of fluid inclusions in marine halite chevrons and interpreted as tied to levels of shelf dolomite(after Zimmermann, 2000a)

progressive subduction of ridges and their flanks along the Pacific rim.

Holland et al. (1996), while agreeing that there are changes in ionic proportion of Phanerozoic seawater and that halite micro-inclusions preserve evidence of these changes, recalculated the effects of changing seafloor spreading rates on global seawater chemistry used by Hardie and others. They concluded changes in ionic proportions from such changes in seafloor spreading rate were modest. Instead, they pointed out that the composition of seawater can be seriously affected by secular changes in the proportion of platform carbonate dolomitised during evaporative concentration, without the need to invoke hydrothermally driven changes in seawater composition. In a later paper, Holland and Zimmermann (2000) suggest changes in the level of Mg in seawater were such that the molar Mg/Ca ratio of the more saline Palaeozoic global seawater (based on dolomite volume) was twice the present value of 5.

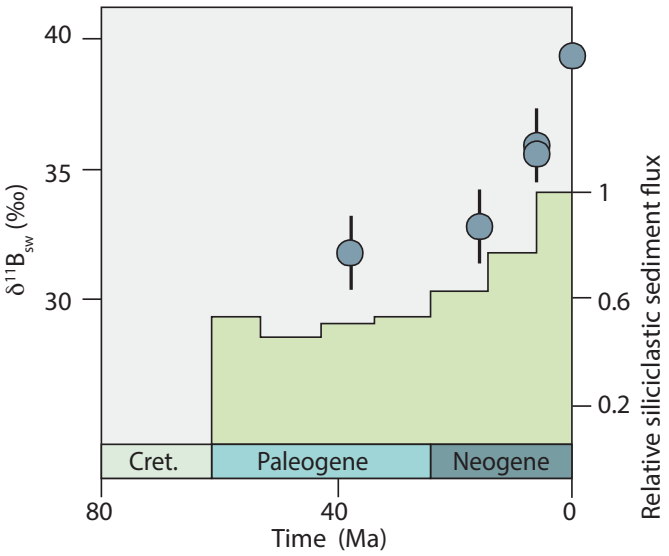

Figure 7. Evolution of boron isotope values in Tertiary-age seawater, based on brine inclusions in chevron halite and plotted against relative siliciclastic input to oceans (after Paris et al., 2010).

Using micro-inclusion studies of halites of varying ages, Zimmermann (2000a, b) has proposed that the evolving chemistry of the Phanerozoic ocean is more indicative of changing volumes of dolomite than it is of changes in the rates of seafloor spreading . Using halite inclusions, she showed that the level of Mg in seawater has increased from ≈38 mmol/kg H2O to 55 mmol/kg H2O in the past 40 million years (Figure 6). This increase is accompanied by an equimolar increase in the level of oceanic sulphate. Over the longer time frame of the Palaeozoic to the present the decrease in Mg/Ca ratio corresponds to a shift in the locus of major marine calcium carbonate deposition from Palaeozoic shelves to the deep oceans, a change tied to the evolution of the nannoplankton. Prior to the evolution of foraminifera and coccoliths, some 150 Ma, the amount of calcium carbonate accumulating in the open ocean was minimal. Since then, a progressively larger portion of calcium carbonate has been deposited on the floor of the deep ocean. Dolomitization of these deepwater carbonates has been minor.

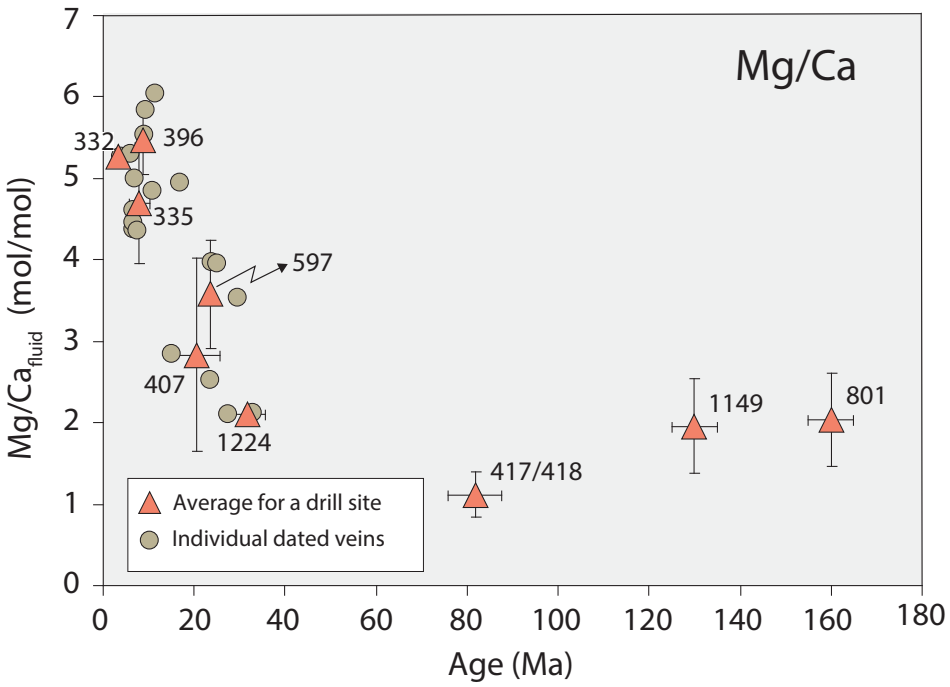

Figure 8. Reconstructed Mg/Ca ratios of past seawater, based on calcium carbonate veins from the ocean crust (after Rausch et al., 2013)

In a study of boron isotopes in inclusions in chevron halite, Paris et al. (2010) mapped out the changes in marine boron isotope compositions over the past 40 million years (Figure 7). They propose that the correlation between $\delta^{11}B_{SW}$ and Mg/Ca reflects the influence of riverine fluxes on the Cenozoic evolution of oceanic chemical composition. Himalayan uplift is a major tectonic set of events that probably led to a 2.5 times increase of sediment delivery by rivers to the ocean over the past 40 m.y. They argue that chemical weathering fluxes and mechanical erosion fluxes are coupled so that the formation of the Himalaya favoured chemical weathering and hence CO2 consumption. The increased siliciclastic flux and associated weathering products led to a concomitant increase in the influx levels of Mg and Ca into the mid to late Tertiary oceans. However the levels of Ca in the world's ocean are largely biologically limited (mostly by calcareous nannoplankton and plankton), so leading to an increase in the Mg/Ca ratio in the Neogene ocean.

In a study of CaCO3 veins in ocean basement, utilising 10 cored and documented drilled sites, Rausch et al. (2013) found for the period from 165 - 30 Ma the Mg/Ca and the Sr/Ca ratios were relatively constant (1.22-2.03 mol/mol and 4.46-6.62 mmol/mol respectively (Figure 8). From 30 Ma to 2.3 Ma there was a steady increase in the Mg/Ca ratio by a factor of 3, mimicking the brine inclusion results in chevron halite. The authors suggest that variations in hydrothermal fluxes and riverine input are likely causes driving the seawater compositional changes. They go on to note that additional forcing may be involved in explaining the timing and magnitude of changes. A plausible scenario is intensified carbonate production due to increased alkalinity input to the oceans from silicate weathering, which in turn is a result of subduction-zone recycling of CO2 from pelagic carbonate formed after the Cretaceous slow-down in ocean crust production rate. However, world-scale factors driving the increase in Mg in the world's oceans over the past 40 million years are still not clear and are even more nebulous the further back in time we look.

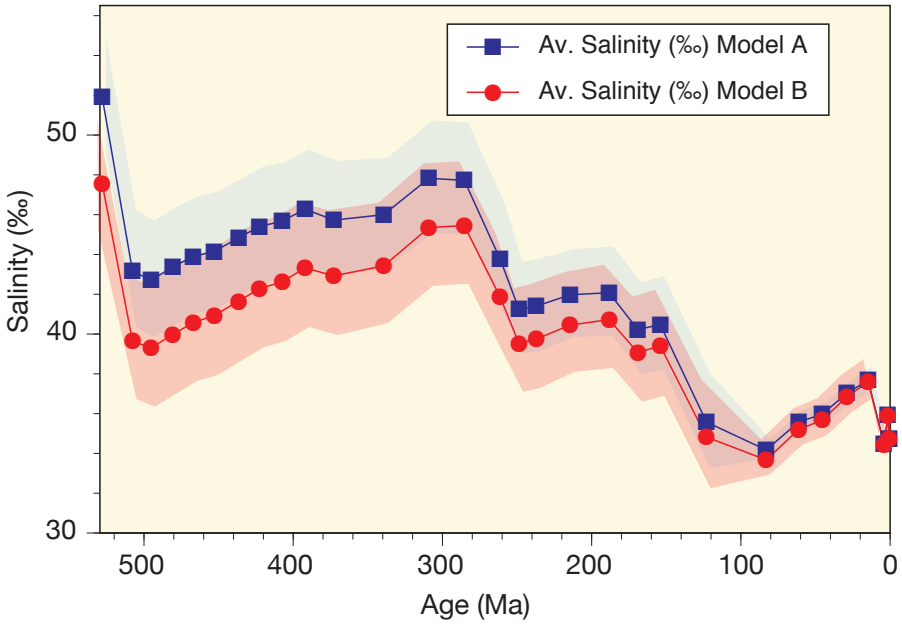

Figure 9. Oceanic salinity changes for the last 500 million years (after Hay et al., 2006).

Changes in Phanerozoic ocean salinity

As well as changes in Mg/Ca and SO4, the salinity of the Phanerozoic oceans shows a fluctuating but overall general decrease from the earliest Cambrian to the Present (Figure 9; Hay et al. 2006). The greatest falls in salinity are related to major extractions of NaCl into a young ocean (extensional continent-continent proximity) or foreland (compressional continent-continent proximity) ocean basins (Chapter 5). Phanerozoic seas were at their freshest in the Late Cretaceous, some 80 Ma, not today. This is because a substantial part of the Mesozoic salt mass, deposited in the megahalites of the circum-Atlantic and circum-Tethyan basins, has since been recycled back into today's ocean via a combination of dissolution and halokinesis. Periods characterised by marked decreases in salinity (Figure 9) define times of mega-evaporite precipitation, while periods of somewhat more gradual increases in salinity define times when portions of this salt were recycled back into the oceans (Chapter 5).

The last major extractions of salt from the ocean occurred during the late Miocene in the various Mediterranean Messinian basins created by the collision of Eurasia with North Africa. This was shortly after a large-scale extraction of ocean water from the ocean to the ice cap of Antarctica and the deposition of the Middle Miocene (Badenian) Red Sea rift evaporites. Accordingly, salinities in the early Miocene oceans were between 37‰ and 39‰ compared to the 35‰ of today (Figure 9). The preceding Mesozoic period was a time of generally declining salinity associated with the salt extractions in the opening North Atlantic and Gulf of Mexico (Middle to Late Jurassic) and South Atlantic (Early Cretaceous) and the earliest Cambrian oceans also had some of the highest salinities in the Phanerozoic. Recently, work by Blättler and Higgins (2014) utilising Ca isotopes studies of selected Phanerozoic evaporites has confirmed the dichotomous nature of Phanerozoic ocean chemistry that was previously defined by micro-inclusion studies of chevron halite (Figure 3).

So what?

In summary, based on a growing database of worldwide synchronous changes in brine chemistry in fluid inclusions in chevron halite, echinoid fragments, vein calcites at spreading centres and Ca isotope variations, most evaporite workers would now agree that there were secular changes in Phanerozoic seawater chemistry and salinity. Ocean chemistries ranged from MgSO4-enriched to MgSO4-depleted oceans, which in turn drove the two potash endmembers What is not yet clear is what is the dominant plate-scale driving mechanism (seafloor spreading versus dolomitisation versus uplift/weathering) that is driving these changes.

In terms of marine bitterns controlling favourable potash ore associations, it is now clear that the variation in ionic proportions in the original seawater controls whether or not potash-precipitating bitterns are sulphate enriched or sulphate depleted. A lack of MgSO4 minerals as co-precipitates in a sylvite ore makes the ore processing methodology cheaper and easier (Warren, 2016). Understanding

the ionic proportion chemistry of Phanerozoic seawater is a useful first-order exploration tool in ranking potash-entraining evaporite basins across the Phanerozoic.

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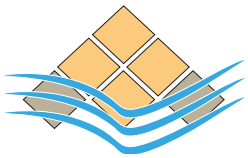

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