Salty Matters

John Warren - Monday August 10, 2015

Seawater chemistry (2 of 2): Pre-cambrian evolution of brine proportions and associated salts

Introduction

We saw in the previous Salty Matters article (part 1 of 2) that ionic proportions of major ions in seawater and oceanic salinity have changed through the Phanerozoic and so influenced the make-up of bittern precipitates once the lower salinity salts (carbonates, gypsum and halite) had precipitated. In the Phanerozoic, seawater was dominantly a Na-K-Mg-Ca-Cl (Ca-rich) brine that changed periodically to a Na-K-Mg-Cl-SO_4 (SO_4-rich) type, as in the modern ocean. This oscillation across 600 million years forces number of questions, for example, do similar oscillations in ocean chemistry extend back across the Precambrian? How consistent is the chemistry of the world's oceans since the early Archean? Does the evaporite evidence in Precambrian sediments support a notion of a primordial reducing atmosphere and/or higher levels of bicarbonate in an early Archean ocean?

Some authors postulate that there have been no significant changes in the major ion proportions in seawater and hence the evaporation mineral series for the past 4 Ga (Morse and Mackenzie, 1998). Others assert that the Archean was dominantly a time of little or no atmospheric oxygen and that ocean waters were reducing anoxic fluids and so sulphate levels were low and sulphide levels high in evaporative marine waters (Krupp et al., 1994). Yet others propose that the bicarbonate to calcium ratio was so high in Archean and Palaeoproterozoic seawater compared to today that all the calcium was used up in widespread abiotic marine aragonite and Mg-calcite precipitates (Sumner and Grotzinger, 2000). In this case trona or nahcolite are likely marine evaporites in the early Archean bitterns (see Figure 1 in part 1). Still others have theorised cyclic changes in oceanic chemistry occurred across much of the Precambrian were similar to those of the Phanerozoic. Such changes were perhaps related to changes in styles and rates of sea floor spreading-hydrothermal circulation in midoceanic ridges (Channer et al., 1997) and the development of tonalitic continents (Knauth, 1998).

Evolution based on brine inclusions

Given that the world's oldest known halites occur in the Bitter Springs Formation in the Amadeus Basin of Australia and that they were deposited some 840 Ma, we can only extend a halite chevron inclusion-based study of ocean chemistry back to that time. These brines were sulphate-depleted, while recrystallised halite from the uppermost Neoproterozoic Salt Range Formation (ca. 545 Ma) in Pakistan, contains solitary inclusions indicating SO_4-rich brines (Kovalevych et al., 2006). This supports a similar late Neoproterozoic ocean chemistry to today, as do proportions derived from primary fluid inclusions from the Neoproterozoic Ara Formation of Oman (ca. 545 Ma). It seems that SO_4-rich seawater existed during latest Neoproterozoic time. In contrast while recrystallised halite from the somehat older Bitter Springs Formation contains brine inclusions that are entirely Ca-rich, implying ambient basin brines and the mother seawater were Ca-rich some 830-840 Mas. These combined data, supported by the timing of aragonite and calcite seas, as preserved in various marine carbonates, suggest that during the Neoproterozoic, significant oscillations of the chemical composition of marine brines, and seawater occurred over the last 250 million years of the NeoProterozoic, and that the end-members were similar to those of the Phanerozoic oceans. It seems that Ca-rich seawater dominated for a substantial period of Late Precambrian time (more than 200 Ma) from 850 Ma, until some 650 Ma, this was replaced by SO_4-rich seawater, returning to Ca-rich seawater at 530 Ma.

Evolution based on pseudomorphs

The detail for much of the remaineder of the Precambrian back to 4 Ga is far less precise than when modelling inclusion chemistries based on actual halites. The oldest documented chevron halite is 850Ma and the oldest bedded anhydrite is 1.2Ga, beyond that, only evaporite pseudomorphs are available to study.

Early Archean seawater precipitated sodium bicarbonate salts along with some halite, but no or very rare gypsum

Ambient seawater was anoxic with elevated bicarbonate due to high levels of atmospheric CO_2

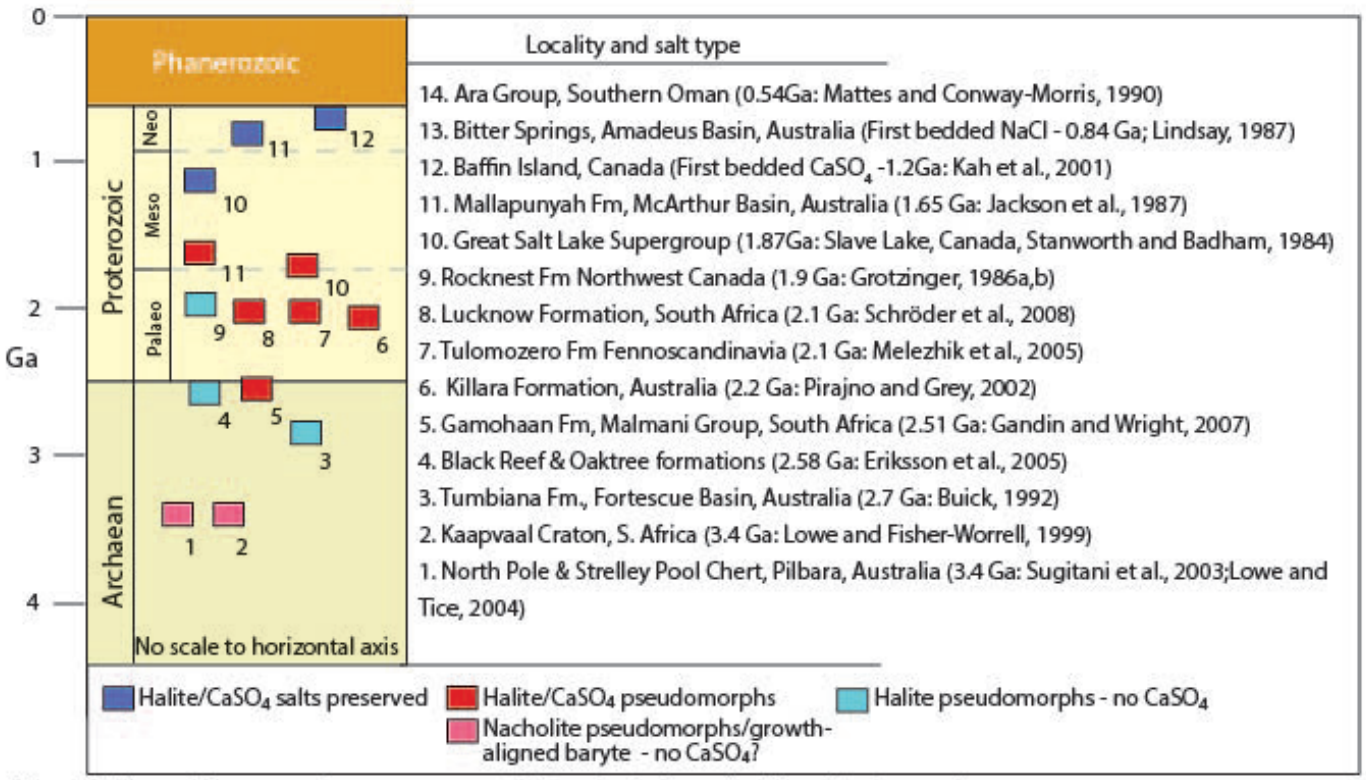

Figure 1. Precambrian evaporite occurrences and mineralogies (compiled from listed sources).

So, beyond the 850 Ma record established by halite inclusions in the Bitter Springs Fm., can other Precambrian evaporites especially the calcium sulphates with a record that extends back patchily to the Mesoproterozoic, give indirect clues as to a chemical scenario for the world's paleo-oceans and brine?

Pseudomorphs, especially of halite hoppers, occur in marine rocks as old as Archean, but are far more common, as are the actual salts, in Proterozoic strata (Figure 1; Warren, 2016). Halite or its pseudomorphs characterise areas of widespread marine chemical sedimentation from the Archean to the present. $CaSO_4$ pseudomorph distribution is more enigmatic. In the 1980s and 1990s, the oldest documented $CaSO_4$ pseudomorphs were thought to cm-sized growth-aligned barytes and cherts in 3.45 Ga metasediments in the Pilbara/North Poleregion of Western Australia. They were interpreted as replacing primary bottom-nucleated gypsum (Figure 2; Barley et al., 1979; Lowe, 1983; Buick and Dunlop, 1990). These barytes and cherts occur in volcaniclastics in association with what are possibly the world's oldest stromatolites (Hofmann et al., 1999; Allwood et al., 2007). Similar growth-aligned baryte crystals, which initially were also interpreted as likely primary gypsum pseudomorphs, occur in the Nondweni greenstones in South Africa, some 3.4 Ga (Wilson and Versfeld, 1994).

Sequences in both regions are now completely silicified or barytised. At the time they were first documented, the recognition of what were considered shallow-water Early Archean gypsum pseudomorphs at North Pole, Pilbara Craton, caused a re-evaluation of models of a totally reducing Archean atmosphere (Dimroth and Kimberley, 1975; Clemmey and Badham, 1982). The presence of free sulphate in surface brines of the Archean world was thought to imply an at least locally oxygenated hydrosphere. Gypsum precipitating in Archean ocean waters also meant calcium levels in the ocean waters were in excess of bicarbonate, as is in the modern oceans. The presence of free-standing gypsum on the seafloor is incompatible with any model of the Early Archean ocean as a "soda lake."

When did marine gypsum evolve?

However, in both the Pilbara and the South African sequences there are no actual calcium sulphate evaporites preserved, onl- growth-aligned crystal textures, now preserved as baryte or chert. Textures in baryte ore from Frasnian sediments in Chaudfontaine,

Gypsum requires the oxidised form of sulphur in the precipitative brine

Oxygenation of the world's oceans becomes obvious in the Mesoproteroiz but is characterised by an early overshoot not a continous gradual rise

Belgium, are near identical to those observed at North Pole, Australia. The Belgian barytes are primary shallow subsea-bottom precipitates with no precursor mineral phase (Figure 2 inset; Dejonghe, 1990). Some workers in the Pilbara feel that the growth-aligned Archean baryte in this region is also a primary seafloor precipitate, formed in the vicinity of hydrothermal vents (Vearncombe et al., 1995; Nijman et al., 1999; Runnegar et al., 2001). As such, it is not secondary after gypsum. A similar hydrothermal discharge model has been developed for aligned barytes in the Barberton Greenstone belt (de Ronde et al., 1994, 1996).

Based on this more recent analysis, levels of Archean sulphate in the world ocean were probably less than a few percent of the current levels and probably remained so until the evolution of a widespread oxygen-producing biota into the Proterozoic (Figures 3, 4; Habicht and Canfield, 1996; Kah et al., 2004). Barium sulphate is highly insoluble in modern oxygenated seawater. To carry large volumes of barium or sulphur (as sulphide) in seawater solution to the precipitation site required anoxic conditions. If the aligned baryte crystals are primary, their formation still requires sulphate to be locally present on the seafloor, at least in the vicinity of the depositional site. A

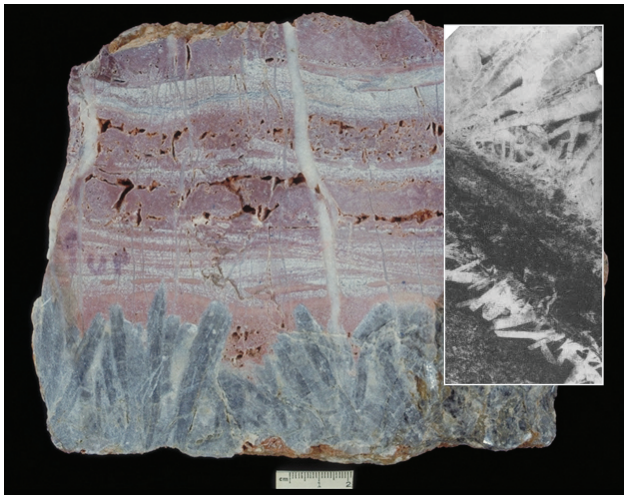

Figure 2. Lower third of this slabbed specimen is composed of growth-aligned baryte (is it a possible replacement of bottom-nucleated evaporite; or, is it a primary baryte precipitate, associated in some areas with silicified marine-derived nahcolite evaporites?). The growth-aligned layer is overlain by current-rippled and silicified volcaniclastic sands. Sample collected from the early Archaean 3.45 Ga Warrawoona Fm. near North Pole, Western Australia. Inset shows Devonian bottom-nucleated baryte from Belgium (see DeJonghe, 1990).

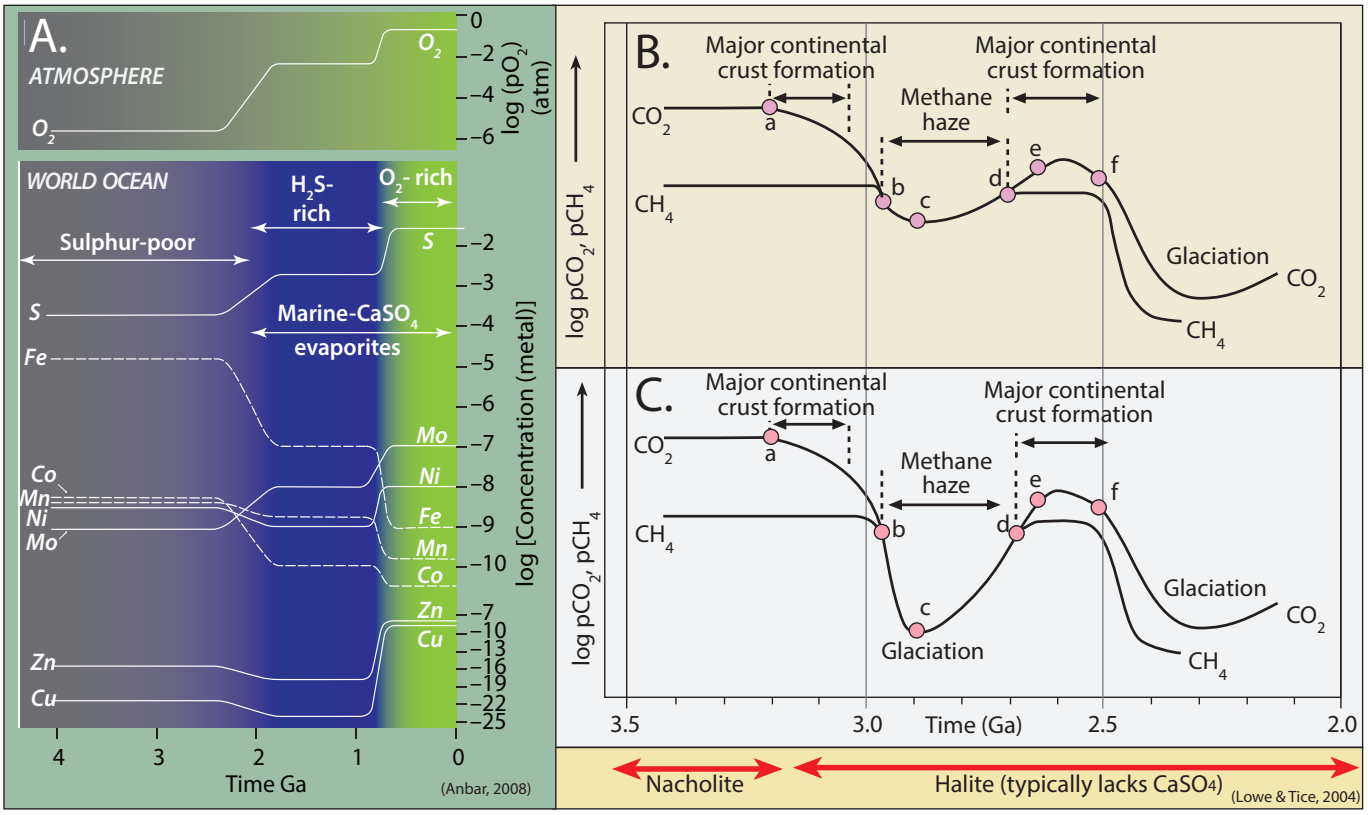

Figure 3. Schematic diagrams showing proposed Earth's oceanic and atmospheric evolution. A) Oxygen, sulphur and metal levels in the world oceans across time. The Archaean ocean was sulphur-poor, an expansion in H2S-rich oceanic regions occurred around 2.4 billion years, which then gave away to fully oxygenated oceans around 800 million years ago. That is, marine-derived sulphate evaporites formed both from mother brines that were sourced in H2S-rich oceans from 2.4-0.8 Ga and from O2-enriched since 0.8 Ga (in part after Anbar, 2008) B) and C) pCH4 and pCO2 evolution during Archaean and earliest Proterozoic, 3.5–2.2 Ga (after Lowe and Tice, 2004). Diagrams show atmospheric evolution B) without and C) with glaciation at 2.9 Ga. High surface temperatures, 70±15°C, were maintained from before 3.5 to at least 3.2 Ga by mixed CO2 and CH4 atmospheric greenhouse with CH4/CO2 << 1. Starting ca. 3.2 Ga (point a), enhanced weathering associated with continent formation began to deplete atmospheric CO2, leading eventually to CH4/CO2 ≈ 1 some. 2.9 Ga (point b) and formation of organic haze, which began to reduce pCH4 along a path defined by CH4/CO2 ≈ 1. Declining pCO2 and pCH4 at 2.9–2.7 Ga resulted in global cooling and possibly glaciation (point c in lower diagram). Reduced weathering and continued tectonic recycling 2.7–2.6 Ga led to increasing pCO2 (line c-d-e), allowing a coupled increase in pCH4 while maintaining CH4/CO2 ≈ 1. When upper limit of CH4 production was reached (point d), CH4/CO2 became <1 and methane haze formation ceased. Enhanced weathering ca. 2.6 Ga (point e) associated with continent building at 2.7–2.5 Ga once again initiated rapid depletion of atmospheric CO2 and decline in surface temperatures. Increased O2 production—associated with latest Archaean spread of oxygenic photosynthetic microbes onto large, shallow-water, continental shelves developed on older (pre–3.0 Ga) blocks of continental crust (point f)—concurrently lowered pCH4, maintaining CH4/CO2 < 1 and preventing the formation of organic haze. Oxygen in this period did not approach levels comparable with the Phanerozoic. Widespread glaciation at 2.4–2.2 Ga resulted from decreasing pCO2 due to weathering and declining pCH4 due to oxidation.

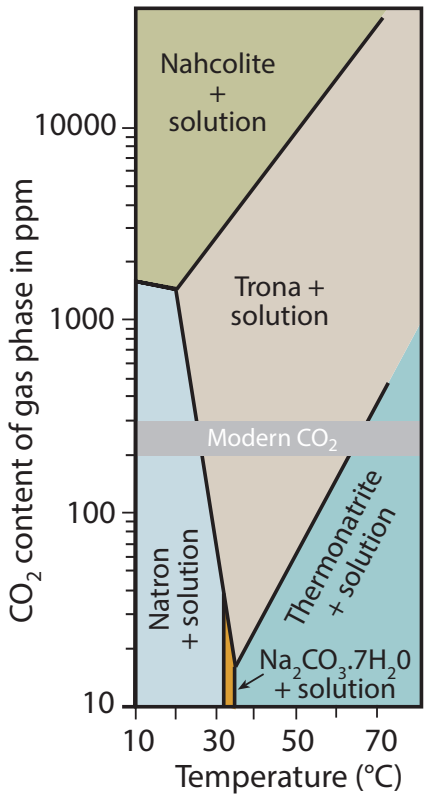

Figure 4. Sodium carbonate phases in equilibrium with a saturated solution as a function of CO2 content of the gas phase and temperature. CO2 content of today's atmosphere is plotted as a grey band (in part after Eugster, 1971).

possible source for local sulphate production in the shallow waters that characterised the North Pole site was shortwave ultraviolet photoxidation of volcanic SO2, indicating an inorganic association (Runnegar et al., 2001). Within barytes in the same 3.47-Ga-old barytes there are microscopic sulphides. These sulphide inclusions show a $\delta^{34}S$ of 11.6‰, possibly indicating microbial sulphate reduction with H2 as electron donor in what was an anoxic seafloor (Canfield et al. 2004; Shen et al., 2009).

According to Nijman et al. (1999) the occurrence of the North Pole barite in sedimentary mounds atop growth faults meant sulphate was locally derived via boiling of escaping hydrothermal vent waters enriched in Ba, Si and sulphide. As these hydrothermal waters vented beneath marine water columns perhaps 50 metres deep, they boiled or violently degassed. Consequent mixing with normally stratified seawater, caused instantaneous oxidization of sulphide into sulphate that then, on cooling, combined with the Ba to precipitate as growth-aligned baryte crystals on the seafloor. Conflicting notions (replaced gypsum versus primary baryte) mean that at this stage of our understanding, the bedded baryte evidence cannot be reliably used to support an evaporite paragenesis of gypsum and so infer an Archean ocean with ionic proportions similar to those of today.

Archean and Proterozoic distributions of gypsum have been further complicated by the misidentification of primary aragonite splays and pinolitic siderite marbles as gypsum replacements (Warren 2016; Chapter 15). When these misidentifications are removed from the record it is obvious that calcium sulphate precipitating directly from Archean seawater to form widespread beds did not occur, and that precipitation of aragonite as thick crusts on the sea floor was significantly more abundant than during any subsequent time in earth history. In contrast to gypsum, halite pseudomorphs are found throughout the Precambrian (Figure 1;e.g. Boulter and Glover, 1986).

Grotzinger and Kasting (1993) argue that high levels of atmospheric CO_2 meant HCO_3/Ca ratios were much higher in the Archean and the Palaeoproterozoic oceans than today. All the calcium in seawater was deposited as marine cementstones and other alkaline earth precipitates well before bicarbonate was depleted and there was no Ca left over to precipitate as gypsum. The early Archean ocean was perhaps a Na–Cl–HCO_3 sea, and not the Na–Cl ocean of today (Kempe and Degens, 1985; Maisonneuve, 1982). This early Archean hydrosphere had a chemistry similar to that found in modern soda lakes like Lake Magadi and Lake Natron (pathway I brines) and hence the term "soda-lake oceans" (see Figure 1 in part 1) This rather different marine brine chemistry would have precipitated halite and trona/nahcolite, not halite/gypsum. It probably meant that if gypsum did ever precipitate from Archean seawater it did so only in minor amounts well after the onset of halite precipitation. Excessive sodium in the ocean may help explain the ubiquity of stratiform albitites in much of the Archean. They would have formed throughout the marine realm as early diagenetic replacements of labile volcaniclastics/zeolites in volcanogenic/greenstone terranes).

Were trona nacholite primary marine salts in the Archean?

A case for nahcolite (NaHCO3) as a primary evaporite, along with halite, in the 3.42 Ga rocks of the Barberton greenstone belt was documented by Lowe and Fisher-Worrell (1999). Sugitani et al. (2003) reported silicified nahcolite (the high CO_2 form of sodium carbonate salts) in ≈3.2 Ga rocks in the northern part of the Eastern Pilbara block, Western Australia. Coarse, upward-radiating, silicified evaporite crystals in the ca. 3.47–3.46 Ga Strelley Pool Chert (Lowe, 1983) show the same habit, geometry, and environmental setting as nahcolite in the Barberton belt and also probably represent silicified $NaHCO_3$ precipitates (Lowe and Tice, 2004).

Marine nahcolite in the 3.5-3.2 Ga sedimentary record is thought to be evidence of surface temperatures around 70±15°C (Figures 3b, c, 4; Lowe and Tice, 2004). Contemporary early Archean nahcolite ($NaHCO_3$) as a primary evaporitic mineral in a very aggressive weathering regime, in the absence of land vegetation, is best explained by a mixed CH_4 and CO_2 atmospheric greenhouse. CH_4/CO_2 ratios were <<1 and pCO_2 was at least 100-1000 times the present value, perhaps as high as several bars (Kaufman and Xiao, 2003). The formation of large areas of continental crust at 3.2-3.0 Ga, including the Kaapvaal and Pilbara cratons, resulted in the gradual depletion of atmospheric CO_2 through weathering and a lack of marine nahcolite since the early Archean. By 2.9-2.7 Ga, declining pCO_2 was associated with climatic cooling and siderite-free soils.

Transitory CH_4/CO_2 ratios of ~1 may have resulted in the sporadic formation of organic haze from atmospheric CH_4, and are reflected in one or more isotopic excursions involving global deposition of abnormally ^{13}C-depleted organic carbon in sediments of this age. Surface temperatures of <60°C after 2.9 Ga may have allowed an increase in the distribution and productivity of oxygenic

photosynthetic microbes (and a decrease in sulphur dependent thermophiles). Eventual lowering of newly formed continental blocks by erosion, reduced loss of atmospheric CO_2 due to weathering, and continued long-term tectonic recycling of CO_2 resulted in rising pCO2 and decreasing CH4/CO2 ratios in the later Archean and eventual re-establishment of a mainly CO_2 greenhouse. Similar events may have been repeated in the latest Archean and earliest Proterozoic, but gradually rising production of O_2 effectively kept CH_4/CO_2 ratios to <<1.

By 2.2-2.0 Ga and perhaps as early as 2.5 Ga, reliable examples of pseudomorphs after primary marine-sourced calcium sulphate first appear in the rock record, but aside from the Karelian beds associated with the Lomagundi Event (LE), widespread stratiform sulphate beds of anhydrite do not appear until 1.2 Ga (Figure 5a). Undeniable $CaSO_4$ nodular and lenticular pseudomorphs are widespread in latest NeoArchean of South Africa and Palaeoproterozoic to Mesoproterozoic sediments of the McArthur Basin, Northern Territory, Australia, and in rocks of Great Slave Lake in northern Canada. For example, in the Malapunyah Formation (1.65 Ga) of the Northern Territory, Australia, the outer portions of numerous decimetre to metre-diameter silicified anhydrite nodules still retain outlines of felted anhydrite laths (pers. obs). The oldest reliable sulphate pseudomorphs after anhydrite and gypsum in Australia come from Palaeoproterozoic cherts in the 2.0-2.2 Ga Bartle Member of the Killara Formation, western Australia (Pirajno and Grey, 2002). These cherts locally retain small amounts of anhydrite (verified by XRD, as well as appearing as highly birefringent flecks in thin sections). Other widespread but younger sulphate pseudomorphs occur in the 1.2 Ga Amundsen Basin in the Canadian Arctic Archipelago. Actual $CaSO_4$ beds outcrop in the 1.2 Ga Society Cliff Formation in Baffin and Bylot Islands of the Canadian Archipelago (Kah et al., 2001, 2004). Sulphate evaporite pseudomophs and nodules in all these Neoproterozoic basins are hosted in sedimentary layers up to tens of metres thick and with lateral extents measured in hundreds of square kilometres. All were laid down in shallow marine, coastal, and alluvial environments under an increasingly oxygenated Meso- to Neoproterozoic atmosphere (Jackson et al., 1987; Walker et al., 1977). After passing from the Archean, by the Mesoproterozoic the hydrosphere contained free sulphate and Ca/HCO_3 ratios were lower, leading to a decrease in molar-tooth, herringbone and other carbonate textures indicative of widespread inorganic calcium carbonate saturation in shallow ocSanic waters (Figure 6). However, oceanic mother brines for these now-widespread calcium-sulphate evaporites were largely H_2S-rich with only moderate levels of oxygen in the atmosphere until some 800 Ma (Figure 3a).

The work of Kah et al. (2004) shows that prior to 2.2 Ga, when oxygen began to accumulate in the Earth's atmosphere, sulphate concentrations in the world's oceans were low, <1 mM and possibly <200 μM (Figure 5). By 0.8 Ga, oxygen and thus sulphate levels had risen significantly. Sulphate levels were between 1.5 and 4.5 mM, or 5–15% of modern values, for more than a billion years after initial oxygenation of the Earth's biosphere some 2.2-2.4 Ga and mid -ocean depth waters were anoxic for most of that time (Brocks et al., 2005). Marine sulphate concentrations probably remained low, no more than 35% of modern values, for nearly the entire Proterozoic. A significant rise in biospheric oxygen, and thus oceanic sulphate, may not have occurred until the latest Neoproterozoic (0.54 Ga), just before the Cambrian explosion, when sulphate levels may have reached 20.5 mM, or 75% of present day levels. This is a time when thick sulphate platforms first characterised the salt basins of Oman, prior to that most actual calcium sulphate is in the form of nodules or relatively thin beds.

Sodium carbonate salts require elevated bicarbonate in excess of Ca in seawater. Nachcolite is the higher temperature sodium carbonate salt in modern trona lakes

Ambient Archean seawater was anoxic with elevated bicarbonate due to high levels of CO_2

Gypsum indicates an oxygen overshoot in the Mesoproterozoic Lomagundi Event

In a refinement of the sulphate model, Bekker and Holland (2012) note that free sulphate bottom-nucleated sulphate evaporites and not just pseudomorphs were present during the Lomagundi Event (2.22 to 2.06 Ga), and then became relatively scarce once more until some 1.2 Ga. For example, there is a 200 m thick stratigraphic interval of sulphate evaporites of Lomagundi-age, preserved in a shallow-water open-marine siliciclastic and carbonate succession (Lower Jatuli informal group) of Karelia, Russia (Morozov et al., 2010). The Lomagundi Event defines the most extreme and longest lasting isotope excursion of carbon in the world's marine carbonate record. Bedded gypsum pseudomorphs in the Malmani Group some 2.5 Ga (Gandin and Wright, 2007; Eriksson and Warren, 1983) implies that elevated oceanic sulphate levels that typify the Lomagundi Event may have extended a little further back in time, at least locally (Figure 5).

At the same time as the Lomagundi event, the average ferric iron to total iron (expressed as $Fe_2O_3/\Sigma Fe_{|Fe2O3|}$) ratio of shales increased dramatically. At the end of the Lomagundi Event (LE), the first economic sedimentary phosphorites were deposited, and the carbon isotope values of marine carbonates returned to ≈0.0‰VPDB (Figure 2.50). Thereafter marine sulphate evaporites and phosphorites

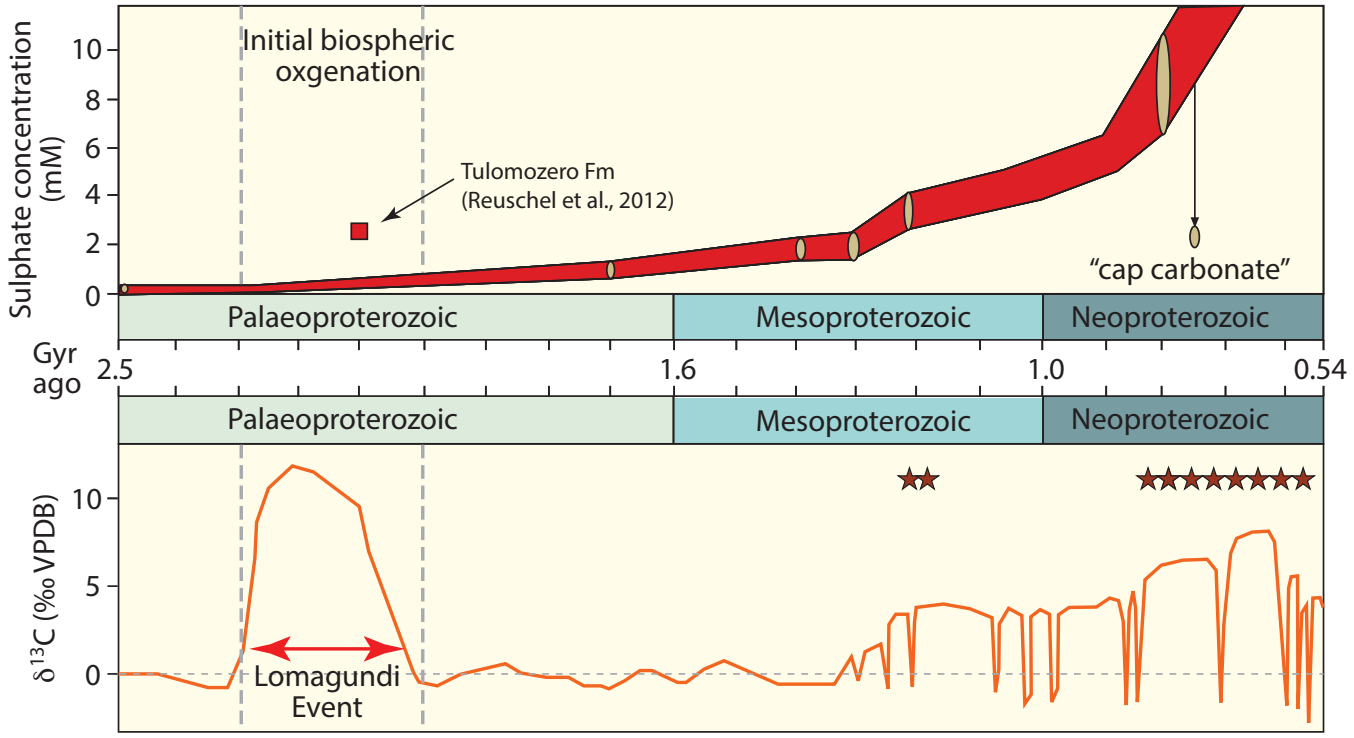

Figure 5. Proterozoic marine sulphate concentrations. Filled ovals mark data determinations (in part after Kah et al., 2004). Marine sulphate concentrations probably remained mostly below 2mM until about 1.3 Gyr ago (except in the Lomagundi event), rose to, 4.5mM by 1.2 Gyr ago, and possibly as high as 7–10mM by the mid-Neoproterozoic, although near-complete reduction of oceanic sulphate may have occurred during Neoproterozoic glacial intervals (arrow). Increased sulphate concentrations coincide with changes in marine $\delta^{13}C$ associated with biospheric oxygenation and are marked by the appearance of bedded gypsum (stars) in the late Mesoproterozoic and more frequent gypsum deposition in the last two-thirds of the Neoproterozoic.

again became scarce, while the average $Fe_2O_3/\Sigma Fe_{|Fe2O3|}$ ratio of shales decreased to values intermediate between those of the Archean and Lomagundi-age shales.

In support of this notion of an "oxygen overshoot," sulphur isotope work by Reuschel et al. (2012) on the 2.1 Ga dolomitic Tulomozero Fm, which entrains abundant $CaSO_4$ pseudomorphs, concluded that there was a minimum level of 2.5 mM sulphate in the world ocean at that time (Figure 5).

Bekker and Holland (2012) argue the short appearance of sulphate evaporites in Logamundi and the other associated events can be regarded as a ca. 200 Ma "glitch" in the gradual oxidation of the atmosphere–ocean system. It was driven by a positive feedback between the rise in atmospheric O_2, the oxidation of pyrite in rocks undergoing weathering, a decrease in the pH of soil and ground water, and an increase in the phosphate flux to the oceans. This sequence led to a major increase in the rate of organic matter burial, a rise in atmospheric oxygen, a large increase in the $\delta^{13}C$ value for marine carbonates, the deposition of marine evaporites containing gypsum and anhydrite, and the formation of the first commercially important phosphorites. The end of the LE was probably brought about by the weathering of sediments deposited during the LE.

In yet another proposal of hydrosphere-atmosphere evolution, Huston and Logan (2004) argue that the presence of relatively abundant bedded sulphate deposits before 3.2 Ga (as the contentious Archean barytes and chert mentioned earlier) and after 1.8 Ga (as $CaSO_4$ salts), and the peak in banded iron formation abundance between 3.2 and 1.8 Ga, and the aqueous geochemistry of sulphur and iron, when taken together suggest that the redox state and the abundances of sulphur and iron in the hydrosphere varied widely during the Archean and Proterozoic. They propose a layered hydrosphere prior to 3.2 Ga in which sulphate was enriched in an upper oceanic layer, whereas the underlying layer was reduced and sulphur-poor. The sulphate was produced by atmospheric photolytic reactions with volcanic gases in a reducing atmosphere. Mixing of the upper and lower water masses allowed the banded barytes to form prior to 3.2 Ga and created an ocean chemistry where nahcolite was a marine evaporite. Between 3.2 and 2.4 Ga, decreasing volcanogenesis and sulphate reduction removed sulphate from the upper layer, producing broadly uniform, reduced, sulphur-poor and iron-rich oceans.

Whatever the origin of the early Archean barite and chert, around 2.2 - 2.4 Ga, as a result of increasing atmospheric oxygenation, the flux of sulphate into the hydrosphere by oxidative weathering was greatly enhanced, producing layered oceans, with sulphate-enriched, iron-poor surface waters and reduced, sulphur-poor and iron-rich bottom waters. Gypsum evaporites were increasingly

likely as marine precipitates. The rate at which this process proceeded varied between basins depending on the size and local environment of the basin. By 1.8 Ga, the hydrosphere was relatively sulphate-rich and iron-poor throughout. Gypsum was now a widespread marine evaporite. Variations in sulphur and iron abundances suggest that the redox state of the oceans was buffered by iron before 2.4 Ga and by sulphur after 1.6 to 1.8 Ga (Figure 1).

From then till now

Gypsum in combination with halite was the marine evaporite association from then until now. Seawater was predominantly a Na-Cl±SO_4 ocean. Neoproterozoic stratiform sulphates along with widespread halokinetic halite, occur in the Bitter Springs Formation of the Amadeus basin, central Australia (0.8 Ga), its equivalents in the Officer Basin, the Callana beds of the Flinders Ranges and the younger Infracambrian salt basins of the Arabian (Persian) Gulf (≈0.545 Ga; Wells, 1980; Cooper, 1991; Mattes and Conway-Morris, 1990; Edgell, 1991).

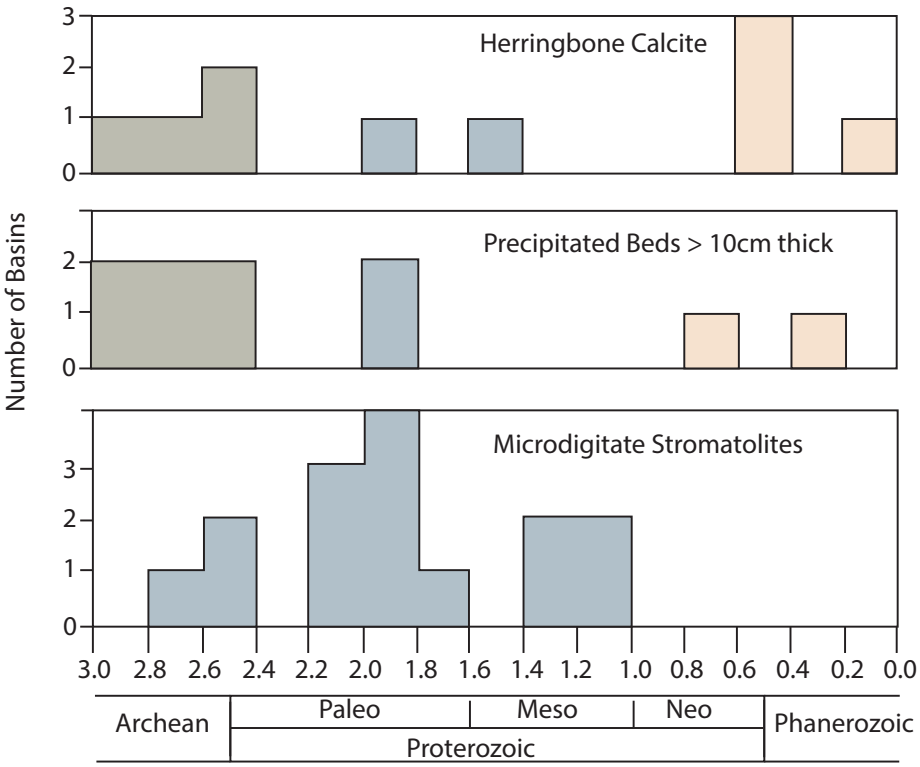

Figure 6. Carbonate precipitation from seawater through time. Brown fill represents basins where the textures are abundant across a range depositional settings. Grey fill represents basins where the textures are present in a limited number of depositional settings. Orange fill indicates textures and minor components with limited extents (after Sumner and Grotzinger, 1996).

The transition to calcium sulphate textures in evaporite pseudomorphs mirrors a marked change in the style of marine carbonates that began around 2.2 to 2.3 Ga when herringbone calcite and precipitated carbonate beds become much less common and the precipitation mode shifted from the seafloor to the water column (Figure 6; Sumner and Grotzinger, 1996, 2000). The boundary also corresponds to the "rusting" of the oceans when oxygen levels became high enough to precipitate widespread banded iron deposits on the seafloor. Microdigitate stromatolites cross this boundary with little effect, suggesting the marked decrease in dissolved iron exerted little influence on them.

The relative scarcity of actual Pre-Phanerozoic salts, not pseudomorphs, especially in the Archean has been used by some to argue that conditions were less favourable for widespread evaporite deposition in the early Precambrian (Cloud, 1972). Others, myself included, feel that the relative scarcity of preserved evaporites in older sequences reflects the greater likelihood of fluid flushing, evaporite dissolution and metasomatism in progressively older rocks. It is likely that oceanic calcium-sulphate evaporites were less common in the Archean, and that sodium carbonates mixed with halite were dominant evaporite salts in the seawater-fed saline giants in appropriate tectonic seepage depressions of the Early Archean. But widespread evaporite deposition from sodium-dominated brines did occur throughout the Archean in large drawdown basins isolated from a surface connection with the ocean. A paucity of preserved bedded evaporite salts in the Precambrian reflects an increased probability of partial or complete evaporite dissolution, remobilization and metasomatism with increasing geological age (see meta-evaporite).

In what is an inclusion study of oldest actual halite, Spear et al., (2014) characterised marine brine chemistry using brine inclusions in the 830 Ma salt of the Browne Formation, Officer Basin, Australia (equiv. to Bitter Springs Fm.). It seems that concentrations of the major ions in these inclusions, except K^+ and possibly SO_4^{2-}, fall within the known range of Phanerozoic seawaters. This ananlysis suggests that mid-Neoproterozoic marine sulphate concentrations were lower (≈90%) than modern values. By the terminal Neoproterozoic, fluid inclusions in halite and evaporite mineralogy from the Khewra Salt of Pakistan and the Ara salt in Oman indicate seawater sulphate levels had risen significantly, to 50%-80% of modern concentrations, which parallels increases in atmospheric and oceanic oxygen.

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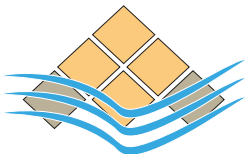

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