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Seawater Chemistry Through Phanerozoic Time

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Keywords

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Abstract

The major ion balance of the ocean, particularly the concentrations of magnesium (Mg), calcium (Ca), and sulfate (SO₄), has evolved over the Phanerozoic (last 550 million years) in concert with changes in sea level and the partial pressure of carbon dioxide (*p*CO₂). We review these changes, along with changes in Mg/Ca and strontium/calcium (Sr/Ca) of the ocean; how the changes were reconstructed; and the implication of the suggested changes for the overall charge balance of the ocean. We conclude that marine Mg, Ca, and SO₄ concentrations are responding to different aspects of coupled tectonic changes over the Phanerozoic and the resulting effect on sea level. We suggest a broad conceptual model for the Phanerozoic changes in Mg, Ca, and SO₄ concentrations along with the seawater ⁸⁷Sr/⁸⁶Sr and sulfur isotope composition.

- Marine concentrations of magnesium, sulfate, and calcium have varied over the last 550 million years in sync with changes in sea level and atmospheric carbon dioxide.
- Seawater chemistry and sea level both respond to supercontinent formation and breakup, age of the ocean floor, and extent of continental shelf area.
- Changes in plate tectonics impact the ocean's chemical balance and the carbon cycle in varied ways, resulting in cyclical changes in key climatic variables over geological time.

INTRODUCTION

pH: a measure of acidity, calculated as $-\log_{10}[\text{H}^+]$; 7 is neutral, <7 is acidic, and >7 is basic; surface ocean pH is 8.2

Inherent to our understanding of the evolution of Earth's surface environment is an understanding of the evolution of the chemical composition of the ocean (Rubey 1951; Holland 1984, 2003). Life began and evolved in the ocean, and, indeed, the presence of liquid water on the planet for the vast duration of Earth history implies the maintenance of conditions habitable for life (Kasting & Catling 2003, Zahnle et al. 2007). The presence of an ocean on our planet means that the majority of carbon (C) at the surface can be in its dissolved forms in the ocean rather than as a greenhouse gas in the atmosphere and that C continually emanating from the deep Earth can be recycled back into it. Over the course of Earth history, many aspects of the chemistry of the ocean have evolved, including the oxidation state, the dominant redox chemistry, the pH, the degree to which it is ventilated and connected with the atmosphere, and the detailed chemical and isotopic composition of its dissolved constituents (Kasting et al. 2006, Jaffres et al. 2007, Gaucher et al. 2008, Haqq-Misra et al. 2009, Scott et al. 2008, Rosing et al. 2010, Halevy & Bachan 2017, Blättler et al. 2018).

The past 550 million years of Earth history (the Phanerozoic eon) is of particular interest because the rocks of this age range contain abundant fossils that document the increasing diversity and evolution of life (Bambach 2006, Alroy et al. 2008). This time period is also represented by extensive accumulations of marine sedimentary rocks on all continents, and those rocks have revealed large-scale cycles in sedimentation patterns that have become a key framework for understanding other global changes (see **Figure 1**; see also the sidebar titled Variations of Global Sea Level). Sedimentary rocks carry with them not only the record of changing life-forms but also the mineralogical and chemical clues to reconstructing past global environments (Heim & Peters 2011, Meyers & Peters 2011, McMahon & Davies 2018). The chemistry of the oceans is one major component of the puzzle of how climate and life have coevolved over Earth history, and the Phanerozoic is the time period where we have the best opportunities for gathering clues that can advance our understanding of the evolution of Earth's surface environment. It is a

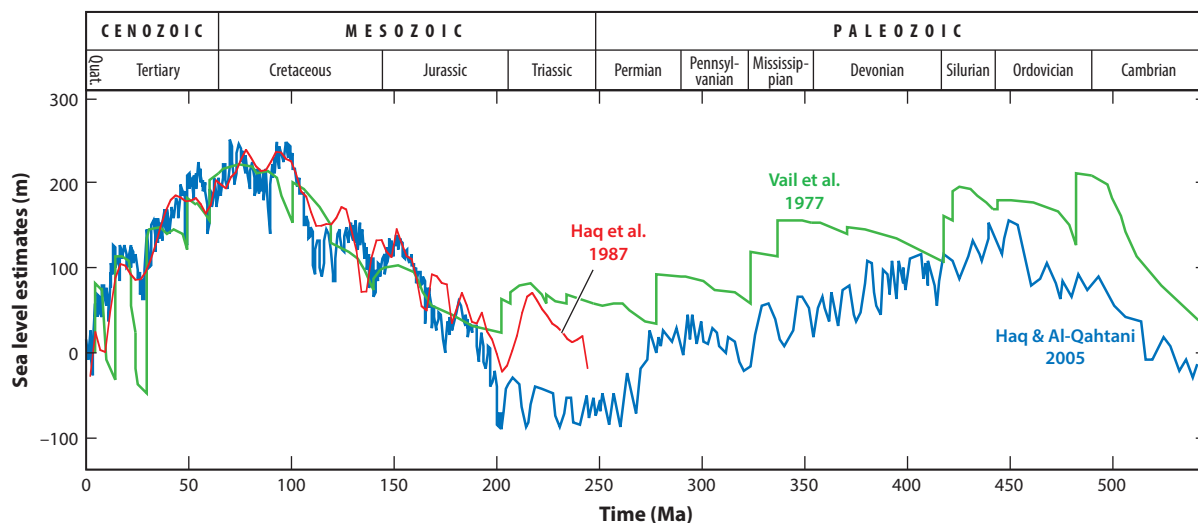


Figure 1

Variations in global sea level over the past 550 million years as inferred from seismic stratigraphy by Vail et al. (1977) and subsequently largely confirmed by further research (Haq et al. 1987). The overall character of this curve resembles that inferred for magnesium/calcium and calcium/sulfate variations in seawater. Figure adapted from Miller et al. (2005) with permission from AAAS.

VARIATIONS OF GLOBAL SEA LEVEL

A profound and obvious characteristic of the continents is that they were more fully covered with marine sedimentary rocks at certain times during the Phanerozoic and less so at other times. This observation suggests that the level of the surface of the oceans has changed systematically over cycles of 100 million years or more, relative to the nominal level of the surface of the continents. Starting in the 1970s, this and other related evidence became more generally accepted as a measure of global sea level (Haq et al. 1987, Hallam 1984). The sea level changes, summarized in **Figure 1**, have been attributed to changes in the shape of the ocean basins, as well as glaciations, which change the volume of ocean water. The former concept led to the inference that variations in the global mid-ocean ridge seafloor generation rate produced the major sea level variations (Gaffin 1987). Berner (1991) used the sea level curve and its implied relation to rates of tectonism to build the first model of the climate history of the Phanerozoic. The pattern inferred for sea level generally corresponds to major cycles in seawater chemistry (Holland 2005).

problem that has been approached several times over the past century, notably by Rubey (1951), who concluded in the president's address to the Geological Society of America that the chemistry of the ocean had not evolved much since early in Earth history. His approach, based on a compilation of the chemistry of rocks that were known to have eroded or formed over time, laid the foundation for decades of further work on both how Earth's chemical surface environment is regulated and how it evolved. Our understanding of this puzzle has grown with our ability to resolve, through geochemical techniques, changes in the chemical composition of sedimentary rocks over time. This was reflected in the seminal book on the subject by Holland (1984).

Of particular interest with regard to the chemical history of the ocean is the mix of elements that are dissolved in the water and make it salty (Pilson 1998). Most of the salt is dissolved sodium chloride (NaCl), but the salt components that receive the most attention in the context of Earth history are less abundant: the cations magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^{+}) and the anion sulfate (SO_4^{2-}). The salinity of the modern ocean is derived 86% from Na and Cl, while Mg, Ca, K, and SO_4 compose the majority of the remaining salt content (Lyman & Fleming 1940, Pilson 1998). The concentrations of these ions in seawater vary only in proportion to that of NaCl, which can be increased by evaporation and decreased by dilution with freshwater. Due to their long residence times, these ions are homogeneously distributed in the modern ocean at constant salinity (Fofonoff 1985). The intriguing and challenging issues involve the extent to which the amounts of these ions in seawater have changed over the long course of Earth history, on timescales of tens of millions of years to hundreds of millions of years. How such variations can be measured, the current understanding of their causes and meaning, and the gaps in both evidence and understanding are the subjects of this review.

The prevailing view is that the salt content of the world's oceans must have evolved over Earth history (Livingstone 1963, Mackenzie & Garrels 1966). The total salt content is assumed to have reached a steady value sometime in the Precambrian and probably has not changed much over the course of the Phanerozoic (Mackenzie & Garrels 1966, Blättler et al. 2018). However, the composition of the salt seems not to be so steady. Cations and anions are added to the ocean from the chemical weathering of rocks on the continents and analogous processes that affect oceanic rocks on the seafloor (Edmond et al. 1979, McDuff & Morel 1980, Walker et al. 1981, Berner et al. 1983, Caldeira 1995, Elderfield & Schultz 1996, Sleep & Zahnle 2001). Cations and anions are removed from the oceans through precipitation of minerals, which is typically mediated by biological activity, and subsequent incorporation into sedimentary rocks forming on the ocean

floor as well as through secondary mineral formation in hydrothermal systems (Edmond et al. 1979, Walker et al. 1981, Berner et al. 1983, Caldeira 1995, Elderfield & Schultz 1996, Sleep & Zahnle 2001). Lithification of marine sediment can be followed by metamorphism and storage in continental crust or subduction back into the mantle. These processes define broad geochemical cycles for the major cations and anions in the ocean (McDuff & Morel 1980, Berner et al. 1983). Although the processes are presumed to be active at all times, there may be subtle imbalances sustained over millions of years, and potentially also feedbacks, that can cause the salt composition of the oceans to oscillate on long timescales.

The sources and sinks of cations and anions to the oceans are linked to the movement of C among various reservoirs at Earth's surface. Chemical weathering of rocks on land supplies both dissolved C, often termed carbonate alkalinity, and cations to the ocean (Berner et al. 1983). This chemical weathering leads to the precipitation and preservation in the ocean of calcium carbonate (CaCO_3) minerals, which form the dominant removal path for C from Earth's surface (e.g., Walker et al. 1981, Raymo & Ruddiman 1992). Chemical weathering of ocean floor rocks also involves the exchange of cations and anions and the sequestering of C as carbonate minerals (Sleep & Zahnle 2001). Our essential understanding is that these processes must have changed and evolved over Earth history, impacting the chemical composition of the oceans.

In terms of Earth's global climate, one ultimate objective is to reconstruct the Phanerozoic history of atmospheric carbon dioxide (CO_2). Proxy measurements of partial pressure of CO_2 ($p\text{CO}_2$) are scarce and have large uncertainties (Cerling 1984, 1991; Royer 2001). Models for Phanerozoic $p\text{CO}_2$ resemble the sea level curve, which is not accidental because sea level is viewed as the master variable that indicates changes in the solid-Earth processes—volcanism, weathering, carbonate sedimentation—that should control atmospheric CO_2 (Berner et al. 1983, McCauley & DePaolo 1997). Insofar as the same processes affect the chemistry of seawater, the major ion chemistry of the ocean should be a sensitive monitor of the processes that control atmospheric CO_2 on long timescales (Sillén 1967, McDuff & Morel 1980, Berner et al. 1983, Berner 2004). However, much of what we know about changes in seawater chemistry, and related changes in atmospheric $p\text{CO}_2$, relies on either uncertain proxies or rather simple models of the long-term C cycle. Independent determination of the chemical history of seawater thus is of prime importance for understanding the evolution of Earth's surface conditions and atmospheric composition (Sillén 1967, McDuff & Morel 1980, Steuber & Veizer 2002). The major focus in this review is on the long timescale shifts in ocean chemistry that are most likely to relate to global tectonics and climate. There are, in addition, other changes that occur on shorter timescales associated with, for example, glacial-interglacial cycles (Stoll & Schrag 1998) and rare events, many associated with mass extinctions (Kump et al. 2009).

Our focus on the major ions Ca, Mg, and SO_4 and to a lesser extent strontium (Sr) stems from their critical roles and properties (Berner & Berner 2012, Sun et al. 2016). Ca is a key biological element, required in the formation of CaCO_3 , that serves as the dominant biomineral used by organisms for the last 550 million years. Ca is added to the ocean through terrestrial weathering of carbonate and silicate minerals and through hydrothermal circulation in oceanic crust, and it is removed through the formation of biogenic and abiogenic CaCO_3 minerals (De La Rocha & DePaolo 2000, Fantle & DePaolo 2005). Mg is the second most abundant cation (to Na) and one of the key elements for tracing the chemical weathering of silicate minerals and the extent of hydrothermal circulation on the seafloor (Mottl & Wheat 1994). The latter process constitutes the dominant removal path for Mg from the ocean due to the formation of highly stable hydroxylated Mg-bearing minerals (Tipper et al. 2006, Higgins & Schrag 2012). Mg removal has also been associated with the formation of dolomite $[\text{Ca,Mg}(\text{CO}_3)_2]$ (Holland & Zimmermann 2000). SO_4 is the second most abundant anion in the ocean (to Cl) and exists in multiple valence states.

Because of the ability of S to change valence states, it has been one of the key redox players over geological time (Halevy et al. 2012). Sr is the most abundant heavier element in seawater. Sr isotopes have been used as a key indicator of the relative importance of terrestrial silicate weathering versus seafloor hydrothermal fluxes to the overall balance of the chemistry of the ocean (Raymo & Ruddiman 1992, McCauley & DePaolo 1997).

As we discuss in this review, evidence for past changes in seawater chemistry must first be established by using indirect (referred to as proxy) measurements of geological materials. While any one proxy may be compromised by a series of assumptions or limitations, through combining multiple proxies, we can reach an emerging consensus on the change in the major ions. Once this emerging consensus is established, the next objective is to understand whether the relative changes in the various ions are internally consistent and the implications for changes in the overall salinity and charge balance of the ocean (Lowenstein et al. 2014).

As proxy records point to semiconsistent changes in the major ion balance, these can then be considered in terms of why the relative amounts of cations or anions may have changed—for example, changes in plate tectonics, the evolution of life, the water cycle, the brightness of the sun, and other related feedbacks (Sillén 1967, McDuff & Morel 1980, Walker et al. 1981, Berner et al. 1983, Raymo & Ruddiman 1992). The other side of this is an understanding of the implications for various processes in sediments and oceanic crust when there is a change in the major ion balance of the ocean. For example, how does changing the major ion balance impact the extent of water-rock interaction during hydrothermal circulation or the relative C fluxes into and out of marine sediments? These processes are discussed in this review, which focuses on the last 500 million years of Earth history, where the record of changes and knowledge of the processes that may have driven these changes are more complete than for earlier periods of Earth history.

mM: millimolar or 10^{-3} mol/L; a unit of concentration commonly used for major and minor ions in the ocean

SEAWATER CHEMISTRY, ALKALINITY, AND CARBON DIOXIDE

The ocean's salinity comprises six major ions: four cations (Na, Mg, Ca, and K) and two anions (Cl and SO_4) (Lyman & Fleming 1940, Pilson 1998). The charge difference between the major cations and major anions is known as total alkalinity, which is given by (Figure 2)

$$\text{TA} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}]. \quad 1.$$

Ultimately, the ocean cannot carry a charge imbalance; therefore, the total alkalinity, roughly 2.2 mM in the modern ocean, comprises largely the dissolved inorganic C species [the bicarbonate

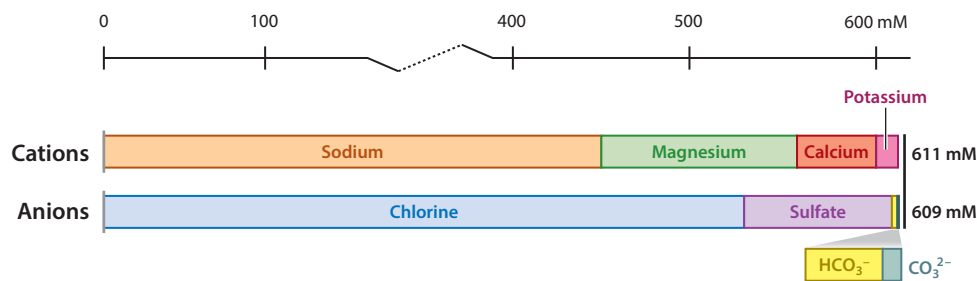


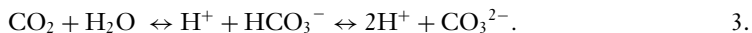
Figure 2

A schematic of the alkalinity, or charge balance, of the oceans. Abbreviations: CO_3^{2-} , carbonate ion; HCO_3^- , bicarbonate ion.

ion (HCO_3^-) and the carbonate ion (CO_3^{2-}) as well as the borate ion $[\text{B}(\text{OH})_4^-]$ and therefore can also be defined as

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] + \text{minor compounds.} \quad 2.$$

These species serve as the primary pH buffer for the oceans over geological time through the chemical equilibrium (Ridgwell & Zeebe 2005, Zeebe 2012)



The goal in trying to resolve changes in the major ion chemistry of the ocean lies in this link among the difference between the cation and anion charge balance, the ocean's alkalinity, and the dissolved inorganic C in the ocean (Zeebe 2012). The alkalinity in the ocean is very small relative to the summed charge balance between the major cations and major anions. But the ocean's alkalinity cannot change dramatically (outside a factor of ~ 2) because the majority of alkalinity is carbonate alkalinity, and major changes in the total alkalinity would quickly change the concentration of atmospheric CO_2 in ways that have not been seen in the geological record, potentially leading to runaway hothouse or icehouse conditions (Ridgwell & Zeebe 2005). For example, if there is a decrease in alkalinity, then the ocean's carrying capacity for C decreases, and Equation 3 shifts to the left, converting the CO_3^{2-} , which carries a double charge (Equation 2), into a HCO_3^- and dissolved CO_2 , and in so doing lowering ocean pH. In an extreme scenario, if alkalinity were to decrease by 1–1.5 mM, then the ocean pH would drop such that the oceans would degas their dissolved inorganic C and the atmospheric CO_2 concentration would rise over 50 times. When there is a change in the concentration of one of the major cations or anions, the marine system compensates through increased preservation or dissolution of CaCO_3 to restore the alkalinity and charge balance of the ocean (Ridgwell & Zeebe 2005, Zeebe 2012).

Furthermore, it has long been thought that the balance of the major cations and anions plays a key role in the type of CaCO_3 polymorph that precipitates, either aragonite or calcite, meaning that as the major ion balance of the ocean changes, there is a significant impact on the ability of organisms to biomineralize (Sandberg 1983, Stanley & Hardie 1999).

HOW ARE CHANGES IN PALEOSEAWATER CHEMISTRY OBTAINED?

The earliest suggestion that there was a change in ocean chemistry over the course of Earth history came from analysis of the primary authigenic minerals, carbonates and evaporates, precipitated from the ocean (Sandberg 1983; Hardie 1991, 1996). These precipitates show cyclical variability, from periods where calcite is the dominant carbonate polymorph and evaporite deposits are dominated by Na-K and chloride salts to periods where aragonite is the dominant carbonate polymorph and evaporite deposits are dominated by Mg- SO_4 salts (Hardie 1996, Stanley & Hardie 1998). Early experimental studies attempting to precipitate different carbonate polymorphs abiotically in the lab showed a strong control of the Mg/Ca ratio of the solution on the CaCO_3 polymorph precipitated, hinting strongly that the observed cyclical changes in ocean mineralogy are linked to changes in the major ion balance of the ocean (Wilkinson & Algeo 1989, Morse et al. 1997, Bots et al. 2011).

This early supposition was confirmed by studies of fluid inclusions in evaporite minerals (see the sidebar Fluid Inclusions in Evaporites) that supported an ocean with higher Mg concentrations and an excess of Ca oversulfate during periods where calcite was the dominant carbonate polymorph. This picture was strengthened through measurements of the trace amount of Mg in preserved carbonate minerals of biomineralizing organisms and abiogenic CaCO_3 veins

FLUID INCLUSIONS IN EVAPORITES

Evaporite minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and halite (NaCl) form from the residual salts left behind as water is removed through evaporation. Because evaporite minerals are highly soluble, they have poor geological preservation; there are only a few time periods in geologic history where there are reliably preserved evaporite deposits. In the late 1980s it was observed that within many evaporite minerals, there are small inclusions of fluid trapped by the precipitating mineral during evaporation. These inclusions, 0.2 mm to 2 mm across, can be opened with a microdrill and the water, or brine, extracted with a micropipette [or scanned directly (Timofeeff et al. 2000)]. The absolute concentration of various elements in that brine will be different from the original parent solution as the concentration increases during evaporation. To determine the chemical composition of the original brine, we assume the potassium (K) and/or bromine (Br) concentration in seawater has not changed over Earth history. This approach is used widely for magnesium (Mg), although it relies on the assumption that no other K-, Mg-, or Br-bearing mineral precipitated during evaporation before formation of the fluid inclusion (Timofeeff et al. 2001).

For calcium (Ca) and sulfate (SO_4) there is more uncertainty because Ca- or SO_4 -bearing minerals precipitate early in evaporite sequences and therefore the concentrations change before fluid inclusions are formed. Typically, fluid inclusions contain either Ca or SO_4 but not both, suggesting which was initially present more than the other. To derive estimates of absolute concentration, we assume that the total concentration of Ca and SO_4 cannot have varied by more than a factor of 2 from the modern value.

in low-temperature hydrothermal and carbonate cements, which showed higher reconstructed fluid Mg/Ca when aragonite was the dominant carbonate biomineral (see the sidebar titled Trace Element Partitioning into Biogenic and Abiogenic Carbonate).

The absolute Mg concentration of the ocean is derived qualitatively from the presence or absence of Mg salts in evaporite successions and semiquantitatively from fluid inclusions (Lazar

TRACE ELEMENT PARTITIONING INTO BIOGENIC AND ABIOGENIC CARBONATE

Calcium carbonate (CaCO_3) minerals provide the primary repository for paleoceanographic information. More recently, it was observed that the other alkaline earth metals, particularly magnesium and strontium, substitute for calcium (Ca) in the carbonate mineral (Nürnberg et al. 1996). The amount of these trace elements in the mineral was initially thought to be solely a function of temperature, which influences partition coefficients. However, more recent work has demonstrated that the composition of the fluid, as well as the rate of mineral growth, greatly impacts the metal-to-Ca ratio in the carbonate mineral. Biogenic carbonate minerals—that is, those that are made by organisms for their skeletons—have been used most extensively for their trace-element ratios. In some ways, organisms exert such a high degree of control on biomineralization that certain compounding effects, such as changes in pH and solution chemistry, may be minimized. However, each organism makes carbonate biominerals in a marginally different way with different degrees of control, and these vital effects confound interpretation.

An alternative to measuring trace elements in CaCO_3 skeletons is measurement in CaCO_3 veins in ancient oceanic crust. Vein carbonate is inorganically precipitated, so much of the ambiguity resulting from vital effects is removed, although there are other analogous issues. The fluid forming CaCO_3 veins is not pristine seawater but rather one that has been altered by heating and interactions with basalt. Corrections can be made for the alteration processes, but there are still substantial uncertainty (Broecker & Yu 2011) and questions regarding equilibrium partition coefficients (see **Figure 4**).

& Holland 1988; Horita et al. 1991, 2002; Kovalevich et al. 1998; Lowenstein et al. 2001, 2003, 2005, 2014; Brennan & Lowenstein 2002; Brennan et al. 2004; Timofeeff et al. 2006). If constant K and bromine (Br) concentration is assumed (and typically assumed to be constant—but see Siemann 2003), the Mg concentration in the hyperevaporated brine and the Mg/K or Mg/Br ratio in the fluid inclusion allow reconstruction of the original seawater Mg concentration (cf. Lowenstein et al. 2014). The Mg/Ca ratio of the ocean can also be estimated from trace element partitioning into biomineralized or abiotically precipitated calcite if independent knowledge exists of the temperature of biomineralization, although this does not yield an absolute number for the Mg concentration of the ocean, just the relative amounts of Mg and Ca (Lear et al. 2000; Dickson 2002, 2004; Ries 2004, 2010; Gothmann et al. 2015).

The absolute Ca concentration of the ocean is derived qualitatively from the presence of Ca salts in evaporite successions (Hardie 1991). In fluid inclusions when there is an excess of Ca relative to SO_4 remaining in the hyperevaporated brine, the Ca concentration is calculated assuming that the ion product of Ca and SO_4 cannot have varied by more than a factor of 2 (higher or lower) from today's value (Lazar & Holland 1988; Timofeeff et al. 2001, 2006; Lowenstein et al. 2003, 2014). The relative amount of Ca to SO_4 has also been qualitatively determined using the range in the Ca isotope composition of Ca salts in evaporite successions (Blättler & Higgins 2014). This latter approach is based on the concept that when Ca is more abundant than SO_4 , there is a smaller range in the Ca isotope composition of the evaporite deposit (Blättler & Higgins 2014). If there is more SO_4 than Ca, then the Ca is quantitatively precipitated as evaporite minerals and there is a larger range in the Ca isotope composition of the minerals from the evolution of the Ca isotope composition of the brine during precipitation.

The SO_4 concentration of the ocean is derived qualitatively from the amount of SO_4 salts within evaporite successions and semiquantitatively from calculating the excess of SO_4 to Ca in fluid inclusions, again assuming that the ion product of Ca and SO_4 cannot have varied by more than a factor of 2 from the modern ocean (Stanley & Hardie 1998, Lowenstein et al. 2014). Modeling approaches have been used to estimate the SO_4 concentration of the ocean and typically use the rate of change in the sulfur (S) isotope composition of the ocean measured in SO_4 minerals deposited in the ocean (Kah et al. 2001). Conceptually, the faster the rate of change is in the S isotope composition of ocean SO_4 , the smaller is the concentration of SO_4 (Kah et al. 2001). While intuitive, these modeling approaches tend to neglect the fact that the rate of S isotope change can be decoupled from the concentration of SO_4 because the isotope composition of the output flux in the S cycle [pyrite (FeS_2)] has a very large range of S isotope composition (Rennie et al. 2018).

An estimate of the absolute Sr concentration of the ocean over Earth history cannot be obtained through fluid inclusions as for Mg, Ca, and SO_4 , but a reasonable understanding of the Sr/Ca ratio has emerged through the measurement of the Sr/Ca ratio in biomineralized and abiotic carbonate minerals (Stoll & Schrag 1998, Lear et al. 2003, Coggon et al. 2010, Gothmann et al. 2015). Assuming, or measuring, a temperature of precipitation using the defined partition coefficient for Sr into the carbonate mineral allows us to calculate the Sr/Ca ratio of the precipitating fluid (Lear et al. 2003, Coggon et al. 2010).

For the other major ions, such as Cl, K, and Na, several assumptions are made. The consensus is that there has been no change to the Cl or K concentration of the global ocean over the last 500 million years (Horita et al. 2002, Demicco et al. 2005; cf. Lowenstein et al. 2014). For Cl this is because the residence time is sufficiently long (>100 million years) that the assumption is that it is difficult to change the amount of Cl in the ocean. For K, this assumption derives from the fact that the K/Br ratio in fluid inclusions has been invariant over time, and there is an assumption that the Br concentration in the ocean has not changed, again due to its long residence time (Horita et al. 2002; Lowenstein et al. 2003, 2014). Na concentrations are typically determined through

a charge balance, assuming that the relative amount of the cations versus anions has not varied much over Earth history (see the next section).

EMERGING CONSENSUS ON SEAWATER CHEMISTRY OVER PHANEROZOIC TIME

The calculated estimates based on fluid inclusions in evaporate minerals for the absolute concentrations of Mg, Ca, and SO_4 in the ocean over the last 500 million years are shown in **Figure 3**. The only estimates of the absolute concentrations of these cations are from the extrapolation from the hyperevaporated inclusions in evaporite minerals, subject to the constraints described above. This yields a picture of the general shape of the relative changes in Mg, Ca, and SO_4 . It is important to note that the samples shown in **Figure 3** come from five time periods where there are evaporites available for sampling, and there are large gaps in the record (Lowenstein et al. 2005, Blättler & Higgins 2014). In general, the relative changes suggest that when Mg and SO_4 concentrations are high, Ca concentrations are low, and vice versa. These changes in major seawater ion concentrations are quite large and must be driven by changes in global geologic processes. The correspondence of the inferred chemical cycles with the reconstructions of global sea level and atmospheric CO_2 is noteworthy.

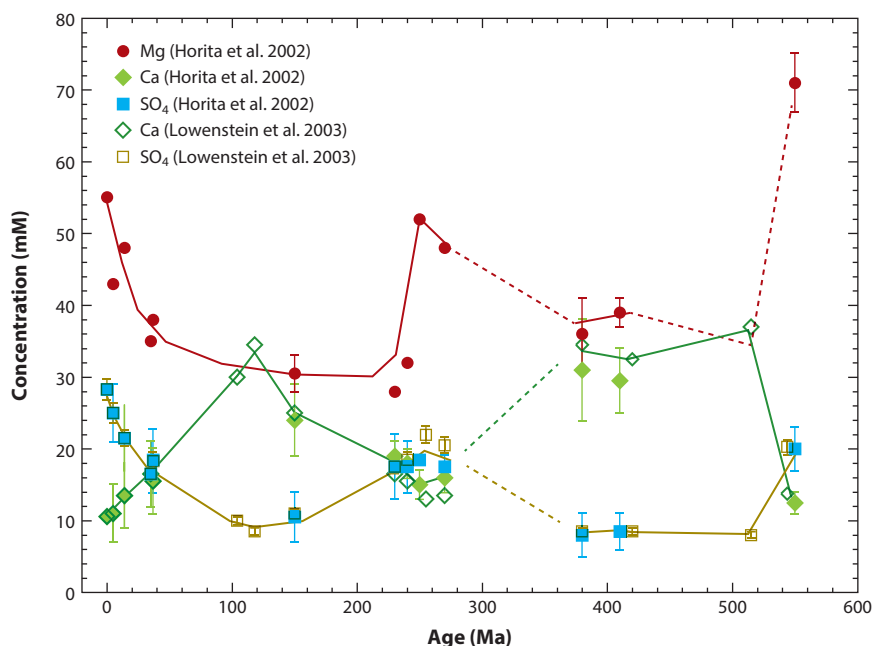


Figure 3

Reconstruction of seawater concentrations of Mg, Ca, and SO_4 reported by Horita et al. (2002) and Lowenstein et al. (2003). The error bars on the values approximate those reported by the authors; the lines are hand-drawn fits to the data. The data mostly cover five limited time periods, each spanning about 40–50 million years. The lines represent modest interpolations and are similar to those used by the authors and by Lowenstein et al. (2014). The gap between 270 and 380 Ma is left here because the concentrations apparently changed substantially during that time period, but the data do not constrain when a similar gap is left for the Mg trend between 410 and 550 Ma. Abbreviations: Ca, calcium; Mg, magnesium; SO_4 , sulfate.

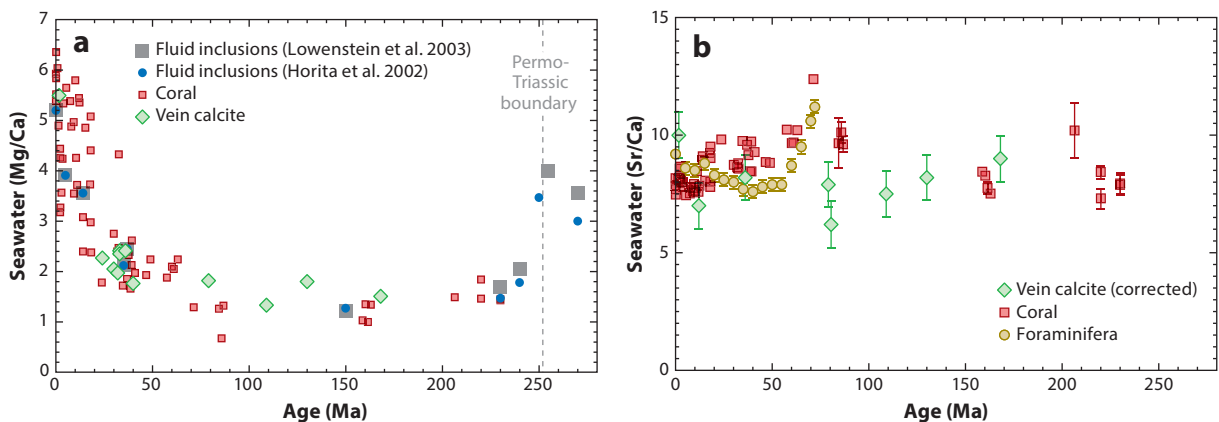


Figure 4

(a) Mg/Ca and (b) Sr/Ca over the past 240 million years. The data plotted here show results from three different approaches using three different types of carbonate mineral genesis that give reasonably consistent results. The Sr/Ca data from Coggon et al. (2010) have been recalculated using a value of $K_{Sr/Ca}$ (0.026 at 10°C) that is more consistent with experimental and other data (Zhang & DePaolo 2018). Abbreviations: Ca, calcium; K, potassium; Mg, magnesium; Sr, strontium. Figure redrawn from Gothmann et al. (2015), Lear et al. (2003), Coggon et al. (2010), and references therein.

When it comes to what biogenic and abiogenic carbonates can add to this picture, only ratios of the various elements can be obtained (**Figure 4**). This work has mostly used measurements of Mg/Ca or Sr/Ca in fossil calcite and aragonite (Lear et al. 2000, 2003; Dickson 2002, 2004; Ries 2004, 2010), or abiogenic carbonate veins from the oceanic crust (Coggon et al. 2010) or sedimentary carbonate cements (Hasiuk & Lohmann 2008), and then an estimate of the seawater ratio by application of an effective distribution coefficient that can be denoted as, for example, K_{Sr} , is defined as

$$K_{Sr} = \frac{Sr/Ca_{\text{carbonate}}}{Sr/Ca_{\text{seawater}}}.$$

If the value of K_{Sr} (or K_{Mg}) can be estimated, then it is possible to calculate the seawater Sr/Ca (or Mg/Ca) ratio from measurements of these ratios in carbonate minerals. Records of seawater Mg/Ca reconstructed from fluid inclusions and biogenic and abiogenic carbonate minerals are semiconsistent (**Figure 4**), reflecting a modern ocean with a relatively high Mg-to-Ca ratio (Mg/Ca = 5.4), while in the mid-Cretaceous these ratios are substantially different (Mg/Ca \approx 1). In the late Paleozoic, it appears that the Mg/Ca ratio is high again, exceeding 2, while for most of the Paleozoic the ratio is low, around 1, although the data are sparse. The Mg/Ca ratio has what has come to be known as a classic W shape.

The geochemistry of Sr has been the subject of extensive study for many decades because it is the most abundant trace metal in the oceans. It also substitutes for Ca in carbonate minerals, and its isotopic composition is one of only a few available measures of weathering fluxes and sources (Raymo & Ruddiman 1992, McCauley & DePaolo 1997). Reconstruction of the paleoseawater Sr concentration has not been pursued independently, but there have been multiple studies of seawater Sr/Ca (Lear et al. 2003, Tripathi et al. 2009, Coggon et al. 2010, Gothmann et al. 2015). Most of the work done has used biominerals, which is challenging because biogenic carbonate minerals do not form at equilibrium and hence the K_{Sr} value is quite different from the equilibrium K_{Sr} (Watkins et al. 2013). If the mineral is aragonite, this difference is minimal because K_{Sr} is

close to unity (Gaetani & Cohen 2006). For biogenic calcite the effective K_{Sr} is typically four to five times larger than the equilibrium value and strongly dependent on calcite growth rate and probably also on pH (Nehrke et al. 2007, Tang et al. 2008).

The majority of available data for Sr/Ca apply to the past 200 million years and involve biogenic aragonitic corals, calcitic benthic foraminifera, and abiogenic low-temperature hydrothermal calcite veins formed in oceanic crust (Elderfield et al. 2000, Lear et al. 2003, Tripathi et al. 2009, Coggon et al. 2010, Gothmann et al. 2015) (**Figure 4b**). A subset of the deep-sea coral data (Gothmann et al. 2015) that includes only those deemed to have the highest reliability is close to the modern Sr/Ca ratio of 8.4 mM/mol for much of the last 200 million years, except for a short period in the Late Cretaceous where reconstructed Sr/Ca appears to be as high as 12 mM/mol. The record is far from continuous, however. For deep-sea corals, the difference between the measured Sr/Ca ratio and that inferred for seawater is a factor of 1.1 ($K_{Sr} = 1.1$), and the equilibrium K_{Sr} for abiogenic aragonite is also close to 1.1 (Gaetani & Cohen 2006, Gothmann et al. 2015). The inferred seawater Sr/Ca ratio based on the extensive data set of Lear et al. (2003) on benthic foraminifera is similar to the Sr/Ca ratio reconstructed from coral, even though the difference between the measured Sr/Ca ratio in the benthic foraminifera and that calculated for seawater is a factor of 6 ($K_{Sr\text{-forams}} = 0.165$), a value that is far different from the equilibrium K_{Sr} for abiogenic calcite, which is about 0.02 to 0.04 at bottom water temperatures (see the section titled Carbonate Mineral Growth and Seawater Chemistry below). The constant K_{Sr} used by Lear et al. (2003) is calibrated from modern foraminifera, which could be a problem for older samples. The generally warming ocean temperatures and lower pH at earlier times could cause the effective K_{Sr} to drift downward and hence the reconstructed seawater Sr/Ca to be systematically higher further back in time. Overall, however, the deep-sea coral and benthic foraminifera records are in relatively good agreement.

The seawater Sr/Ca estimates based on calcite vein data as published by Coggon et al. (2010) appear to be drastically different from the estimates based on corals and benthic foraminifera. However, this discrepancy may be mainly a result of an inappropriate choice of K_{Sr} . Available experimental data (Lorens 1981, Tesoreiro & Pankow 1996, Malone & Baker 1999) and estimates based on pore fluids from deep-sea sediments (Richter & Liang 1993, Zhang & DePaolo 2018) suggest that the appropriate K_{Sr} values at 0–20°C, which control their estimates, are in the range 0.02–0.04 rather than the higher values (0.8–0.9) used in the Coggon et al. (2010) study. Recalculating their data (approximately) yields estimates of seawater Sr/Ca that are not so different from those based on the biogenic carbonate materials and provides additional evidence supporting the supposition that seawater Sr/Ca has not changed much over the past 240 million years.

PRIMARY ISSUES WITH THE EMERGING CONSENSUS: PALEOSEAWATER AND CHARGE BALANCE

The cyclical changes in the relative amounts of Mg, Ca, and SO_4 are also, based on the currently preferred numbers for the absolute concentrations as shown in **Figure 3**, associated with substantial changes in the charge sum of these major ions. The shifts in the summed total of 2^*Mg , 2^*Ca , and $2^*SO_4^{2-}$ are depicted in **Figure 5** in terms of the inferred effect on charge balance of the major cations and anions in the oceans. Total alkalinity, or the ocean's charge balance (Equation 1), can be written approximately as

$$m_{Na} + m_K + 2m_{Mg} + 2m_{Ca} - m_{Cl} - 2m_{SO_4} - alk = 0, \quad 4.$$

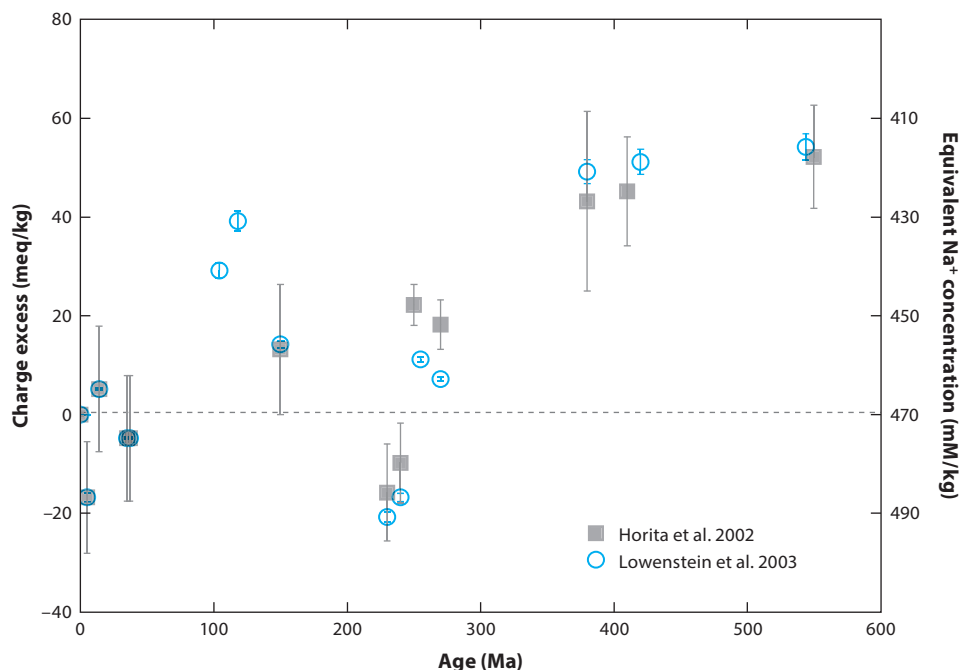


Figure 5

Charge excess relative to the modern ocean calculated from the inferred concentrations of Ca, Mg, and SO_4 as shown in **Figure 3**. If this charge imbalance was compensated solely by changes in seawater Na, the corresponding inferred Na concentration values are shown on the right scale. Abbreviations: Ca, calcium; Mg, magnesium; Na, sodium; SO_4 , sulfate.

where m_x refers to the concentration of the various cations and anions in seawater. As shown in **Figure 5**, assuming no changes in Na, Cl, or alkalinity, the inferred compositions of paleoseawater result in this sum varying from about -20 to $+50$ meq/kg. Given that alkalinity and Cl changes are likely to be minimal, as are changes in the K concentration of the ocean, such changes could be compensated only by concurrent changes in Na concentrations. There is evidence in the data of Lowenstein et al. (2001) that Na concentrations may have been different in the past oceans. Although Lowenstein et al. do not report estimates of Na concentrations and their approach may give only lower limits to the Na concentration, their data suggest that the seawater Na concentration could have been substantially lower in the Cretaceous, Silurian, and Cambrian. The apparent requirement for substantial changes in m_{Na} in the paleo-oceans raises questions about how this might occur and also about whether the current estimates for the concentrations of Mg, Ca, and SO_4 should be further scrutinized with this in mind.

WHAT MIGHT DRIVE THESE CHANGES IN SEAWATER CHEMISTRY?

Ultimately, an understanding of what drives changes in seawater chemistry would help us understand the consequences of the proposed changes in the major ion balance of the ocean, particularly as they link to changes in the C cycle. There have been several proposals as to what could explain the simultaneous decrease in Mg, Na, and SO_4 and increase in Ca (Hardie 1996, Stanley & Hardie 1998, Steuber & Veizer 2002, Hansen & Wallman 2003). What is remarkable is the extent to which these changes in the chemistry of the ocean correlate with changes in sea level and $p\text{CO}_2$ for the

Phanerozoic (see **Figure 1**; see also the sidebar titled Variations of Global Sea Level). When sea level is high, the Mg, SO₄, and Na concentrations of the ocean are low while the Ca concentration is high; when sea level is low, the Mg, SO₄, and Na concentrations of the oceans are high while the Ca concentration is low (Holland 2005). This correlation exists—presumably—because all are responding to the same tectonic drivers. In addition, we need to consider that there are internal chemical controls, especially for Ca, where it is unlikely that the product of the concentrations of Ca²⁺ and CO₃²⁻ depart greatly from the calcite solubility limit over long timescales (Ridgwell & Zeebe 2005).

What Processes Influence Sea Level?

Interpretation of the sea level curve is somewhat complicated because both ocean floor processes and continental tectonics can affect sea level (Vail et al. 1977, Stanley & Hardie 1999, Bradley 2011). One of the most striking and established aspects of the ocean floor is that its depth is proportional to the square root of its age due to cooling and contraction as the crust moves away from the ridge. Consequently, when the average age of the ocean floor is relatively young, the oceans are less deep for the same area, sea level is higher, and the oceans cover more of the continents with shallow seas (Gaffin 1987). When the average age of the ocean crust is older, sea level is lower and more of the continents, and continental shelf, is exposed above sea level.

Additional factors in assessing sea level are the total volume of the ocean and the average thickness of the continental crust. Continents tend to be thinned during rifting, increasing their total area but resulting in some fraction of the continental area being submarine shelf. Continental collisions, in contrast, tend to convert thin crust into much thicker crust that takes up less area. In the simplest form, when continents are rifting, they are thinning and increasing in areal extent, causing sea level to rise. Continental collisions compress the continents laterally, increase the area of the ocean basins, and cause sea level to fall. Hence, when there are many continents dispersed throughout the ocean, their continental shelf area displaces a larger volume of water, and this contributes to sea level being high; when continents are collected together into one supercontinent, there is less shelf area, displacing less ocean water, and sea level is lower (Bradley 2011). In addition, when there is a single supercontinent, the width of the ocean is large and there is a likelihood that the average age of the oceanic crust will be high; therefore, the oceans will be deep and sea level will be low (Rennie et al. 2018).

The concepts described above can be used to explain the general shape of the sea level curve and how it relates to the supercontinent cycle over the Phanerozoic (Bradley 2011). In the Paleozoic, during the accretion of Pangea and the closing of the Rheic Ocean, there were multiple spreading centers, the average age of the oceanic crust was young, and sea level was relatively high. However, sea level became systematically lower as the supercontinent was assembled. The major shorter-term drops in sea level (**Figure 1**) relate to the continental collisions that accreted Baltica onto Laurentia, and then Avalonia onto Laurentia, and finally the closing of the Rheic Ocean and the accretion of Gondwana onto Laurentia, forming Pangea (Nance et al. 2010). The sea level decrease in the latest Paleozoic through the early Mesozoic represents the time when Pangea was fully formed, and the age of the oceanic crust would have been old, both effects leading to a deepening of the ocean basin and a relatively low sea level. The sea level increase in the Mesozoic relates to the breakup of Pangea, the creation of the Mid-Atlantic Ridge, and a lowering in the overall age of the oceanic crust as well as an increase in submarine shelf area of the continents. A potential additional consideration is that during the Cretaceous superchron, there was excess midplate seafloor volcanism in the form of large igneous provinces, further helping to displace sea level higher (Seton et al. 2009). Modern sea level is low, likely because of the India-Asia collision

and the entire Alpine-Himalayan mountain building episode. Furthermore, the continents are far enough apart and spreading sufficiently slowly on the Mid-Atlantic Ridge that the average oceanic crust is relatively old (Rennie et al. 2018).

A consequence of the tectonics that result in changes in sea level is that as mountains are built, either through the accretion of oceanic terranes onto continental crust or through the collision of continental crust, there will be enhanced chemical and physical erosion of high topography, especially when that topography is at low latitudes (Raymo & Ruddiman 1992). This enhanced weatherability of continental rocks leads to increasing carbonate sedimentation on the ocean floor, decreasing atmospheric CO₂, and higher ocean pH over millions of years (Kump & Arthur 1997, Maher & Chamberlain 2014). The weatherability increase is typically correlated with the amount or rate of increase of radiogenic Sr (⁸⁷Sr) in the ocean, which is well recorded in marine carbonate minerals. Because radiogenic ⁸⁷Sr [from radioactive decay of rubidium (⁸⁷Rb)] is enriched in old silica-rich continental rocks such as granite, high seawater ⁸⁷Sr/⁸⁶Sr tends to correspond to more weathering of old granitic continental rocks. Continental collision is generally required to produce mountain ranges that expose such old rocks. Therefore, continental amalgamations simultaneously impact sea level, drive the ocean to higher pH and the atmosphere to lower CO₂, and increase the ⁸⁷Sr/⁸⁶Sr ratio of seawater and marine carbonate minerals (Raymo & Ruddiman 1992, McCauley & DePaolo 1997).

Why Should Sea Level Correlate with Changes in Ocean Chemistry?

The same processes that lead to sea level change are likely to affect seawater chemistry either directly or indirectly. For example, as mentioned above, continental collisions should lead to enhanced erosion and chemical weatherability increasing the efficiency of alkalinity delivery to the oceans while at the same time contributing to the lowering of sea level. Enhanced seafloor generation (younger average age of the oceans), which promotes high sea level, should be associated with increased removal of Mg from the oceans by fixation in Mg-bearing hydroxylated silicates in hydrothermal systems, a modest increase in the supply of Ca to the oceans associated with the same hydrothermal processes, and changes in removal rates of ions due to sediment formation and burial in shallow continental seas.

A logical explanation for a decrease in the Mg concentrations, of the ocean and a concomitant increase in the Ca concentration would relate to enhanced production of oceanic crust, which would draw down Mg into hydrothermal alteration minerals and leach Ca from the ocean floor rocks into the ocean (Berner 2004). This hypothesis could be tested by comparing the production rate of Cretaceous oceanic crust to the modern ocean floor and investigating the effect this would have in seafloor generation rate, but the results of a comparison of seafloor generation rate between the Cretaceous and modern have been ambiguous (Müller et al. 2008, Rowley 2008). But in any case, any increases in oceanic crust generation should produce a substantial perturbation to the Mg cycle in the oceans, particularly because they are concurrent with a reduced continental weathering input due to continental fragmentation. Finally, the formation of Ca,Mg(CO₃)₂, the dominant sedimentary sink for Mg, would be enhanced in shallow, epicontinental seas favored during high sea level (Holland & Zimmermann 2000, Holland 2005, Arvidson et al. 2011). Therefore, at times when sea level is high, two removal pathways for Mg, hydrothermal and Ca,Mg(CO₃)₂, are enhanced, and the main source for Mg (terrestrial weathering) is suppressed, leading to overall lower Mg concentrations in the ocean.

Na concentrations in hydrothermal vent fluids positively correlate with Mg and negatively correlate with Ca, implying that hydrothermal systems are also a sink for Na. Demicco et al. (2005) modeled the effects of changing exchange rates between submarine basalt and seawater, and they

found that there is reason to expect that seawater Na concentrations would decrease in concert with decreasing seawater Mg concentrations, although at a slower rate. Na is also supplied to the oceans by weathering of continental rocks, and this might decrease in concert with decreased Mg delivery when sea level is high (Livingstone 1963, Sun et al. 2016).

Of the seawater components we have been discussing, Ca is the only one that is limited by solubility, and its residence time is much shorter (1 million years versus >10 million years for the others). The Ca input flux to the ocean is large and dominated by continental weathering sources, and the output flux is also large and dominated by carbonate sedimentation. The concentration of Ca in seawater is therefore likely to mainly reflect the indirect effect of ocean pH (cf. Zeebe 2012). For example, if there were an increase in ocean pH, this would be associated with both a lowering of atmospheric $p\text{CO}_2$ and an increase in dissolved CO_3^{2-} (Ridgwell & Zeebe 2005, Zeebe 2012). Increased CO_3^{2-} should lead to a lowering of seawater Ca concentrations if the oceans are to stay near to carbonate mineral saturation. Similarly, a lowering of ocean pH would lead to degassing of C from the ocean to the atmosphere, higher $p\text{CO}_2$, lower CO_3^{2-} , and high seawater Ca concentrations. Broadly speaking, continental collisions should increase the alkalinity flux to the oceans, thus increasing pH, while concomitantly lowering sea level and leading to lower marine Ca concentrations. In a like manner, younging of oceanic crust and a paucity of continental collisions should lead to a lower continental alkalinity flux, lower ocean pH, higher sea level, and higher marine Ca concentrations. Hence, seawater Ca concentrations are anticorrelated with seawater Mg and Na not because of changes in the Ca fluxes but because the processes that affect Mg and Na correlate with atmospheric $p\text{CO}_2$ and seawater pH.

The controls on SO_4 concentrations are also likely to be indirectly correlated with the controls on seawater Mg and Na concentrations, even though there are apparent direct correlations as well. SO_4 is indeed removed from hydrothermal fluids through the formation of anhydrite (CaSO_4), which is highly insoluble at temperatures above 150°C (Edmond et al. 1979, Alt 1995, Elderfield & Schultz 1996). However, it has been debated whether CaSO_4 that precipitates from circulating seawater in mid-ocean ridges is a permanent sink for S from the ocean. Because CaSO_4 becomes soluble again as the oceanic crust cools, it has been suggested that it redissolves and may be returned to the oceans (McDuff & Edmond 1982, Elderfield & Schultz 1996), although this is contradicted by the presence of CaSO_4 in cooler, 10-million-year-old crust (Alt et al. 1989, Alt 1995). Within hydrothermal systems, SO_4 is also reduced thermochemically to sulfide and can precipitate as FeS_2 , which is facilitated by the release of ferrous iron that is leached from ocean floor rocks. There is also igneous S derived from the mantle that is available in oceanic crust and that may also be leached and added to the oceans at low-temperature conditions (Alt 1995). An S isotope mass balance of hydrothermal vent fluids suggests that the S emitted from vents during high-temperature circulation is a mixture of thermochemically reduced seawater SO_4 and S leached directly from the basalt (Alt 1995).

Whether hydrothermal systems are a net source or sink of S to the ocean remains unresolved (e.g., Halevy et al. 2012). In the modern ocean, where the SO_4 concentration is much higher than the Ca concentration, it may be that the Ca supply cannot keep up with the SO_4 available for titration from the hydrothermal fluids as CaSO_4 (Turchyn et al. 2013). As a first pass, only 10 mM of the 28 mM of the SO_4 from seawater can precipitate as CaSO_4 because there are only 10 mM of Ca available, unless more is leached from basalt before the fluids reach the moderate-temperature parts of the hydrothermal systems. The low Ca concentration leaves an excess of SO_4 that enters the high-temperature arm of the hydrothermal system, yielding S-rich hydrothermal vent fluids (largely in the form of sulfide). The behavior of SO_4 during hydrothermal circulation could be fundamentally different in an ocean where the Ca concentration exceeds the SO_4 concentration,

where it is then likely that all the seawater SO_4 will precipitate at 150°C and very little of it will enter the high-temperature part of the hydrothermal system (Antonelli et al. 2017).

Higher sea level, associated with young oceanic crust and/or fragmented continents, could also impact seawater SO_4 concentration because of the increase in the extent of continental shelf area, similar to what was discussed above for Mg (Holland 2005). The dominant removal process for SO_4 in the modern ocean is the reduction of SO_4 to sulfide and then precipitation with iron as FeS_2 . In the modern ocean the formation of FeS_2 is limited by the supply of iron; it could be that with higher sea level and flooded continental interiors close to terrestrial sources of iron, there could be enhanced removal of SO_4 as FeS_2 . This hypothesis is broadly consistent with the S isotope record from carbonate-associated SO_4 and evaporites over the Phanerozoic, which shows relatively high $\delta^{34}\text{S}$ for seawater SO_4 in the Paleozoic, an indicator of enhanced removal of low $\delta^{34}\text{S}$ as FeS_2 or organosulfur molecules (Claypool et al. 1980, Strauss 1999, Rennie et al. 2018). Hence, the correlation of low seawater SO_4 concentration with high sea level may be due to the increase in continental shelf area rather than increased SO_4 removal in seafloor hydrothermal systems.

CONSEQUENCES OF CHANGES IN SEAWATER CHEMISTRY

Global Biogeochemical Cycles

Ultimately, apart from the causes of the variations, higher concentrations of Ca and decreased concentrations of seawater Mg, Na, and SO_4 have implications for other processes across Earth's surface environment. These processes may serve as positive or negative feedbacks within Earth's coupled biogeochemical cycles and their ultimate link to the C cycle.

One consequence of lower absolute Mg concentration in the ocean is lower acidity generated during hydrothermal circulation, since it is the fixing of Mg into Mg-hydroxide minerals that generates protons from water and lowers pH. This lowering of pH enhances weathering and alteration of the oceanic crust. Hence, lower seawater Mg may decrease the overall efficiency of chemical exchange between seawater and seafloor basalt. As mentioned above, the excess of Ca to SO_4 will change the reactive flow path of both through hydrothermal systems—excess Ca, rather than SO_4 , will be supplied to the high-temperature arm of hydrothermal systems, and SO_4 will be quantitatively removed (Turchyn et al. 2013). Since excess Sr as well as Ca may be supplied to the high-temperature parts of the hydrothermal systems, the change in seawater chemistry may have a particularly marked effect on the Sr isotope effects in hydrothermal systems (Antonelli et al. 2017). Since SO_4 reduction at high temperatures is responsible for the removal of electrons from the oceanic crust (the oxidation of the oceanic crust), it is possible that the lower SO_4 concentrations would result in oceanic crust with a lower $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (Stolper & Keller 2018). It is likely that the change in the major ion balance therefore would greatly influence the reactive flow path and alteration products within seafloor hydrothermal systems (Coogan 2009, Turchyn et al. 2013, Coogan & Dosso 2015, Antonelli et al. 2017).

The change in the major ion balance will also have a dramatic impact on sedimentary diagenesis and the deep biosphere. In the modern ocean, marine SO_4 supplies the most dominant electron acceptor to the anoxic oxidation of organic C; microbial SO_4 reduction is responsible for most sedimentary-based organic C oxidation and nearly all anaerobic methane oxidation. The canonical view is that organic C deposited within sedimentary systems will be oxidized by SO_4 -reducing bacteria, and any organic C that escapes oxidation may be made into methane. In modern sedimentary environments, the alkalinity produced by both processes can be titrated by Ca to make

sedimentary, authigenic carbonate. However, in the modern ocean there is a large excess of alkalinity relative to the diffusive supply of Ca to the sediment column; this is because there is so much SO_4 available to oxidize organic matter. In the past ocean, where the Ca concentration is so much higher than the SO_4 concentration, it is likely that subsurface alkalinity generation would be much lower, and methane production would be much higher. This methane production and the oxidation of the methane would promote the formation of authigenic carbonate, and it could be that the supply of alkalinity from sediments to the overlying ocean could be lower.

Carbonate Mineral Growth and Seawater Chemistry

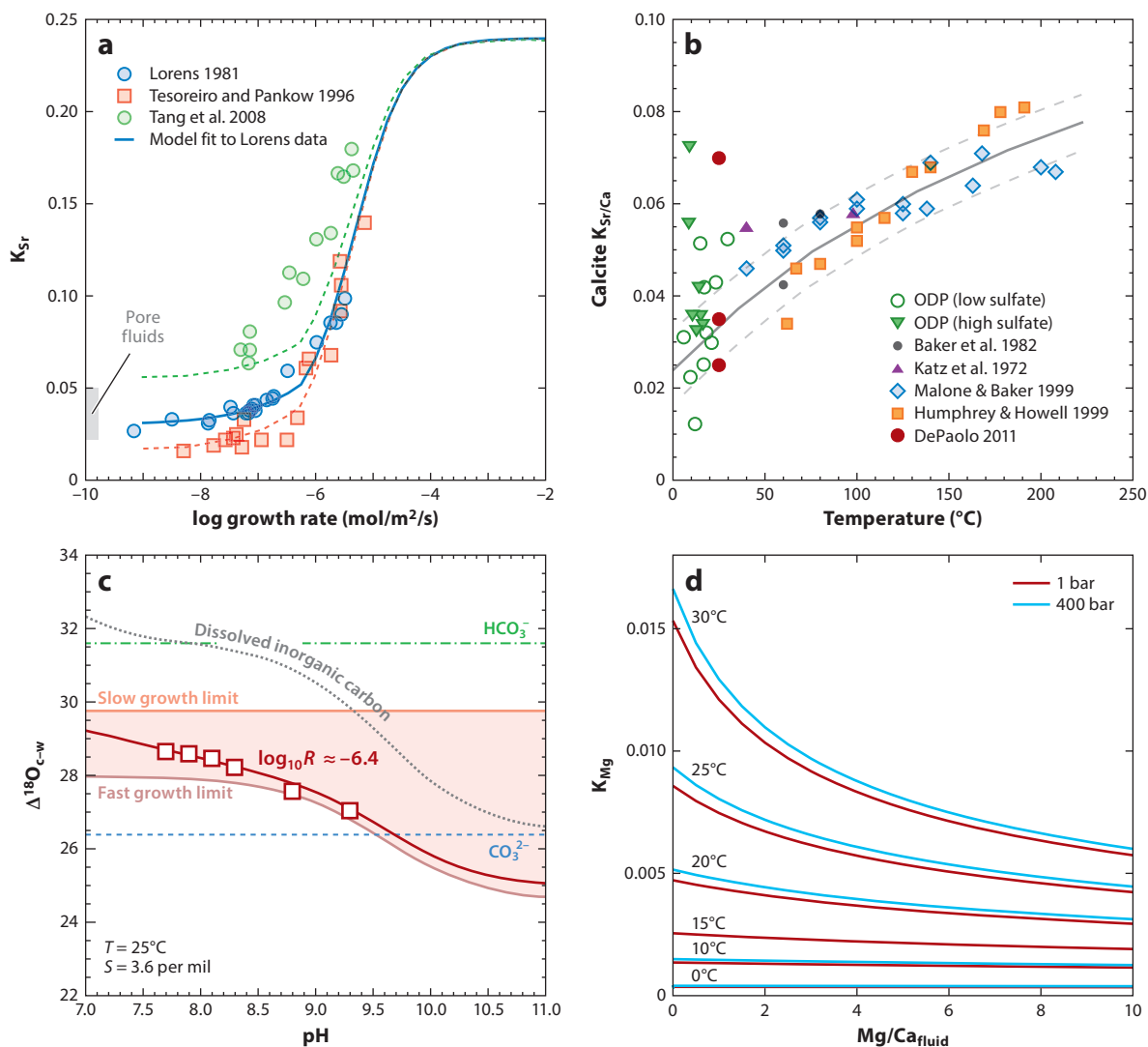
Changes in seawater chemistry can also affect how biogenic and authigenic carbonate minerals grow and how they record the conditions of their growth with their impurity concentrations and isotopic composition (e.g., DePaolo 2011, Nielsen et al. 2013, Watkins et al. 2013). Because biogenic calcite (and aragonite) generally grow from solutions in which the mineral is oversaturated by a factor of 5 to 10, the minerals do not grow in equilibrium with the aqueous solution but instead reflect kinetics of precipitation that is typically controlled by the organism that is biomineralizing. Awareness of this fact is critical to understanding the uncertainties associated with biomineral proxies for past ocean chemistry and to evaluating how our increasing understanding can be used to improve them. In contrast to biominerals, authigenic, or sedimentary, carbonate minerals typically grow at slow enough rates (orders of magnitude more slowly than biominerals) that they form close to chemical equilibrium with the fluid from which they precipitate. This presents an additional challenge—establishing the equilibrium distribution coefficients.

The kinetic, or nonequilibrium, effects on trace element incorporation (Mg/Ca or Sr/Ca, for example) or oxygen isotope ($\delta^{18}\text{O}$) composition can be dramatic. Laboratory studies show, for example, that Sr/Ca partitioning into calcite is a strong function of growth rate and temperature (Nehrke et al. 2007) (**Figure 6**). Mg/Ca partitioning into calcite is a function of both temperature and the Mg/Ca ratio of the fluid phase. Finally, the $\delta^{18}\text{O}$ of calcite is sensitive to growth rate and pH as well as temperature (Watkins et al. 2013). Although the understanding of these nonequilibrium effects is still incomplete, as is how laboratory studies translate to biominerals, they suggest that some proxy record interpretations may need modification and that others could yield additional information about the paleo-oceans.

Calcite growth is also inhibited by high concentrations of aqueous Mg and SO_4 . The relatively high concentrations of these elements in the modern oceans may partially account for why the surface ocean can remain oversaturated with respect to calcite by more than five times; this means that calcite precipitates way out of equilibrium with the ocean. At other times in Earth history, as in the Cretaceous, for example, if concentrations of both Mg and SO_4 were much lower relative to Ca, this inhibitory effect may have been smaller. The implication would be that calcite growth could occur at smaller solution oversaturations and thus closer to equilibrium. Perhaps counterbalancing the effect of the change in the major ion balance, the ratio of Ca to CO_3^{2-} ($\text{Ca}^{2+}/\text{CO}_3^{2-}$) is also inferred to be higher in the Cretaceous, assuming the likely case that pH was lower. It has been shown experimentally that calcite growth rate is dependent on $\text{Ca}^{2+}/\text{CO}_3^{2-}$ as well as on the product $[(\text{Ca}^{2+})(\text{CO}_3^{2-})]$ and tends to decrease as $\text{Ca}^{2+}/\text{CO}_3^{2-}$ gets farther from unity (Larsen et al. 2010). If carbonate mineral growth rates in the Cretaceous were similar to modern but the conditions included both lower ocean pH and conditions closer to carbonate mineral equilibrium, we might expect the Sr/Ca partition coefficient, for example, to be smaller, perhaps by a factor of 2 (**Figure 6a**). It has not yet been demonstrated that these effects can be applied in paleoseawater reconstructions due to the expectation that organisms can create microenvironments to control the conditions of mineralization.

DOES IT ALL FIT TOGETHER?

The conclusion from our discussion is that the chemistry of seawater responds to several different global processes, and the concentrations of some constituents are affected directly and others indirectly. The processes driving seawater chemistry variations are themselves only partially constrained and understood. Nevertheless, it is possible to construct a plausible qualitative model to explain the interrelationships among sea level, continental tectonics, atmospheric CO_2 , and seawater chemistry. Our conceptual model emphasizes geochemical observations of the seawater Mg, Ca, and SO_4 concentration, using as indicators of the driving processes the observed changes in sea level, the S isotope composition of marine SO_4 ($\delta^{34}\text{S}$), and the Sr isotope composition of seawater Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) (Figure 7).



(Caption appears on following page)

Figure 6 (Figure appears on preceding page)

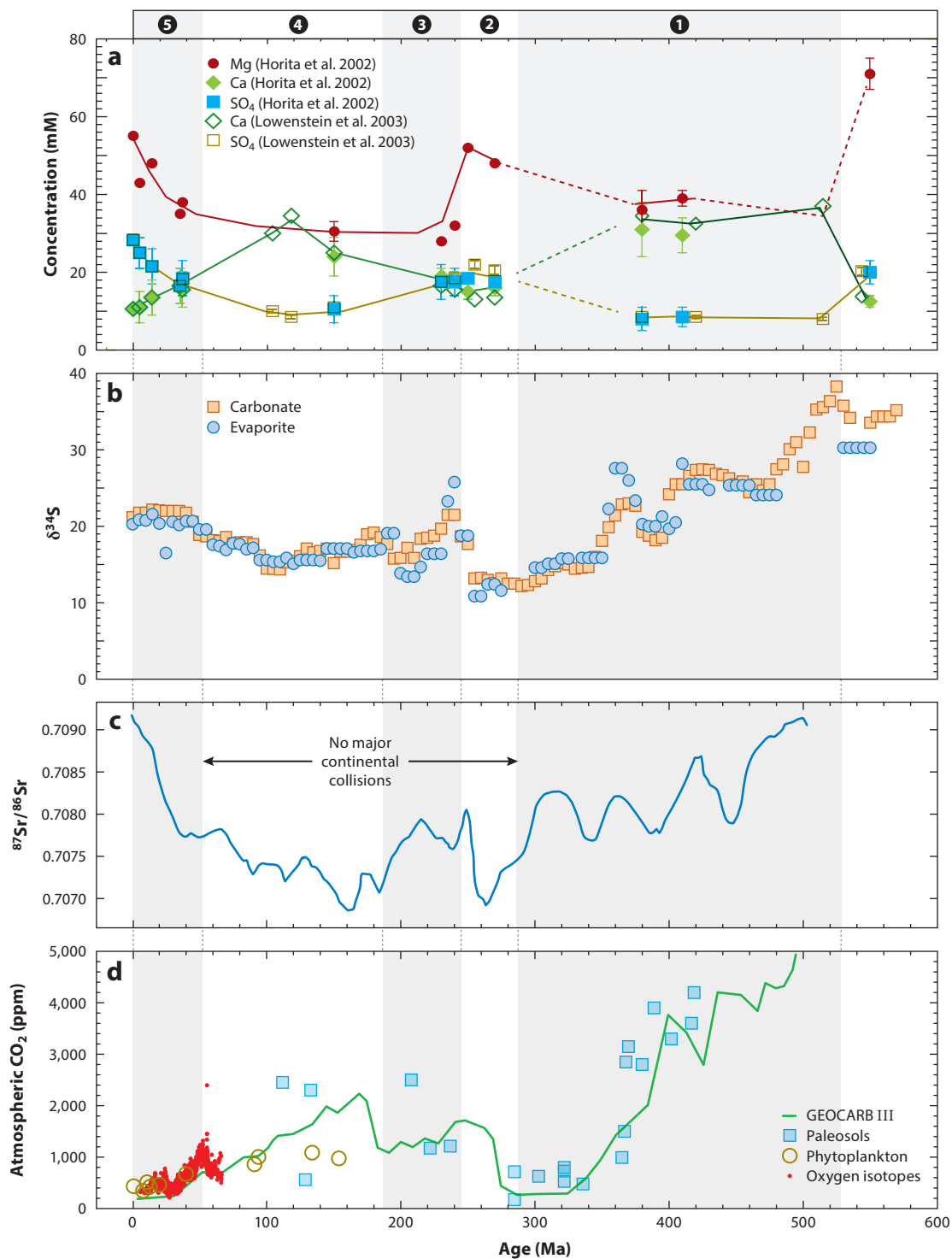
Summary of recent work on kinetic effects related to reconstruction of Sr/Ca, Mg/Ca, and $\delta^{18}\text{O}$ (paleotemperature) from biomineralized and hydrothermal calcite. (a) Dependence of Sr/Ca partition factor (K_{Sr}) on calcite growth rate at 25°C. Typical biogenic growth rates are near 10^{-6} mol/m²/s, and inferred biogenic K_{Sr} values are near 0.15. The solid heavy blue line represents the model fit to the data of Lorens (1981). The gray rectangle indicates the range of values inferred from deep-sea pore fluids (from panel b). The equilibrium value is the value at an infinitely slow growth rate, which in effect is a growth rate slower than about 10^{-9} mol/m²/s. Data are from Lorens (1981), Tesoreiro & Pankow (1996), and Tang et al. (2008) normalized to a constant pH according to the model of DePaolo (2011). (b) Dependence of the equilibrium K_{Sr} on temperature based on data from the literature and inferred from deep-sea pore fluids from carbonate-rich ooze sections. ODP values shown are those inferred from the Sr and Ca concentration of pore fluids. Low and high SO_4 refer to pore fluid SO_4 concentration. DePaolo (2011) refers to the equilibrium values inferred from the data of Lorens (1981), Tesoreiro & Pankow (1996), and Tang et al. (2008) as shown in panel a. The solid gray line is an approximate fit of the data; the dashed gray lines are ± 0.01 from the solid line. The low values of K_{Sr} and temperature dependence as shown require that the SrCO_3 - CaCO_3 solid solution be highly nonideal and with progressively larger departures from ideality at lower temperature. Panel b data taken from Zhang & DePaolo (2018). (c) Theoretical variation of $^{18}\text{O}/^{16}\text{O}$ fractionation in calcite as a function of pH and growth rate, showing the pH effect at constant growth rate of approximately 5×10^{-7} mol/m²/s based on experiments where T is temperature and S is salinity. Panel c adapted from Watkins et al. (2014). (d) Dependence of the equilibrium K_{Mg} on temperature, pressure, and the Mg/Ca of the fluid based on available data and the model of Lammers & Mitnick (2019). Abbreviations: C, carbon; Ca, calcium; H, hydrogen; K, potassium; Mg, magnesium; O, oxygen; ODP, Ocean Drilling Program; SO_4 , sulfate; Sr, strontium.

The ultimate driver of changes to the chemical composition of the ocean is, as others have suggested, changes in global sea level driven by the broad tectonic arc of the Wilson cycle over the Phanerozoic. The changes in reconstructed sea level reflect the accretion phase of the supercontinent Pangea during the Paleozoic. Continents were still substantially fragmented, which resulted in high but generally decreasing sea level followed by the supercontinent phase in the late Paleozoic and early Mesozoic when the continents were fully assembled, the ocean floor was relatively old, and sea level was low. This period of low sea level was followed by the breakup of Pangea in the early Mesozoic, which resulted in high sea level again, and then the Himalayan orogeny starting in the early Cenozoic, which then lowered sea level again. The changes in sea level reflect both the degree of fragmentation or amalgamation of the continents and the rate of generation of younger seafloor or other submarine volcanism.

Seawater chemistry responds to the tectonic driver either directly because it is affected by the nature of submarine volcanism or seafloor generation, or the chemical weathering after generation of continental mountain ranges, or indirectly because it is affected by changes in solubility or the change in the extent and distribution of continental shelf area. Thus, when we think about how this tectonic driver, or resulting sea level change from this tectonic driver, influences the major ion balance or isotope composition of the ocean, we must consider how this driver influences the input or output fluxes associated with the various geochemical cycles.

We suggest that Mg, Ca, and SO_4 concentrations are responding to different aspects of the coupled tectonics and sea level drivers and that Na must be included in these discussions. Mg and SO_4 concentrations largely reflect changes in the removal rates of these ions relative to the delivery rates from continents. Ca is also affected by the delivery and removal rates during this broad cycle, but its seawater concentration is ultimately controlled by carbonate saturation limits, which are set by atmospheric $p\text{CO}_2$ and ocean pH, which in turn change in response to the tectonic drivers.

Mg is delivered to the oceans in rough proportion to continental weathering, but its removal responds directly to the generation of oceanic crust, which provides the dominant sink, through either the fixation of Mg during on-axis or ridge-flank hydrothermal circulation or the enhanced reaction of Mg during clay authigenesis associated with ridge-flank reactions. It has also been suggested that the sink of Mg into authigenic clays is heavily temperature dependent, and as temperature in the ocean scales with $p\text{CO}_2$ in the atmosphere, then when temperatures are higher, the removal of Mg into authigenic clays or off-axis crustal alteration increases (Dunlea et al. 2017).



(Caption appears on following page)

Figure 7 (Figure appears on preceding page)

Summary graphs relating (a) seawater chemistry, (b) the S isotope composition of seawater sulfate, (c) seawater $^{87}\text{Sr}/^{86}\text{Sr}$, and (d) atmospheric $p\text{CO}_2$. Seawater chemistry data from Horita et al. (2002) and Lowenstein et al. (2003), panel c adapted from McArthur et al. (2012), and panel d constructed using selected data and GEOCARB III curve summarized by Royer (2001), plus a reconstruction of CO_2 for the Cenozoic from benthic foraminifera $\delta^{18}\text{O}$ data following the approach of McCauley & DePaolo (1997) and S isotope data from Kampschulte & Strauss (2004). Abbreviations: Ca, calcium; Mg, magnesium; O, oxygen; $p\text{CO}_2$, partial pressure of carbon dioxide; S, sulfur; Sr, strontium.

$\text{Ca}_2\text{Mg}(\text{CO}_3)_2$ formation is another mechanism of Mg removal and is enhanced when sea level is high. Therefore, the conditions under which sea level is high and temperatures are warm will be ones that favor enhanced removal of Mg from the ocean and lower resultant seawater Mg concentrations.

Although SO_4 removal is partly linked to seafloor generation, our hypothesis is that the SO_4 concentration is more likely responding to changes in the removal rate that depend on the extent of shelf area. SO_4 concentrations are low when sea level is high and shallow areas are flooded, and they are high when sea level is low and the primary burial flux of SO_4 as FeS_2 is limited. To support this, we note the broad shape of the curve of $\delta^{34}\text{S}$ of SO_4 over the Phanerozoic (**Figure 7**), which reflects the changes in the burial environment for S and thus the relative amount of ^{32}S removed from the ocean as FeS_2 (Fike et al. 2015, Rennie et al. 2018). There is also a rough correlation between the $\delta^{34}\text{S}$ of SO_4 and the $^{87}\text{Sr}/^{86}\text{Sr}$ of the ocean over the Phanerozoic. While we posit that the $\delta^{34}\text{S}$ of SO_4 is responding to the change in the sulfide burial environment due to changes in sea level and the exposure/submergence of continental shelf area, we suggest that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is responding to the prevalence or absence of large continental collisions that result in the creation of extensive mountain ranges and, ultimately, deep erosion and weathering of ancient ^{87}Rb -rich continental crystalline rocks.

Seafloor hydrothermal processes are a source for seawater Ca rather than a sink as they are for Mg and possibly also for SO_4 . For Ca, however, seafloor processes provide substantially less of the Ca delivered to the ocean than does continental weathering (De La Rocha & DePaolo 2000). Therefore, although it is tempting to think of seafloor processes acting to elevate Ca concentration as they lower Mg, it is more likely that the seawater Ca concentration is controlled by other factors. In particular, changes in $p\text{CO}_2$ directly impact the Ca concentration of the ocean. Higher $p\text{CO}_2$, all else being equal, will lead to a lower ocean pH, which will decrease the CO_3^{2-} concentration in the ocean (Zeebe 2012). Lower CO_3^{2-} concentration means that Ca concentration must be higher to maintain carbonate saturation. For a simple model of seawater carbonate equilibrium, a decrease in pH of 0.5 units should correspond to an increase of Ca by a factor of about 3, which is exactly what the inferences are for the mid-Cretaceous oceans (Zeebe 2012) (**Figure 7**). Indeed, the Ca cycle, the most dynamic of all the biogeochemical cycles discussed in this review, responds nearly directly and entirely to changes in the carbonate saturation state of the ocean.

Our model for the variation of seawater chemistry over the past 500 million years can be summarized with reference to **Figures 7** and **1**. We divide the Phanerozoic eon into five periods marked in **Figure 7**. In period 1 (**Figure 7a**) sea level is generally high but decreasing, Ca is high due to high atmospheric $p\text{CO}_2$ and low pH, Mg is relatively low due to young ocean floor and $\text{Ca}_2\text{Mg}(\text{CO}_3)_2$ formation in shallow seas, and SO_4 is low and $\delta^{34}\text{S}$ high due to extensive shallow seas and enhanced FeS_2 formation removing ^{32}S from the ocean. The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ shows generally high values, with peaks corresponding to major continental collisions, indicating that continental weathering fluxes were more heavily influenced by weathering of old continental silicate rocks. High $p\text{CO}_2$ was gradually lowered due to slow forcing from the enhanced weatherability of continental rocks from rapid erosion associated with mountain building, perhaps further

enhanced by the evolution of land plants in the Devonian. In period 2 (**Figure 7b**) sea level is low because the continents have been amalgamated and the seafloor is older, Mg is high due to slow ocean floor generation and less $\text{Ca, Mg}(\text{CO}_3)_2$ formation, Ca is low due to low $p\text{CO}_2$ and high pH, and SO_4 is somewhat elevated due to smaller available shelf area for FeS_2 removal. The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ reaches a near minimum due to decreased weatherability of the supercontinent, and $p\text{CO}_2$ rises for the same reason. Period 3 (**Figure 7c**) is enigmatic in that there is an apparent large decrease in seawater Mg with little change in Ca or SO_4 ; both $^{87}\text{Sr}/^{86}\text{Sr}$ and S isotopes have positive excursions, coupled with the transient environmental perturbation at the Permian-Triassic Boundary; and CO_2 maintains an intermediate value. In period 4 (**Figure 7d**) the continents are dispersing, so sea level is high and Mg is low due to enhanced seafloor generation and overall ocean floor weathering, Ca is higher due to high $p\text{CO}_2$ and low pH, and SO_4 concentrations are low due to a larger area of shallow seas and continental shelf for FeS_2 removal. Delivery of ^{87}Sr to the oceans is low because of the lack of major continental collisions, and $p\text{CO}_2$ is high due to reduced continental weatherability. The $\delta^{34}\text{S}$ remains low in spite of enhanced burial environments for FeS_2 at this time because it has been suggested that the S isotopic composition of FeS_2 buried in epicontinental seas would be higher, removing less ^{32}S from the ocean (Rennie et al. 2018). In period 5 (**Figure 7d**) sea level is decreasing due to a major continental collision, slowing seafloor generation, and ice cap formation. Mg concentrations increase from increased continental weathering and slower removal, Ca decreases as pH increases, and SO_4 concentrations increase as continental shelf area is lost. The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ increase reflects the source of ^{87}Sr due to continental mountain building, and a correlative increase in overall continental weatherability could account for decreasing $p\text{CO}_2$.

CONCLUSIONS

That seawater chemistry has changed substantially through the last 500 million years is now quite well established, and as we have attempted to show, there is at least a qualitative understanding of how these changes arise and what the consequences are. Models can be constructed that relate seawater chemistry to sea level, continental amalgamation and dispersal, and atmospheric $p\text{CO}_2$. As we have presented them, such models are plausible and mostly self-consistent, and there have been efforts to make them quantitative as well (e.g., Berner 2004, DeMicco et al. 2005). However, the testing of the models is still limited by a paucity of reliable data on both seawater chemistry and its potential drivers, with the accuracy and time resolution needed to distinguish between competing hypotheses. The data on past seawater composition remain minimal, as does documentation of sea level and its meaning for seafloor hydrothermal processes, paleoatmospheric $p\text{CO}_2$ and ocean pH, and past continental weathering rates. There are better constraints for the past 100 million years than for earlier times, but there is still difficulty in rationalizing the data for the more recent period and more difficulty in applying the insights to earlier periods of Earth history. However, there are new approaches being applied using other isotopic systems such as lithium, Ca, and Mg, among others, and continuing improvement in our ability to interpret proxy data from rocks and minerals that suggest that ultimately a holistic view of the coupled evolution of the lithosphere and hydrosphere is possible.

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