

The Role of Seafloor Hydrothermal Systems in the Evolution of Seawater Composition During the Phanerozoic

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Seafloor hydrothermal systems clearly have played an important role in controlling the composition of seawater over geologic time. However, controversy exists concerning their role as drivers of secular variability in major element composition of seawater during the Phanerozoic. The history of Phanerozoic changes in calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentration has been reconstructed through analysis of fluid inclusions in evaporites, and this history is inconsistent with global geochemical cycling models that link both volcanic CO_2 release and Mg^{2+} uptake/ Ca^{2+} release to inferred rates of seafloor production. These models generate little variability in Mg^{2+} concentrations because of compensating effects. Some models that recreate the observed trends either do not conserve alkalinity or do not link seafloor spreading, inferred from past variations in continental flooding presumed to reflect changing mid-ocean-ridge volumes, to volcanic CO_2 production. The most comprehensive models reproduce the variations in seawater $\text{Mg}^{2+}/\text{Ca}^{2+}$ through time quite well, but not because this ratio is tied to variations in seafloor spreading rate, and despite considerable mismatches to the Mg^{2+} record. This cacophony arises in part from our lack of quantitative understanding of fundamental relationships between heat flow, seafloor production rates, sea level, hydrothermal circulation rates, volcanic CO_2 release rates, and ocean chemical changes. Nevertheless, the current fluid inclusion data seem to indicate that ocean composition has an “attractor” that drives Ca^{2+} and Mg^{2+} toward equilibration with seafloor hydrothermal mineral assemblages [20 mm (millimolal) Ca^{2+} and 0 mm Mg^{2+}], thwarted by other processes (weathering and riverine inputs, biogenic mineral precipitation) that drive the system away from this attractor.

1. INTRODUCTION

The evolution of the chemistry of the ocean has been a topic of great interest for many decades. Recurring themes include calculations about the age of Earth based on the notion of accumulating salt [Joly, 1923], the question of equi-

librium vs. kinetic control of seawater chemistry [Broecker, 1971; Holland, 1972; Rubey, 1951; Sillen, 1961], and evolving thoughts about how variations in continental weathering, riverine delivery, and sediment deposition might alter ocean composition on geologic time scales [Mackenzie and Garrels, 1966].

A relative latecomer to the debate has been the role of seafloor hydrothermal fluids in determining the composition of the ocean. Before the discovery of black smokers, efforts to balance the inputs and outputs of the elements for the ocean (presuming steady state) often came up short. The most notorious of these

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was the “Mg problem,” best highlighted by the classic work of Drever [1974]. In this work, Drever showed that the input of Mg from rivers greatly exceeds the output of Mg from the ocean associated with the deposition of Mg-containing marine carbonates (calcite and dolomite) and authigenic clays. The discovery of seafloor hydrothermal systems debauching hot waters with chemical compositions quite distinct from seawater immediately raised the possibility that interaction with hot oceanic crust served as a sink for some elements and a source of others. The fact that these waters were essentially depleted of Mg seemed to once and for all solve the enigma of the missing Mg sink [e.g., Wolery and Sleep, 1976]. More recent analyses of the Mg budget highlight the significant uncertainties associated with off-axis hydrothermal and low-temperature alteration of seafloor basalt [Wolery and Sleep, 1988; Elderfield and Schultz, 1996]. These uncertainties affect the crustal Ca balance, which shows excess Ca that could reflect the cumulative effects of Ca release from basalt during hydrothermal alteration at both high and low temperatures [de Villiers, 1998].

One thing seems certain: over billion year time scales the influence of seafloor hydrothermal systems on ocean chemistry has diminished. Veizer *et al.* [1982] developed the notion that the Precambrian ocean was a “mantle-dominated” ocean because of higher seafloor production rates in the distant geologic past. The best demonstration of mantle dominance was the Sr isotopic composition of seawater, recorded in marine carbonates, which evolved from the mantle end-member to a mix of continental and mantle inputs over the course of geologic time (Figure 1). High hydrothermal Fe fluxes have also been invoked to explain the abundance of “banded iron formations” in the Archean and Paleoproterozoic [Isley, 1997], and these fluxes were likely strongly enhanced by the generally more reduced nature of hydrothermal fluids at that time given the likelihood that the oceans were essentially devoid of sulfate, a major oxidant in modern hydrothermal systems [Kump and Seyfried, 2005]. What little sulfate entered seafloor hydrothermal systems would have been reduced to sulfide and deposited in vent chimneys. Gradually, with time, heat flow, and thus, presumably, fluxes from seafloor hydrothermal systems diminished. Also with the growth of continents, chemical weathering fluxes increased, so the ocean’s $^{87}\text{Sr}/^{86}\text{Sr}$ deviated from the mantle evolution line, reflecting a balance between these two end-member compositions.

The focus of research on Precambrian ocean chemistry has been redox evolution: the progressive oxygenation of the deep sea, and associated changes in sulfur and nitrogen cycling. The general notion is that the Archean ocean was oxygen free except for “oxygen oases,” certain regions of the surface ocean where cyanobacterial blooms may have supported spatially and temporally limited buildups of mo-

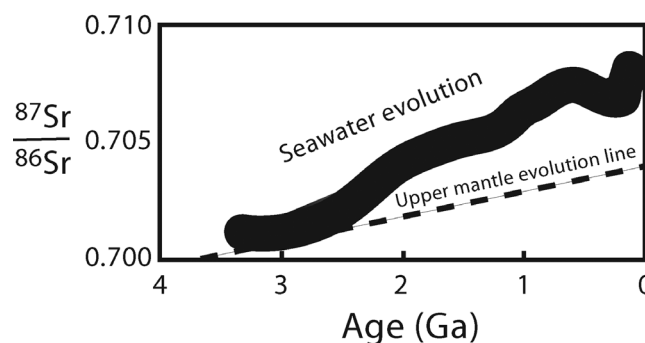


Figure 1. Schematic of the evolution of Sr isotopic composition of seawater as recorded in marine carbonate rocks through geologic time [after Veizer and Compston, 1982], demonstrating the “mantle dominance” of Archean seawater and a shift to crustal weathering dominance in the Proterozoic and Phanerozoic.

lecular oxygen in an otherwise reducing ocean/atmosphere system [Kasting, 1991]. There is a strong evidence in the mass-independent fractionation of sulfur isotopes preserved in pyrites for oxygenation of the atmosphere at about 2.4–2.5 Ga [Bekker *et al.*, 2004], and this likely led to deep-ocean oxygenation. However, oxidative weathering would have provided a new source of sulfate to the ocean. In a somewhat counterintuitive way, this may have promoted (by at least 1.8 Ga) a deep ocean enriched in hydrogen sulfide through the activity of sulfate-reducing bacteria [Canfield, 1998]. The consequences of a euxinic ocean during the Proterozoic have been pursued by a number of investigators [Anbar and Knoll, 2002; Poulton *et al.*, 2004; Shen *et al.*, 2003].

Consideration of changes in ocean chemistry during Phanerozoic time (the last 542 million years) has focused on cyclical variations in seafloor hydrothermal activity tied to the Wilson cycle of supercontinent assembly, breakup, dispersal, and reassembly. This paper reviews the evolving thoughts concerning the role of seafloor hydrothermal fluxes in driving ocean chemistry on this timescale. It is motivated by recent analyses of fluid inclusions from evaporites that have been interpreted to demonstrate substantial variations in the major element composition of seawater during the Phanerozoic, and controversy over whether these fluctuations could be driven by variable rates of seafloor production and hydrothermal activity. Arguments linking the two often have been advanced without comprehensive consideration of the intricate couplings among the element cycles and between them and climate. Models that link the cycles generate little variability in major element (especially Ca^{2+} and Mg^{2+}) composition driven by variations in seafloor hydrothermal activity. The reasons why, and implications for our understanding of these cycles, are explored below.

2. MODELING THE MG AND CA CHEMISTRY OF THE OCEANS

The notion that variation in the rate of circulation of seawater through mid-ocean ridges might drive changes in ocean chemistry was first quantified with the so-called BLAG model [Berner *et al.*, 1983]. In BLAG, the Mg^{2+} content of seawater, for example, depended on inputs from weathering of Mg-containing silicates and dolomite and outputs from dolomite formation (considered by BLAG to be unimportant from mid-Cretaceous to present) and uptake at mid-ocean ridges (presumed to be balanced stoichiometrically by release of Ca^{2+}). BLAG was a fully coupled model, so the weathering flux of Mg^{2+} was linked to the consumption of carbon dioxide from the atmosphere and transfer of bicarbonate (alkalinity) to the ocean. Thus, any conclusions one would draw from the results of BLAG concerning changes in the Mg^{2+} or Ca^{2+} content of seawater would be consistent with the strict constraints imposed by alkalinity balance in the ocean (a constraint that cannot be violated on time scales longer than the alkalinity adjustment time of the ocean, approximately 10 ka; Broecker and Peng [1987]).

One of the key attributes of BLAG, its predecessor model by Walker *et al.* [1981], and many subsequent models, is the parameterized sensitivity of chemical weathering rates to climate, and thus, through the greenhouse effect, to changes in atmospheric $p\text{CO}_2$. The first models ignored the organic carbon subcycle, thus changes in atmospheric CO_2 were driven solely by slight imbalances in the input of carbon dioxide from volcanism and output via silicate-rock weathering. Because volcanic activity was presumed to be linearly dependent on seafloor production rate, an increase in the global average seafloor spreading rate was modeled to drive a proportional increase in the volcanic CO_2 release rate, silicate weathering rate, and finally, CaCO_3 deposition rate [Berner *et al.*, 1983].

To assess the implications of varying seafloor-spreading rates on ocean chemistry, Berner *et al.* [1983] made the further assumption that seafloor hydrothermal fluxes would be linearly proportional to seafloor spreading rates. More specifically, the uptake of Mg was proportional to the seafloor production rate and the concentration of Mg^{2+} ($[\text{Mg}^{2+}]$) of seawater, and the release rate of Ca^{2+} was equal to that of Mg^{2+} uptake. Finally, various reconstructions of spreading rates in the geologic past were used as forcing functions of the model (together with reconstructed changes in land area available for weathering). The result of this modeling effort was “postdictions” of the evolution of ocean chemistry, specifically changes in Ca^{2+} and Mg^{2+} concentrations over the last 100 Ma (Figure 2). According to BLAG, oceanic $[\text{Mg}^{2+}]$ rose in the Late Cretaceous and then fell through the

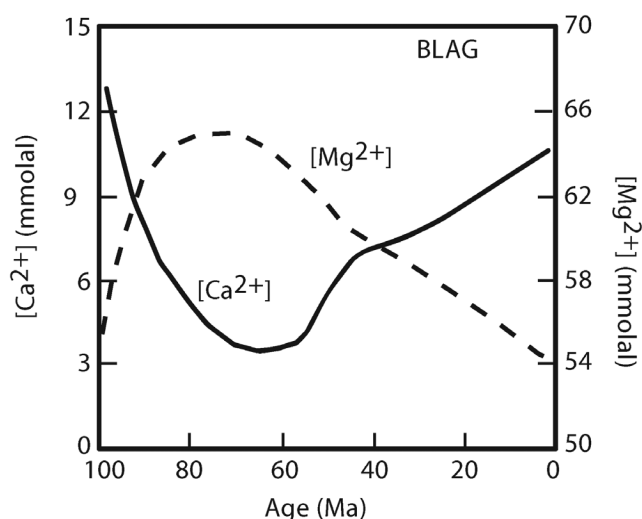


Figure 2. Calculated variations in calcium and magnesium seawater concentrations over the last 100 Ma with a model that couples volcanic CO_2 release and hydrothermal uptake of magnesium and release of calcium to seafloor spreading rates (the so-called BLAG model; Berner *et al.*, 1983).

Cenozoic, whereas $[\text{Ca}^{2+}]$ displayed a mirror-image pattern, as one might expect from a system that was dominated by seafloor hydrothermal exchange of Mg^{2+} for Ca^{2+} .

3. RECONSTRUCTING ANCIENT SEAWATER CHEMISTRY FROM BRINE INCLUSIONS IN SALT DEPOSITS

Subsequent to BLAG there has been a considerable amount of modeling by Berner and his colleagues (the generations of GEOCARB models), and by others, aimed both at refining the estimates of ancient levels of atmospheric CO_2 and O_2 and at improving our understanding of the processes that drive long-term evolution in ocean and atmospheric chemistry [e.g., Arvidson *et al.*, 2006; Berner, 2006; Berner and Kothalava, 2001; Godderis *et al.*, 2007; Wallmann, 2001]. Little attention has been paid, until recently, to improving the calculation of secular changes in major element (e.g., Ca^{2+} and Mg^{2+}) composition of seawater. The most significant breakthrough in the past 20 years of research on ancient-ocean chemistry has instead been the analysis of brine inclusions in salt and their interpretation in terms of changes in ocean chemistry through geologic time. Two groups have worked in parallel to establish these trends: the “Harvard” group led by H. D. Holland [e.g., Horita *et al.*, 2002, and references therein] and the “Johns Hopkins/Binghamton” group led by L. Hardie, T. Lowenstein, and R. Demicco (see references in Lowenstein *et al.* [2003]). These workers

extract minute quantities of evaporated seawater that have been retained and preserved in salt crystals. Analyses of the composition of these fluids are then corrected for inferred evaporation paths and mineral precipitation sequences so that ancient seawater compositions can be estimated.

The latest results from both groups are quite consistent, especially in terms of mirror-image variations in Ca and Mg concentrations (Figure 3) not unlike those of BLAG. The early Paleozoic and mid-Mesozoic were times of high $[Ca^{2+}]$ and low $[Mg^{2+}]$. These results are consistent with the finding that marine carbonates deposited during this time were largely originally calcite, a mineral that is kinetically favored over its polymorph aragonite when $[Mg^{2+}]/[Ca^{2+}]$ ratios are low [e.g., Stanley and Hardie, 1998]. In contrast, the Late Paleozoic/Early Mesozoic and much of the Cenozoic were times of high $[Mg^{2+}]/[Ca^{2+}]$, with abundant evidence for primary aragonite.

Two interpretations of these trends have been proposed:

1. They represent variations in the rates of Mg uptake and Ca release during high-temperature hydrothermal circulation of seawater through mid-ocean ridges [e.g., Spencer and Hardie, 1990; Demicco *et al.*, 2005]. For the Cretaceous to Recent, these rates are estimated based on measured variations in seafloor production rates. For earlier times, the extent of flooding of the continents is used as a proxy for

sea level, itself an assumed proxy for seafloor spreading (production) rates [Gaffin, 1987]. Times of maximal continental flooding (e.g., the early Paleozoic and mid-Mesozoic) were times of high sea level caused by broad, shallow mid-ocean ridges created by fast seafloor spreading. Fast seafloor spreading supported high rates of Ca release and Mg uptake at mid-ocean ridges, and thus low ratios of $[Mg^{2+}]/[Ca^{2+}]$ in the ocean. Intervals during which the continents were maximally exposed were times of low sea level, slow seafloor spreading, and low rates of cation exchange leading to high ratios of $[Mg^{2+}]/[Ca^{2+}]$.

2. They represent variations in the rates of dolomitization of preexisting limestones or contemporaneously deposited limestones [Holland, 2005]. Times of maximum continental flooding are times when shallow, restricted marine basins should be abundant; these types of environments are presumed to be ideal for the development of dolomitizing basinal fluids.

The seafloor hydrothermal interpretation was proffered first, and provided what seemed to be a self-consistent explanation for secular variations in seawater chemistry, biogenic mineralogy, and sea level. However, any celebrations were short-lived; the analysis of seafloor production rates through time by Rowley [2002] concluded that the present-day distribution of ages and areas of seafloor is entirely consistent with a constant rate of production of seafloor through time (over the last 150 Ma or so) coupled to age-independent seafloor destruction rates. Indeed, it was the work of Rowley [2002] that prompted the second explanation for inverse covariation of $[Mg^{2+}]$ and $[Ca^{2+}]$ through the Phanerozoic. Moreover, a reanalysis of eustatic sea level variations by Miller *et al.* [2005] downscaled the amplitude of Mesozoic-Cenozoic variations from 200 to 300 m to much closer to that explainable by glacioeustasy (100–200 m). If Rowley is correct [cf. Demicco, 2004], and seafloor spreading rates have been essentially invariant in time, then variations in hydrothermal fluxes cannot be invoked to explain the pattern of variation of $[Mg^{2+}]/[Ca^{2+}]$.

4. RECONCILING MODELS AND PROXIES OF $[Mg^{2+}]$ AND $[Ca^{2+}]$ VARIATION

Although much-improved models exist, the BLAG model is the simplest expression of an important concept: secular variations in seafloor spreading rates drive changes in volcanic CO_2 release that lead to climate change on long time scales. Moreover, these variations are also reflected in changes in the Mg/Ca ratio of seawater. Curiously, the BLAG model calculations of oceanic $[Mg^{2+}]$ and $[Ca^{2+}]$ bear little resemblance to the time histories derived from the study of brine inclusions. The data clearly indicate that

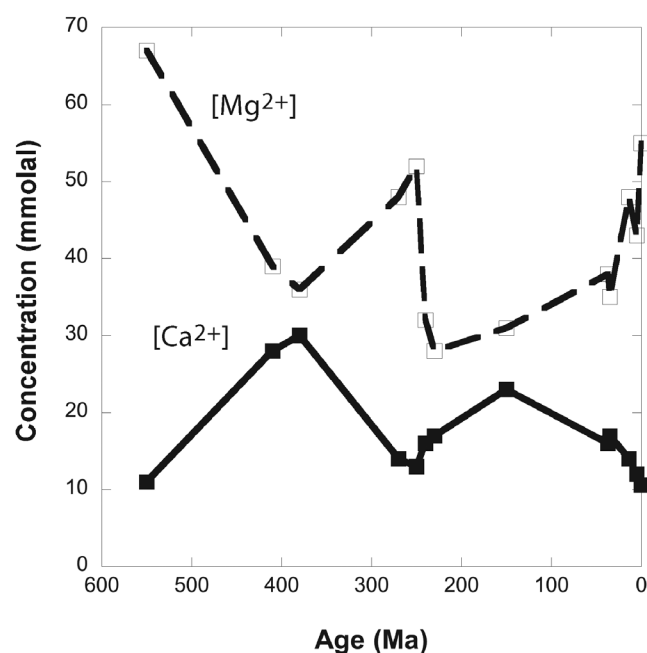


Figure 3. Evolution of seawater concentration of Mg^{2+} and Ca^{2+} reconstructed from the analysis of fluid inclusions in marine evaporites [Horita *et al.*, 2002].

[Mg²⁺] has increased and [Ca²⁺] has decreased from the mid-Cretaceous to Recent, whereas the BLAG calculation shows just the reverse. This is even more peculiar when one realizes that modeling done by the Hopkins/Binghamton group [e.g., *Demicco et al.*, 2005] reproduces the secular variations quite closely. How can two classes of numerical model, both driven by essentially the same presumed secular variation in seafloor spreading rates, generate such different results?

Even more baffling are the recent modeling predictions of [Mg²⁺] and [Ca²⁺] again by *Berner* [2004] that reproduce the observed trends from fluid inclusions quite closely. What is the key difference between BLAG of *Berner et al.* [1983] and *Berner* [2004]?

First, we must delve into the modeling of *Berner* [2004]. In this work, *Berner* utilized the fact that, over long time scales (>10⁴ years), the alkalinity inputs to and outputs from the ocean must be balanced. When that constraint and the exchange of Ca for Mg at mid-ocean ridges are applied to the balance equations for Mg²⁺ and Ca²⁺, an interesting result emerges: secular variations in Ca²⁺ must mirror those of Mg²⁺ except to the extent that imbalances of the sulfur cycle allow Ca to vary independently of Mg²⁺:

$$\frac{d[\text{Ca}^{2+}]}{dt} = -\frac{d[\text{Mg}^{2+}]}{dt} + (\text{gypsum weathering} - \text{deposition}) + 0.7 (\text{pyrite weathering} - \text{pyrite burial}).$$

Pyrite burial and weathering are involved because the acidity produced by pyrite oxidation is in part involved in Ca mineral weathering, whereas the alkalinity generated during sulfate reduction drives the precipitation of CaCO₃ (0.7 represents the fraction of the sulfuric acid generated that reacts with Ca-bearing minerals). *Berner* [2004] uses the C and S isotope modeling of *Berner* [2001] to provide the C and S fluxes necessary to drive calculations of Ca and Mg variation through time. These generate mirror-image trends that match observations quite well. The calculations represent an improvement over those of the Hopkins/Binghamton group because they explicitly conform to alkalinity mass balance.

However, both the *Berner* [2004] and the Hopkins/Binghamton group models lacked the explicit link between seafloor spreading and volcanic CO₂ emission of BLAG and GEOCARB models. In models where this link is included, an increase in seafloor spreading rate drives proportional increased hydrothermal uptake of Mg²⁺, and [Mg²⁺] tends to fall, as in all other models. However, increased spreading drives proportionally higher weathering rates (i.e., Mg²⁺ input rates). Thus, the tendency toward lower [Mg²⁺] from increased hydrothermal uptake is countered by increased riverine Mg²⁺ delivery, and [Mg²⁺] remains relatively unchanged

(as long as the weathering adjustment is fast relative to the Mg²⁺ residence time of the ocean). [Ca²⁺] variability is also damped, but for a different reason: increased spreading increases both the weathering and hydrothermal inputs, which would tend to increase [Ca²⁺]. However, the ocean remains near saturation with respect to CaCO₃, so this excess Ca input is quickly countered by increased CaCO₃ burial.

This tendency toward damping is best illustrated in a highly simplified model. Here the simplified carbonate-silicate geochemical cycle model of *Payne and Kump* [2007] is modified to also calculate changes in Ca and Mg with time. The oceanic reservoir of Mg²⁺ changes through time according to:

$$\frac{d(\text{Mg}^{2+})}{dt} = F_{\text{wMgsil}} + F_{\text{wdol}} - F_{\text{hydrMg}}$$

where F_{wMgsil} and F_{wdol} are the weathering flux of Mg²⁺ from silicates and dolomite, respectively, each calculated by the model to depend on changes in atmospheric pCO₂ [*Payne and Kump*, 2007], and F_{hydrMg} is the rate of hydrothermal uptake of Mg²⁺, expressed as:

$$F_{\text{hydrMg}} = F_{\text{hydrMg}}^0 \cdot f_{\text{SR}} \cdot \frac{[\text{Mg}^{2+}]}{[\text{Mg}^{2+}]^0}.$$

Here, F_{hydrMg}^0 is the present-day steady state hydrothermal uptake rate of Mg²⁺, 5.2×10^{18} mol/yr [*Berner et al.*, 1983], f_{SR} is the seafloor spreading rate according to *Gaffin* [1987] as presented by *Demicco et al.* [2005], and $[\text{Mg}^{2+}]^0$ is today's Mg²⁺ concentration [55 mm (millimolal)]. Similarly, the oceanic reservoir of Ca²⁺ changes through time according to:

$$\frac{d(\text{Ca}^{2+})}{dt} = F_{\text{wCasil}} + F_{\text{wdol}} + F_{\text{wcarb}} + F_{\text{hydrCa}} - F_{\text{bcarb}}$$

where F_{wCasil} , F_{wdol} , and F_{wcarb} are the weathering fluxes of Ca²⁺ from silicates, dolomites, and limestones, respectively, each calculated by the model to depend on changes in atmospheric pCO₂ [*Payne and Kump*, 2007], and F_{hydrCa} is the rate of hydrothermal uptake of Ca²⁺, expressed as:

$$F_{\text{hydrCa}} = F_{\text{hydrCa}}^0 \cdot f_{\text{SR}} \cdot \frac{41 - [\text{Ca}^{2+}]}{31}.$$

Here, F_{hydrCa}^0 is the present-day steady-state hydrothermal uptake rate of Ca²⁺, 5.2×10^{18} mol/yr [*Berner et al.*, 1983], and the numbers 31 and 41 are selected to (1) give a value of the quotient of 1 for the modern [Ca²⁺] of 10 mm, and (2) be consistent with the vent fluid composition chosen by *Demicco et al.* [2005] (41 mm; see below).

In the fully coupled model, changes in spreading rate drive changes in volcanic CO₂ outgassing and proportional changes in Mg uptake and Ca release from hydrothermal

systems. This system behaves as described above: even with spreading rates $2.5\times$ higher than present, the Ca^{2+} and Mg^{2+} contents of the ocean are essentially identical to today (Figure 4) and unchanging in time (this model does not include the sulfur cycle dependencies of *Berner* [2004]). Only with the dependence of CO_2 outgassing on seafloor spreading disabled do fluctuations in seafloor spreading drive variations in Ca^{2+} and Mg^{2+} that mimic the observed record (Figure 4).

What then explains the temporal variability of $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ in BLAG? There are two factors involved:

(1) *Berner et al.* [1983] initiated their model at 100 Ma far from steady state, so $[\text{Mg}^{2+}]$ increased and $[\text{Ca}^{2+}]$ decreased for the first 30 Ma of the simulation as the system sought steady state [*Kasting*, 1984]; and

(2) the quasi-steady state $[\text{Mg}^{2+}]$, once achieved, declined from 100 Ma to the present because the sedimentary dolomite Mg reservoir shrunk, and so the weathering input of Mg^{2+} , presumed proportional to the reservoir size, diminished as the input of Ca^{2+} increased. The dolomite reservoir decreased (and limestone reservoir increased) over this interval because *Berner et al.* [1983] specified that no dolomite formation has occurred during this interval of time (a common presumption). If, instead, dolomite production and

weathering were closely balanced, BLAG would dictate that $[\text{Mg}^{2+}]$ was essentially invariant in time.

The MAGic model of *Arvidson et al.* [2006] provides a state-of-the-art box model of the geochemical cycling of the elements, highly evolved from BLAG, fully coupled, and comprehensive, including factors like dolomite formation that were not part of BLAG. *Arvidson et al.* [2006] use MAGic to address important issues in ocean chemical evolution such as the impact of the evolution of pelagic carbonate production, the importance of dolomite formation and whether it occurs during early diagenesis or deep burial, and the impact of authigenic silicate mineral formation in the ocean (reverse weathering). In the standard MAGic simulations, spreading rate variations drive changes in volcanic CO_2 outgassing and mid-ocean ridge hydrothermal fluxes. Interestingly, although MAGic fits the fluid inclusion $[\text{Ca}^{2+}]$ and Mg/Ca ratio quite closely, $[\text{Mg}^{2+}]$ variations deviate from observed levels: whereas observed $[\text{Mg}^{2+}]$ reaches a minimum at the end of the Paleozoic, MAGic reaches a maximum. Likewise, the Mesozoic trends are generally inverted. Similarly, the model of *Hansen and Wallmann* [2003] predicts little variation in $[\text{Mg}^{2+}]$ from seafloor spreading variations because of compensating changes in riverine Mg input. The modeled Cenozoic rise in $[\text{Mg}^{2+}]$ is rather the result of intensified carbonate weathering caused by increased exposure of carbonate terrains.

Where does this leave us? Models that incorporate a tight coupling between seafloor spreading, volcanism, climate, and weathering predict a less variable seawater composition (especially for Mg) than reconstructed from the brine inclusion record because of compensating effects. However, there is a compelling correspondence between the extent of continental flooding and the observed $[\text{Mg}^{2+}]$ and $[\text{Ca}^{2+}]$ of seawater. Either seawater chemistry is indeed driven by variations in seafloor hydrothermal fluxes reflected in inferred sea level fluctuations, and the seafloor spreading-volcanism- CO_2 link is much weaker than previously thought (i.e., the modeling of the Hopkins/Binghamton group is largely correct), or the chemistry of seawater instead has been driven primarily by other factors, for example, variations in rates of dolomitization modulated by secular changes in the extent of continental inundation [*Holland*, 2005] resulting from some factor other than seafloor spreading-driven mid-ocean ridge volume changes [*Rowley*, 2002]. Of course, this option also lessens the importance of the relationship between seafloor spreading and volcanic CO_2 emission anyway, because seafloor spreading rates do not vary. In either case, changes in atmospheric CO_2 driven by variations in volcanic CO_2 release not tied to seafloor spreading, and tectonic changes driving variations in the rate of CO_2 consumption during weathering, both important factors in subsequent GEOCARB mod-

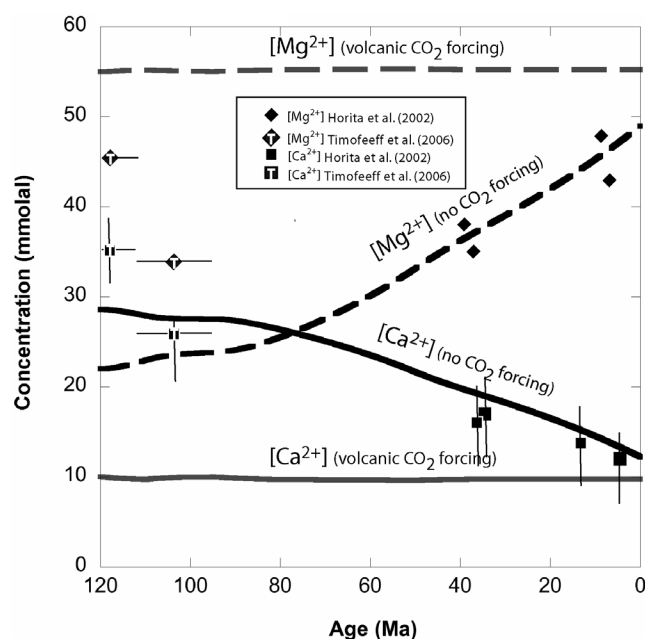


Figure 4. Modeled and observed variations of Mg^{2+} and Ca^{2+} from 120 Ma ago to the present. Two simulations are shown; one in which variations in seafloor spreading rate drive changes in atmospheric CO_2 as well as in Ca^{2+} and Mg^{2+} , and another in which the link to CO_2 is removed. Data from *Horita et al.* [2002] and *Timofeeff et al.* [2006].

eling by Berner and colleagues [e.g., *Berner and Kothalava*, 2001], together with biotically driven changes in the organic carbon cycle, remain as likely climate drivers over Phanerozoic time scales. Indeed, sensitivity analysis of the most recent models, including GEOCARB and MAGic, produces atmospheric CO₂ curves that match the proxy record quite well while specifying constant seafloor spreading rates.

Perhaps the answer to the question of what drives coupled variations in [Mg²⁺ and Ca²⁺] still resides in the evaporite brine inclusion record. The Phanerozoic data, recast in phase space, reveal an interesting pattern (Figure 5): [Mg²⁺] and [Ca²⁺] are inversely related when [Ca²⁺] is <~20 mm, and positively related above this concentration. One possible explanation of this behavior is that seafloor hydrothermal activity is indeed driving ocean chemical composition toward an “attractor,” a fluid equilibrated with hot basalt. This attractor would have an equilibrium [Ca²⁺] of ~20 mm (based on Figure 5) and an equilibrium [Mg²⁺] of 0. Interestingly, the observed [Ca²⁺] of vent fluids, corrected for phase separation by normalizing to seawater salinity, is 20 mm [*Seyfried et al.*, 1991] (note that this is considerably smaller than the 41 mm used by *Demicco et al.* [2005]). Hypothetically, when [Ca²⁺] in the oceans is <20 mm, seawater circulating through the ridges loses Mg²⁺ and accumulates Ca²⁺ with

$$\frac{d[\text{Mg}^{2+}]}{d[\text{Ca}^{2+}]} = -\frac{[\text{Mg}^{2+}]}{20 - [\text{Ca}^{2+}]},$$

or a slope with [Mg²⁺] = 50 mm and [Ca²⁺] = 10 mm of -5 (approximately the slope through this range of [Ca²⁺] in Figure 5). When [Ca²⁺] exceeds 20 mm, seafloor alteration acts as a sink for both Ca and Mg; the slope of this relationship for a [Mg²⁺] = 40 mm and [Ca²⁺] = 30 mm is +4, again compatible with the observed slope of the relationship at these higher concentrations of Ca.

Of course, this mechanism is highly speculative, and requires considerably more investigation. If secular variations in seafloor hydrothermal activity need to be invoked to explain the Ca and Mg chemical evolution of the oceans, and if these variations tend to correlate with extent of continental flooding, then we need to address the mechanism that relates these phenomena [cf. *Rowley*, 2002; *Demicco*, 2004]. Alternatively, if the “attractor” idea has merit, then perhaps other variables such as rates of dolomitization [*Holland*, 2005] or rates of sulfur cycling [*Berner*, 2004] drive the system away from the attractor, and then hydrothermal activity (possibly relatively invariant) carries the system back toward the attractor.

In any event, the notion that the rate of volcanic CO₂ release scales proportionately to seafloor production rates is challenged by the observed variations in seawater chemis-

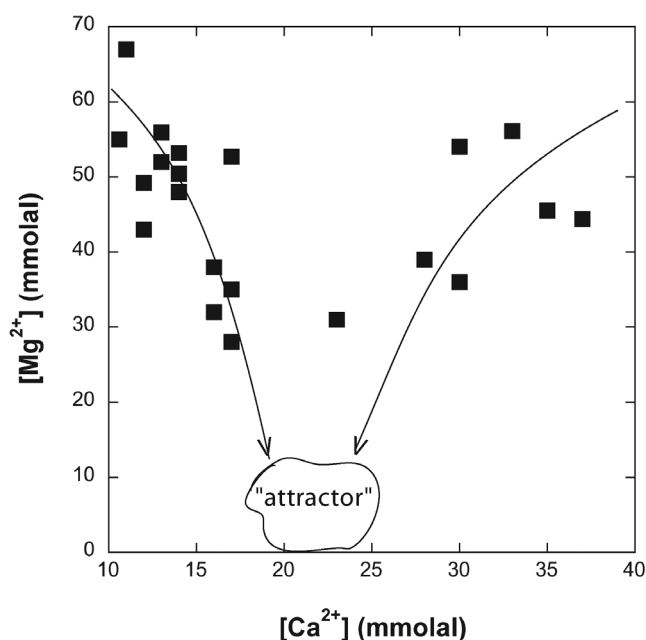


Figure 5. Relationship between Mg²⁺ and Ca²⁺ concentrations in Phanerozoic seawater (data from *Horita et al.* 2002; *Lowenstein et al.* 2003) showing an inferred “attractor” for seawater composition determined by the equilibrium composition of seafloor hydrothermal vent fluids.

try through time, causing us to look elsewhere, for example, tectonically driven changes in metamorphic degassing and continental weatherability, biological innovations that affect carbon cycling, that is, the multitude of other factors that go into the current GEOCARB, MAGic, and related models. Progress on understanding seawater chemical evolution depends on fundamental breakthroughs in our understanding of the relationships between variations in seafloor production rate (if they exist), seafloor spreading rates, sea level, hydrothermal fluid fluxes and compositions, and volcanic CO₂ release rates.

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