

# Seawater chemistry driven by supercontinent assembly, breakup, and dispersal

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## ABSTRACT

**Global oceans are known to have alternated between aragonite and calcite seas. These oscillations reflect changes in the Mg/Ca ratios of seawater that control biomineralization and the composition of marine carbonates, and are thought to be caused mainly by the time dependence of crustal accretion at mid-ocean ridge crests and the associated high-temperature mid-ocean ridge fluid flux. Here we use global ocean basin reconstructions to demonstrate that the fluctuations in hydrothermal ocean inputs are instead caused by the gradual growth and destruction of mid-ocean ridges and their relatively cool flanks during long-term tectonic cycles, thus linking ocean chemistry to off-ridge low-temperature hydrothermal exchange. Early Jurassic aragonite seas were a consequence of supercontinent stability and a minimum in mid-ocean ridge length and global basalt alteration. The breakup of Pangea resulted in a gradual doubling in ridge length and a 50% increase in the ridge flank area, leading to an enhanced volume of basalt to be altered. The associated increase in the total global hydrothermal fluid flux by as much as 65%, peaking at 120 Ma, led to lowered seawater Mg/Ca ratios and marine hypercalcification from 140 to 35 Ma. A return to aragonite seas with preferential aragonite and high-Mg calcite precipitation was driven by pronounced continental dispersal, leading to progressive subduction of ridges and their flanks along the Pacific rim.**

## INTRODUCTION

The major ion chemistry of the world's oceans has oscillated dramatically during the Phanerozoic Eon (Hardie, 1996; Sandberg, 1983). These changes are seen in the mineralogy of marine carbonates (Dickson, 2002; Hardie, 1996; Sandberg, 1983), composition of fluid inclusions in marine halite (Horita et al., 2002; Lowenstein et al., 2001), mineralogy of marine potash evaporites (Hardie, 1996), the polymorph mineralogy of hypercalcifying marine organisms (Ries, 2010), and the composition of calcium carbonate veins in oceanic basalt (Coggon et al., 2010). Geochemical evidence indicates that the oscillations between aragonite seas, during which aragonite and high-Mg calcite precipitate, and calcite seas, during which low-Mg calcite precipitates, are controlled by changes in the Mg/Ca ratio of seawater (Hardie, 1996).

Hydrothermal fluid flow and chemical exchange between seawater and mid-ocean ridge basalt are known to be linked (Staudigel, 2003), exerting a strong control on the Mg/Ca ratio of seawater (Alt, 1995; Elderfield et al., 1999; Mottl, 2003). Through its interaction with seawater, ocean crust is a sink for Mg and a source of Ca, predominantly via the formation of smectite, chlorite, and saponite due to alteration of pillow basalts, sheeted dikes, and gabbros (Alt, 2003, 1995; Elderfield et al., 1999). Additional removal of Mg and Ca occurs during the formation of vein and vesicle-filling carbonate and carbonate-cemented breccias in basalt from low-temperature fluids (Alt, 1995; Coggon et al., 2010). High crustal production rates and the associated increase in total global hydrothermal

fluid flux driven by magmatic heat associated with the formation of hot, young, permeable oceanic crust (Mottl, 2003) are thought to lower the Mg/Ca ratio of seawater (Hardie, 1996), but geological observations alone cannot be used to validate this hypothesis or elucidate the mechanisms driving these changes.

Secular shifts in the Mg/Ca ratio of seawater have been linked conceptually to cycles in crustal production (Coggon et al., 2010; Hardie, 1996; Horita et al., 2002; Stanley and Hardie, 1998). Here we investigate the tectonic forces driving these changes and their time dependence by developing a model for crustal production rates and fluid flux through time. Analyses of residual oceanic heat flow (the difference between heat flow predicted from a conducting thermal boundary layer model and observed heat flow) suggest that the crustal hydrothermal reservoir becomes isolated from seawater near 65-m.y.-old crust (Stein and Stein, 1994). There is strong additional observational evidence that alteration of ocean crust at low temperatures persists to a crustal age of at least 65 Ma, including cumulative vein mineral ages based on the distribution of isotopic ages of secondary minerals from the Troodos ophiolite and various Deep Sea Drilling Project sites, ranging from 0 Ma to older than 30 Ma (Booij et al., 1995), and a decrease in the macroporosity and matrix density paralleled by an increase in crustal seismic velocity in ocean crust older than 65 Ma (Jarrard, 2003), reflecting continuing precipitation of carbonate and clay minerals. There is additional evidence from local heat flow observations (Von Herzen, 2004) that hydrothermal

alteration may continue in ocean crust older than 65 Ma, but because residual heat flow is close to zero in these regions, there is no basis for modeling the associated fluid flux here.

The oceanic hydrothermal fluid flux through mid-ocean ridges and their flanks on crust as much as 65 m.y. old can be approximated as a function of residual heat flow and basement temperature (Johnson and Pruis, 2003). Our approach is based on the observation that only ~30% of the total global hydrothermal fluid flux (Stein and Stein, 1994) occurs in crust younger than 1 Ma via active vents along mid-ocean ridge crests at mean temperatures of 350 °C ± 30 °C (Mottl, 2003). The majority of heat loss occurs by passive convection on ridge flanks (Mottl, 2003; Stein and Stein, 1994) and involves low-temperature hydrothermal circulation driven by heat conducted in 1–65-m.y.-old crust (Stein and Stein, 1994) through lithospheric cooling (Mottl, 2003) as long as permeability remains (Stein and Stein, 1994). This involves a loss of >80% Mg from seawater-derived hydrothermal fluids during fluid-rock interaction at temperatures >45 °C and <10% at temperatures ≤25 °C (Mottl and Wheat, 1994).

The fact that the majority (60%–70%) of heat loss occurs as a result of passive circulation through older oceanic crust indicates that ridge flank contributions to global geochemical budgets may be significant. Differing from previous models based on inferred changes in hydrothermal fluid flux through time derived entirely from geochemical observations and proxies, we forward model global changes in both the axial and ridge flank hydrothermal fluid fluxes since 200 Ma, and relate them to observed variations in marine calcification that reflect changing ocean chemistry.

## METHODOLOGY

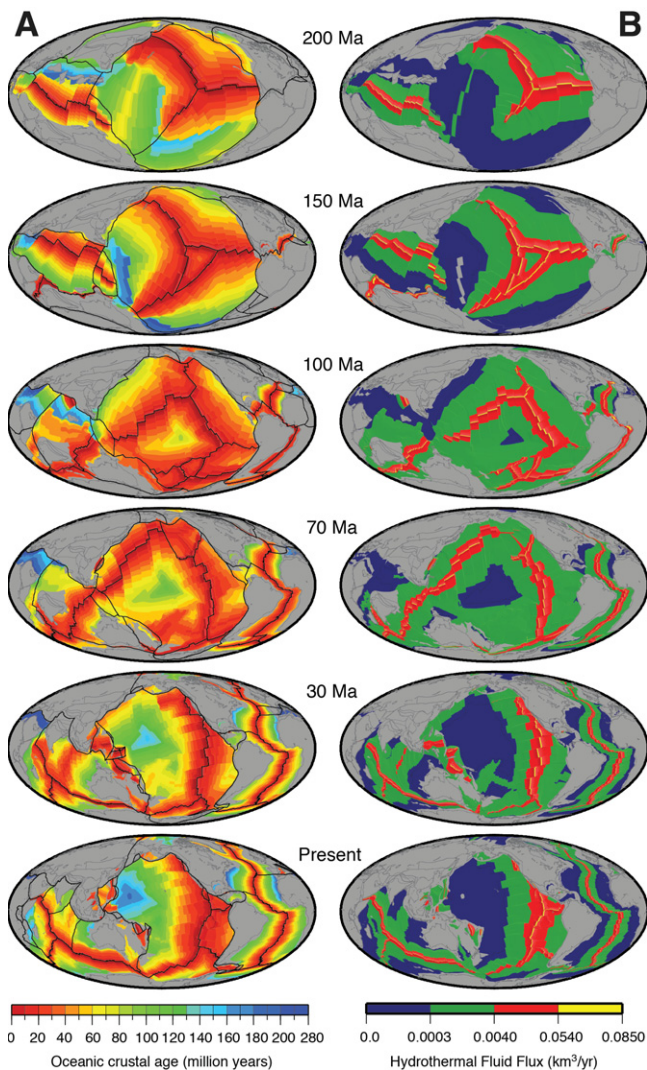
We combine two methodologies (Johnson and Pruis, 2003; Müller et al., 2008b) to quantify the hydrothermal fluid flux through time via reconstructions of the area of 0–65-m.y.-old ocean crust from 200 Ma to the present. Johnson and Pruis (2003) used a compilation of crustal porosities, heat flow, and sediment thickness to compute hydrothermal reservoir temperatures and mean hydrothermal flux into the deep ocean as a function of crustal age. We follow the assumption that the relationship between observed oceanic heat flow and that expected from a conductive plate model, representing

two-way advection of heat and fluid between the crustal reservoir and overlying seawater (Stein and Stein, 1994), holds for past oceanic age-area distributions. We compute past hydrothermal fluid flux as a function of oceanic heat flow derived from reconstructions of the age-area distribution of the global ocean floor (Fig. 1), based on the plate model in Seton et al. (2012). This provides the basis for computing residual heat flow, basement temperature, and fluid flux through time. The errors of our computed fluid flux include uncertainties in the age-area distribution of all ocean floor, including now-subducted crust, through time, following the methodologies of Müller et al. (2008a, 2008b). In addition, there are uncertainties in mapping hydrothermal fluid flux as a function of crustal age (Johnson and Pruis, 2003). However, these are relatively small compared to the very substantial tectonic reconstruction uncertainties mainly due to uncertainties in reconstructing now-subducted ocean floor.

## RESULTS

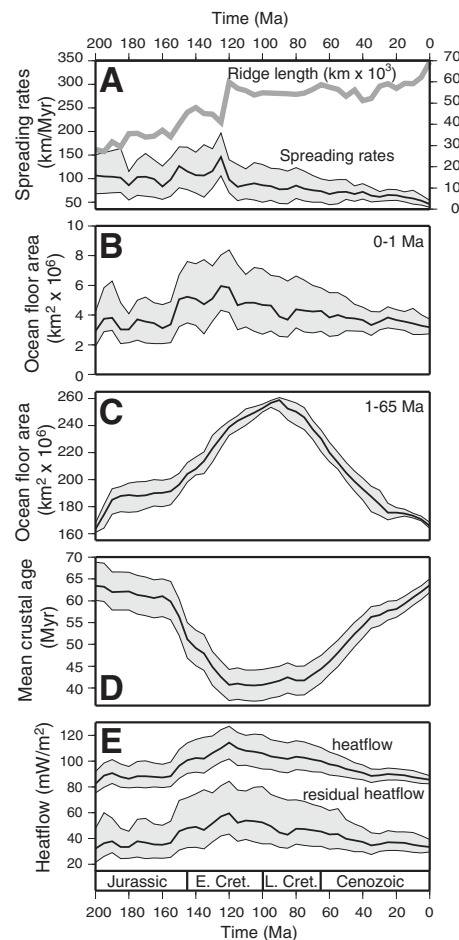
Computed oceanic heat and fluid flow, ocean-floor area, and mean age of the crust over the past 200 m.y. (Fig. 2) correlate with major transitions in ocean chemistry in the Late Jurassic–Early Cretaceous and late Cenozoic, consistent with geological observations (Stanley and Hardie, 1998) (Fig. 3). Aragonite seas in the Jurassic were associated with a mid-ocean ridge system only about half as long (~30,000 km) as the present-day system (Fig. 2A). The origin for the transition from aragonite to calcite seas ca. 140 Ma was in the breakup of the supercontinent Pangea in the central North Atlantic ca. 200 Ma and the subsequent formation of the Pacific plate ca. 190 Ma, resulting in a 25% increase in ridge length between 200 Ma and 140 Ma. These events contributed toward a substantial increase in the production rate of ocean crust and thus an increase in the volume of basalt being altered.

Between 200 Ma and 120 Ma, the area of ocean floor 1–65 m.y. in age increased from



**Figure 1. Oceanic crustal age and hydrothermal fluid flux since 200 Ma. A: Crustal age-area distribution. B: Resulting hydrothermal fluid flux (in units of  $\text{km}^3/\text{yr}$  per unit area sized  $0.1^\circ \times 0.1^\circ$ ), taking into account average size (in  $\text{km}^2$ ) of this area given global latitudinal distribution of grid cells contributing to fluid flux. Lithospheric cooling causes basalt alteration via percolation of seawater in crust aged 0–1 m.y. (yellow) at high temperatures to  $400^\circ\text{C}$  and in crust aged 1–20 m.y. (red) and 20–65 m.y. (green) at low temperatures between  $30^\circ\text{C}$  and  $60^\circ\text{C}$ . Hydrothermal fluid flux in crust older than 65 m.y. (blue regions) is negligible. Note dramatic fluctuations in ocean-floor area 1–65 m.y. old, highlighting time-dependent contribution of ridge flanks to hydrothermal fluid flux. Thin black lines denote plate boundary locations.**

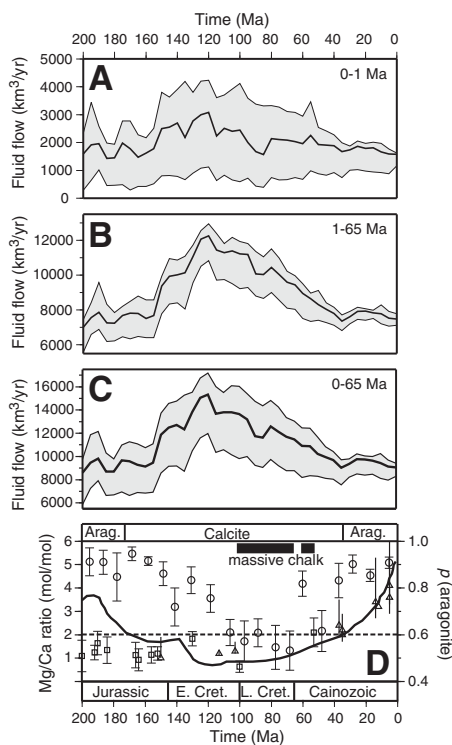
~ $170 \times 10^6 \text{ km}^2$  to  $260 \times 10^6 \text{ km}^2$  (Fig. 2C). In contrast, the crustal area 0–1 m.y. in age stayed relatively constant because a long-term increase in ridge length was roughly compensated for by a concurrent decrease in spreading rates (Figs. 2A and 2B). The ridge flank area of ocean floor 1–20 m.y. old, known to be subject to substantially more vigorous fluid flow than older crust (Gillis and Coogan, 2011), peaked in the Cretaceous Period (Fig. 1), ca. 120 Ma (Fig. DR4 in the GSA Data Repository<sup>1</sup>). From 120 to 65 Ma, ridge length and crustal production remained



**Figure 2. Key seafloor spreading parameters 200 Ma to present day. A: Mean global spreading rates and mid-ocean ridge length (scale  $0\text{--}70 \text{ km} \times 10^3$ ). B: Global ocean-floor area aged 0–1 m.y. C: Global ocean-floor area aged 1–65 m.y. D: Mean crustal age. E: Top—global mean oceanic paleo-heat flow based on paleo-age-area distribution and heat flow–age relationship (Stein and Stein, 1994). Bottom—residual paleo-heat flow is based on present-day residual heat flow–age relationship, expressing difference between observed oceanic heat flow and that predicted by a cooling plate model as function of age (Johnson and Pruis, 2003). Error envelopes are based on estimated oceanic crustal paleo-heat flow reconstruction errors.**

<sup>1</sup>GSA Data Repository item 2013249, additional details on methodology and results, is available online at [www.geosociety.org/pubs/ft2013.htm](http://www.geosociety.org/pubs/ft2013.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.





**Figure 3. Hydrothermal fluid flux and carbonate geochemistry.** A: Global mean fluid flux in ocean crust aged 0–1 m.y.; uncertainties in gray. Note that these fluctuations are all within model uncertainties. B: Global mean fluid flux in ocean crust aged 1–65 m.y.; uncertainties in gray. C: Global mean fluid flux in ocean crust aged 0–65 m.y.; uncertainties in gray. D: Calculated oceanic Mg/Ca ratio through time (Stanley and Hardie, 1998); horizontal dashed line at Mg/Ca ratio of 2 represents boundary between low-Mg calcite (Mg/Ca < 2) and aragonite (Arag.) + high-Mg calcite (Mg/Ca > 2) nucleation fields (Hardie, 1996). Proportional abundance ( $p$ ) of aragonitic reef builder fossils through time (circles) (Kiessling et al., 2008) and Mg/Ca ratio of seawater estimated from fluid inclusions (triangles) (compiled by Hönisch et al., 2012) and echinoderms (squares; Dickson, 2002) provide uncertainties on seawater Mg/Ca ratio estimates through time. Age range of massive chalk deposits (Stanley and Hardie, 1998) is also shown. Cret.—Cretaceous; E.—early; L.—late.

more or less constant. The area of 1–65-m.y.-old ridge flank crust peaked at 90 Ma (Fig. 2C), followed by a gradual decline in crustal production by ~25% during the Paleogene and Neogene. However, there was a dramatic decrease to ~160 × 10<sup>6</sup> km<sup>2</sup> in the ridge flank area of ocean floor 1–65 m.y. in age after 100 Ma. This decline is associated with a reduction in ridge flank-hosted fluid flux from ~10,500 to ~7500 km<sup>3</sup>/yr, whereas the high-temperature fluid flux associated with young 0–1-m.y.-old ocean floor declined insignificantly during the Cenozoic.

Our model results in a gradual fluid-flow decrease after a peak at 120 Ma, driven by successive subduction of ridge flanks. A distinct

inflection point in fluid flux at 35 Ma (Fig. 3C) marks the end of the slow Paleogene decline in the total global hydrothermal fluid flux, in agreement with observations constraining the transition from calcite to aragonite seas occurring at about that time (Stanley and Hardie, 1998; Fig. 3D).

## DISCUSSION

We observe good agreement between our computed total global hydrothermal fluid flux history and published data on crustal alteration. Approximately 75% of all secondary minerals in ocean crust (Booij et al., 1995) and ~80% of void-filling carbonates (Coggon et al., 2010) are observed to form within 20 m.y. of crustal emplacement; this is in excellent agreement with our model, predicting between 73% (at present) and 78% (at 100 Ma) of fluid flux occurring in ocean floor <20 m.y. old over the past 200 m.y. (Fig. DR7 in the Data Repository). Our model (Fig. 3C) results in a high global hydrothermal fluid flux throughout the Cretaceous, corresponding to a Phanerozoic minimum in oceanic Mg/Ca, calcite seas, and the formation of massive coccolith chalk deposits in the Late Cretaceous (Stanley and Hardie, 1998) (Figs. 3C and 3D). Periods when the total hydrothermal flux falls below ~10,000 km<sup>3</sup>/yr (Fig. 3C) and the global average oceanic heat flow is <~90 mW/m<sup>2</sup> (Fig. 2E) correspond to aragonite seas, with preferential aragonite and high-Mg calcite precipitation. Low-Mg calcite precipitation is favored when the total hydrothermal flow and heat flow are above this modeled fluid flux threshold, leading to calcite seas.

Relatively short ridge lengths and relatively small ridge flank areas, resulting from low spreading rates, lead to low hydrothermal fluid fluxes and to elevated Mg/Ca in seawater. Experiments combined with seawater composition models suggest that if this ratio is >~2 for warm surface seawater, then aragonite ± high-Mg calcite precipitates instead of low-Mg calcite (see Ries, 2010, for a review of the experiments involved), as in the Early Jurassic and Neogene aragonite oceans. Conversely, relatively long mid-ocean ridge systems and/or relatively large ridge flank areas, resulting from fast spreading rates, produce high hydrothermal fluid fluxes and lower the Mg/Ca mole ratio in seawater; if this ratio drops to <~2, then low-Mg calcite precipitates instead of aragonite ± high-Mg calcite (Ries, 2010). Changes in the global age-area distribution of the ocean crust reflect fluctuations in the generation of new crust at mid-ocean ridges, modulated by changes in the average age of the crust that is being subducted globally. In the Jurassic and Cretaceous relatively little crust younger than 65 Ma was subducted compared to the Cenozoic, when large sections of ridge flanks produced during the Late Cretaceous growth of the Pacific plate were gradually subducted (Fig. 1). Thus subduction

had a relatively lower impact on the chemistry of seawater during the Cretaceous, when the growth of mid-ocean ridge system and flanks represented the dominating factor. Instead, subduction processes had a major impact on ocean chemistry during the Cenozoic, driving the return to aragonite seas.

A remaining enigma is that calcareous nanoplankton attained high taxonomic diversity in the Early Cretaceous, but failed to produce massive chalk deposits (Stanley and Hardie, 1998). We suggest that the reason for this time lag lies in the Early Cretaceous co-occurrence of low seawater Mg/Ca (Stanley and Hardie, 1998) and abundant, diverse chalk producers with relatively low sea levels and cooler climate (Frakes et al., 1992) compared to the Late Cretaceous (Fig. 3D). This combination led to a shortage of warm shallow epicontinental seas, preventing massive chalk from being deposited and preserved despite the existence of calcite seas.

Even though there is good agreement on the timing of secular changes in oceanic Mg/Ca between models and observations, the magnitude of these fluctuations is controversial. The Mg content of foraminifera shells yields a change in oceanic Mg/Ca by a factor of 1.7 since the early Cenozoic (Broecker and Yu, 2011), whereas fluid inclusions (Lowenstein et al., 2001) and CaCO<sub>3</sub> mineralogy observations suggest at least a three-fold increase during this time (Coggon et al., 2010). Our computed change in total fluid flux between the Cretaceous maximum at 120 Ma and the present is ~1.7. However, it is unclear how a relatively small (1.7×) change in oceanic Mg/Ca could have precipitated a shift from calcite to aragonite seas since the early Cenozoic, unless it was coupled to a major change in  $p$ CO<sub>2</sub> and thus seawater pH, leading to a change in ocean state. The conversion of hydrothermal fluid fluxes to chemical fluxes is not trivial, as hydrothermal chemical fluxes are dependent on both the partitioning of the fluid flux with respect to temperature, and the temperature dependence of hydrothermal fluid chemistry (Schultz and Elderfield, 1997). Furthermore, the contemporaneous ocean chemistry and conditions may also have had a significant effect on the nature and extent of fluid-rock reaction, preventing us from quantitatively converting the critical threshold in global hydrothermal fluid flux to an equivalent threshold in chemical fluxes that corresponds with the aragonite-calcite sea transition.

## CONCLUSIONS

Our results suggest that it is not necessary to invoke the conventionally accepted idea that high-temperature mid-ocean ridge hydrothermal flux has been the primary driver of seawater Mg/Ca ratios throughout Phanerozoic time. The novel concept that ridge flanks are a key driver of this process is supported by our modeling effort and marks a departure from our current

understanding of how tectonics are thought to control seawater Mg/Ca ratios over geologic time scales. Our results have far-reaching implications for many aspects of understanding long-term biochemical cycles. They demonstrate the impact of global tectonic processes on ocean chemistry and carbonate sedimentary cycles such as reef building and chalk deposition. Because Neoproterozoic and Proterozoic seawater underwent similar oscillations in Mg/Ca ratios (Hardie, 2003), our improved understanding of the underlying tectonic processes controlling the major ion chemistry of oceans can ultimately provide insights into the earliest and poorly constrained cycles of coalescence and dispersal of continents.

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