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**Key Points:**

- At 1000 ppm $CO_2$ and modern Ω, Eocene ocean had modern DIC and low pH of 7.65
- For given Ω, [Mg] increase slightly raises and [Ca] strongly lowers buffering
- Cenozoic [Ca] decline drives evolution and stabilizes climate against $CO_2$ release

**Supporting Information:**

- Figures S1–S4 and Texts S1–S4
- Table S1
- MyAMI model source code

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# The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering

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**Abstract** Reconstructed changes in seawater calcium and magnesium concentration ([$Ca^{2+}$], [$Mg^{2+}$]) predictably affect the ocean's acid/base and carbon chemistry. Yet inaccurate formulations of chemical equilibrium "constants" are currently in use to account for these changes. Here we develop an efficient implementation of the MIAMI Ionic Interaction Model to predict all chemical equilibrium constants required for carbon chemistry calculations under variable [$Ca^{2+}$] and [$Mg^{2+}$]. We investigate the impact of [$Ca^{2+}$] and [$Mg^{2+}$] on the relationships among the ocean's pH, $CO_2$, dissolved inorganic carbon (DIC), saturation state of $CaCO_3$ (Ω), and buffer capacity. Increasing [$Ca^{2+}$] and/or [$Mg^{2+}$] enhances "ion pairing," which increases seawater buffering by increasing the concentration ratio of total to "free" (uncomplexed) carbonate ion. An increase in [$Ca^{2+}$], however, also causes a decline in carbonate ion to maintain a given Ω, thereby overwhelming the ion pairing effect and decreasing seawater buffering. Given the reconstructions of Eocene [$Ca^{2+}$] and [$Mg^{2+}$] ([$Ca^{2+}$] ~20 mM; [$Mg^{2+}$]~30 mM), Eocene seawater would have required essentially the same DIC as today to simultaneously explain a similar-to-modern Ω and the estimated Eocene atmospheric $CO_2$ of ~1000 ppm. During the Cretaceous, at ~4 times modern [$Ca^{2+}$], ocean buffering would have been at a minimum. Overall, during times of high seawater [$Ca^{2+}$], $CaCO_3$ saturation, pH, and atmospheric $CO_2$ were more susceptible to perturbations of the global carbon cycle. For example, given both Eocene and Cretaceous seawater [$Ca^{2+}$] and [$Mg^{2+}$], a doubling of atmospheric $CO_2$ would require less carbon addition to the ocean/atmosphere system than under modern seawater composition. Moreover, increasing seawater buffering since the Cretaceous may have been a driver of evolution by raising energetic demands of biologically controlled calcification and $CO_2$ concentration mechanisms that aid photosynthesis.

## 1. Introduction

Changes in the major ion composition modify ocean chemistry by affecting the thermodynamic activity of dissolved ions and the saturation state of dissolved salts such as calcium carbonate, $CaCO_3$. The concentrations of dissolved magnesium [$Mg^{2+}$] and calcium [$Ca^{2+}$] are of particular importance for the carbon cycle because these ions greatly reduce the activity of carbonate ion [$CO_3^{2-}$] via strong anion-cation interaction [e.g., *Garrels and Thompson*, 1962; *Millero and Schreiber*, 1982] and because [$Ca^{2+}$] is a direct factor in the saturation state of $CaCO_3$ [e.g., *Harvie et al.*, 1984]. Both [$Ca^{2+}$] and [$Mg^{2+}$] are reconstructed to have changed substantially in the geologic past, with evidence for almost 2 times higher [$Ca^{2+}$] and ~40% lower [$Mg^{2+}$] during the Eocene and up to ~4 times higher [$Ca^{2+}$] during the Cretaceous (Figure 1) [*Lowenstein et al.*, 2001, 2003; *Dickson*, 2002, 2004; *Horita et al.*, 2002; *Lear et al.*, 2002; *Steuber and Veizer*, 2002; *Timofeeff et al.*, 2006; *Coggon et al.*, 2010; *Rausch et al.*, 2013; *Gothmann et al.*, 2015]. These large changes must be considered when attempting to reconstruct the evolution of the ocean's acid/base chemistry from observations [e.g., *Demicco et al.*, 2003; *Tyrrell and Zeebe*, 2004; *Foster et al.*, 2012], and carbon cycle models should account for the full range of aqueous chemical effects as accurately as practically possible until their impacts are fully understood.

The basic problem addressed here relates to the conventional oceanographic use of "conditional equilibrium constants" (denoted by appending an asterisk to the equilibrium constant; e.g., $K^*$), which define the equilibrium points of acid/base reactions in terms of "stoichiometric concentration" (square bracket notation; e.g., [$CO_3^{2-}$])

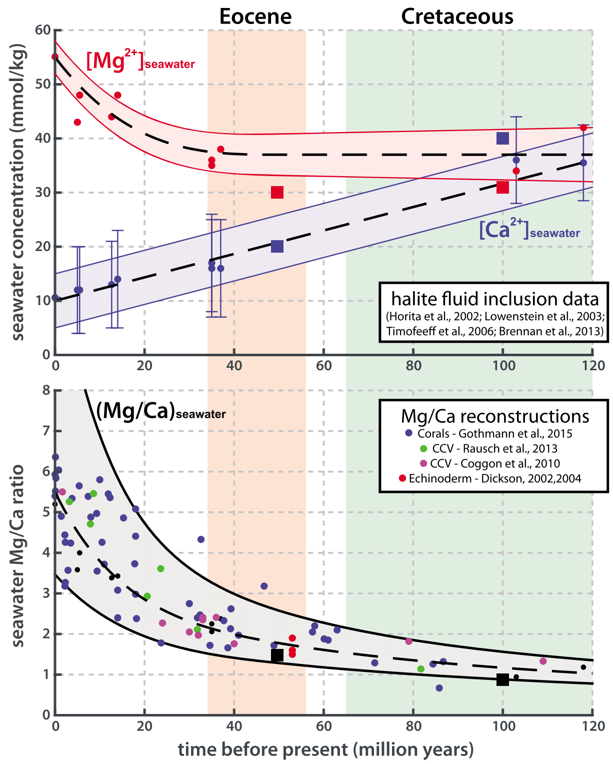


**Figure 1.** Reconstructed changes in (top) seawater calcium and magnesium concentration, and (bottom) seawater Mg/Ca-ratio.

as a function of temperature and salinity ($T$ and $S$). This usage is different from common "thermodynamic equilibrium constants," which define the equilibrium points of acid/base reactions in terms of "activity" (curly bracket notation; e.g., $\{CO_3^{2-}\}$) as a function of temperature, ionic strength ($I$) and solution composition ($X$) (see also Table 1 for terms and symbols used in this study). To formally convert between the two systems ($K^*$ versus $K$) requires calculating the activity coefficients for all involved chemical species, which can be done on the basis of existing experimental data sets and theory [e.g., *Pitzer,* 1973, 1991; *Harvie et al.*, 1984; *Felmy and Weare*, 1986; Greenberg and Møller, 1989; *Campbell et al.*, 1993; *Millero and Roy*, 1997; *Millero and Pierrot*, 1998]. However, due to limitations of the various existing computer models, most current efforts to simulate or reconstruct the carbon cycle of the geologic past rely on simple but inaccurate correction factors for $[Ca^{2+}]$ and $[Mg^{2+}]$ sensitivities of the thermodynamic constants (Figure 2) [i.e., *Ben-Yaakov and Goldhaber*, 1973; *Tyrrell and Zeebe*, 2004]—or they ignore seawater major ion change altogether [e.g., *Heinze and Ilyina*, 2015]. Herein, we recode the part of the MIAMI Ionic Interaction Model (Millero and Pierrot, 1998) that is required for marine acid/base chemistry in order to assist easy incorporation into carbon cycle models and other algorithmic calculations for seawater of different major ion composition than today. The Python source code of our model, MyAMI, is made available in the supporting information (MyAMI source code available at https://github.com/MathisHain/MyAMI).

Finally, as a demonstration of the importance of secular changes in seawater composition, we consider a ~50 Ma "Eocene" and a ~100 Ma "Cretaceous" scenarios, both based largely on *Demicco et al.* [2005]. Three consequences of seawater composition change are analyzed in detail: (1) the effect on the conditional equilibrium constants, (2) the effect on the $CO_2$-pH-DIC-$\Omega$ relationships for surface waters, and (3) changes in the ocean's buffer capacity. We find that changes in the conditional equilibrium constants are on the order of a few tens of percent, but the direct effect of elevated $[Ca^{2+}]$ on $CaCO_3$ saturation dominates the effects on speciation and equilibrium constants because it shifts the $CO_2$-$\Omega$ relationship toward low pH and low DIC. Our best understanding of the Eocene is that atmospheric $CO_2$ was as high as ~1000 ppm [e.g., *Beerling and Royer*, 2011], while reconstructions of the calcite compensation depth (CCD) require that $\Omega$ was not many fold different than in the modern ocean [e.g., *Pälike et al.*, 2012; *Ridgwell*, 2005; *Tyrrell and Zeebe*, 2004]. If reconstructions of elevated $[Ca^{2+}]$ and ~10°C higher temperatures in the Eocene are correct, then the atmospheric $CO_2$ and $\Omega$ constraints are attained by a DIC concentration similar to that of the modern ocean. Mainly due to elevated $[Ca^{2+}]$, seawater during the Eocene and Cretaceous must have been very poorly buffered, thereby making seawater acid/base chemistry, atmospheric $CO_2$, and climate more sensitive to perturbations of the global carbon cycle. The increase in the buffering capacity of the carbonate system in seawater toward the present has potentially important implications for biological systems as it would have made it progressively more energetically demanding for organisms to manipulate their internal acid/base chemistry.

## 2. Methods

Calculating equilibrium constants for seawater with a composition different from today requires a "Pitzer model" [e.g., *Pitzer*, 1973] to predict the activity coefficients of the chemical species involved in the marine

  

**Table 1.** List of Symbols Used in the Text

| | |
|---|---|
| *Concentration Versus Activity* | |
| $[Ca^{2+}]$, $[CO_3^{2-}]$, etc. | Square brackets denote stoichiometric concentration, including both free and complexed ion |
| $\{H^+\}$, $\{CO_3^{2-}\}$, etc. | Curly brackets denote the thermodynamic activity of chemical species |
| $\gamma^F_{SP}$ | "Free ion" activity coefficient of species SP $\gamma^F_{SP} = \{SP\}/[SP]_{free}$ (equations (S4a) and (S4b)) |
| $\gamma^T_{SP} = \gamma^F_{SP} * [SP]_{free}/\left([SP]_{free} + [SP]_{complexed}\right)$ | Stoichiometric "total" activity coefficient: (equations (S5), (S6), and (S8)) |
| *Terms Relating to Seawater* | |
| $CO_2$ | Partial pressure of carbon dioxide in parts per million (ppm) |
| $HCO_3^-$, $CO_3^{2-}$, $H_2CO_3^*$ | Inorganic carbon species: bicarbonate ion, carbonate ion, and carbonic acid |
| DIC | Dissolved inorganic carbon: sum of $[HCO_3^-]$, $[CO_3^{2-}]$, $[H_2CO_3^*]$ (3) |
| ALK | Alkalinity, used here including borate alkalinity: $[HCO_3^-] + 2*[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$ |
| $CaCO_3$ | Calcium carbonate; either calcite or aragonite polymorph |
| $\Omega_{calcite}$, $\Omega_{aragonite}$ | Calcite and aragonite saturation state; $\Omega > 1$ is oversaturation (equations (2) and (3)) |
| pH, $pH_T$ | Total pH scale used throughout: $pH_T = -\log_{10}[H^+]_T = -\log_{10}\left([=H^+]_{free} + [HSO_4^-]\right)$ (equation (S8)) |
| $T$ | Seawater temperature (for equilibrium constant calculation in Kelvin, K) |
| $S$ | Seawater salinity (no units) |
| $X$ | Seawater major ion composition (mole ratio relative to chloride, equation (S7b)) |
| $I$ | Seawater major ionic strength (mol/kg $H_2O$; tied to salinity after *Dickson* [2010]) |
| *Equilibrium Constants* | |
| $K_0^* = [H_2CO_3^*]/CO_2 = K_0\gamma^F_{CO2}/\gamma^F_{H2CO3}$ | See equation (1a)—$CO_2$ solubility |
| $K_1^* = [H^+]_T*[HCO_3^-]/[H_2CO_3^*] = K_1\gamma^F_{H2CO3}/\gamma^T_H/\gamma^F_{HCO3}$ | See equation (1b)—Deprotonation of carbonic acid |
| $K_2^* = [H^+]_T*[CO_3^{2-}]_T/[HCO_3^-] = K_2\gamma^F_{HCO3}/\gamma^T_H/\gamma^T_{CO3}$ | See equation (1c)—Deprotonation of bicarbonate ion |
| $K_{spC}^* = [CO_3^{2-}]_T*[Ca^{2+}]/\Omega_{calcite} = K_{spC}/\gamma^T_{CO3}/\gamma^F_{Ca}$ | See equation (1d)—Saturation of calcite |
| $K_{spA}^* = [CO_3^{2-}]_T*[Ca^{2+}]/\Omega_{aragonite} = K_{spA}/\gamma^T_{CO3}/\gamma^F_{Ca}$ | See equation (1e)—Saturation of aragonite |
| $K_B^* = [H^+]_T*[B(OH)_4^-]/[H_3BO_3] = K_B\gamma^F_{H3BO3}/\gamma^T_H/\gamma^F_{B(OH)4}$ | See equation (1f)—Deprotonation of boric acid |
| $K_w^* = [H^+]_T*[OH^-]_T = K_w/\gamma^T_H/\gamma^T_{OH}$ | See equation (1g)—Autoprotolysis of water |
| $K_{HSO4}^* = [H^+]_T*[SO_4^{2-}]/[HSO_4^-] = K_{HSO4}\gamma^F_{HSO4}/\gamma^T_H/\gamma^F_{SO4}$ | See equation (1h)—Deprotonation of bisulfate ion |
| *Seawater Reference Composition in mmol Per kg Solution* (*Millero et al.* [2008]) | |
| $[Cl^-] = 545.8696 \times S/35$ | |
| $[Na^+] = 468.9674 \times S/35$ | |
| $[Mg^{2+}] = 52.7171 \times S/35$ | Magnesium concentration is being explicitly changed |
| $[SO_4^{2-}] = 28.2352 \times S/35$ | |
| $[Ca^{2+}] = 10.2821 \times S/35$ | Calcium concentration is being explicitly changed |
| $[K^+] = 10.2077 \times S/35$ | |
| $[HCO_3^-] = 1.7177 \times S/35$ | |
| $[CO_3^{2-}] = 0.239 \times S/35$ | |
| $[B(OH)_4^-] = 0.1008 \times S/35$ | |
| $[Sr^{2+}] = 0.0907 \times S/35$ | |
| $[H_2CO_3*]$, $[H_3BO_3]$, $[H^+]$, $[OH^-]$, $[HSO_4^-]$ | Neutral and minor species assume nominal concentration (pH ~8) |

acid/base chemistry. There are a number of models available to carry out these calculations, e.g., (1) PHREEQC distributed by the U.S. Geological Survey [*Parkhurst*, 1995], (2) the EQL/EVP model for evaporation and mineral precipitation of brines (Risacher and Clemant, 2001), (3) commercial software such as MINEQL+, and (4) the MIAMI model [*Millero and Pierrot*, 1998]. Unfortunately, for a number of reasons none of these codes are adequate to be used for carbon cycle modeling. PHREEQC by itself is not intended for brines with ionic strength as high as seawater, and it yields inaccurate results for modern seawater composition when using the included Pitzer model package (Figure 3). EQL/EVP uses (a) outdated Pitzer coefficients for carbon species (with a nominal validity range of only 20–30°C) and (b) an integrated software design that precludes direct access to the Pitzer model part. MINEQL+ is not considered here because it is expensive, not open source, not cross platform, and invalid for ionic strength of seawater. MIAMI is the only existing code that has been successfully validated against empirical equilibrium constants of modern seawater, but it exists embedded in a spreadsheet file (D. Pierrot, personal communication, 2014) making it only appropriate for one-off calculations.

For this study, we recode the part of the MIAMI model that is relevant to the bulk acid/base chemistry of seawater. Our model, MyAMI, yields results that are in good agreement with the original MIAMI model and with the empirical equilibrium constants (see Figures S1 and S2). We note that (1) there are differences

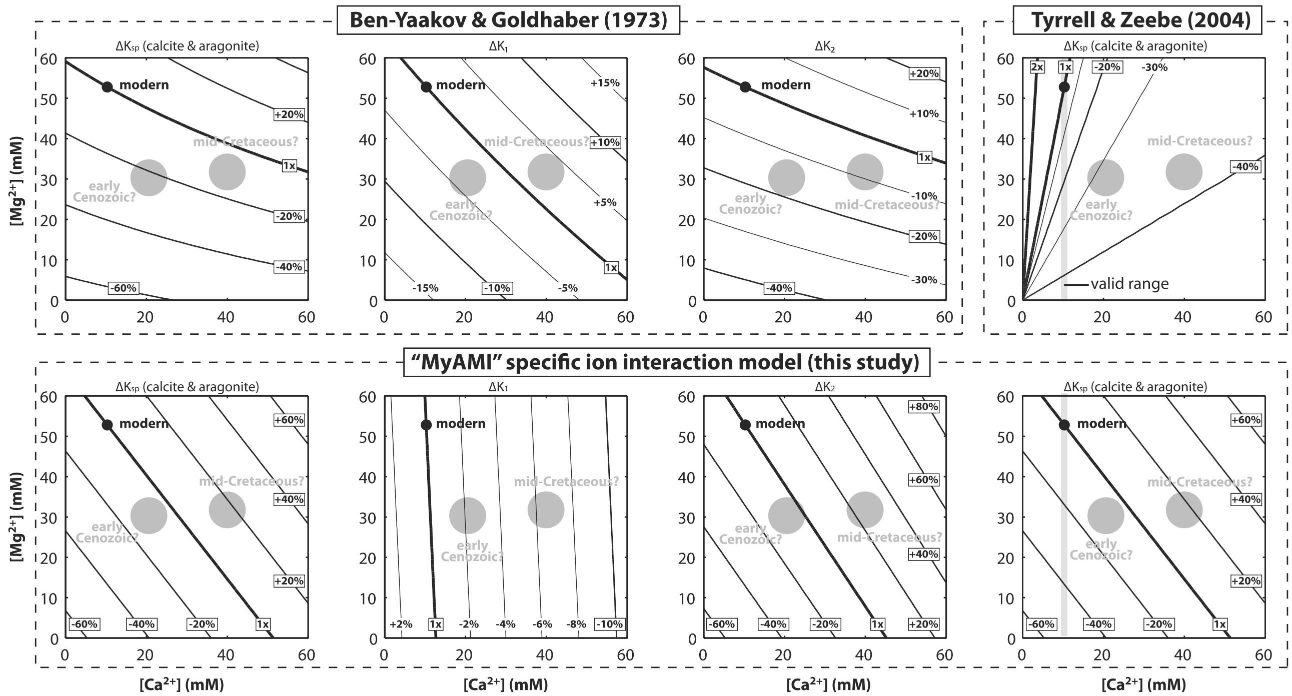


**Figure 2.** The equilibria of acid/base reactions as described by conditional equilibrium constants ($K^*$) change with the ionic composition of the solution, and in particular with changes in the concentration of the divalent cations calcium and magnesium ([$Ca^{2+}$], [$Mg^{2+}$]). Reconstructed [$Ca^{2+}$] and [$Mg^{2+}$] change since the Cretaceous caused significant changes of the conditional equilibrium constants. Predicted change of equilibrium constants ($\Delta K^*/K^*_{\mathrm{empirical}}$) in response to [$Ca^{2+}$] and [$Mg^{2+}$] change based on (top row) previously published corrections differ significantly from (bottom row) Pitzer-type specific ionic interaction model results. The MyAMI ion pairing model used here is a simplified version of the MIAMI model [*Millero and Pierrot*, 1998], drawing on a much larger thermodynamic database than the previous corrections. Moreover, so far corrections are available only for the equilibrium constants shown here: ($K_1$*) the deprotonation of carbonic acid, ($K_2$*) the deprotonation of bicarbonate ion, and ($K_{sp}$*) the solubility product of $CaCO_3$. In this study, we derive conditional equilibrium constants for the entire range of acid/base equilibria required for carbon cycle modeling (see Figures 3). All results here are for 25°C and $S = 35$.

in thermodynamic database used in MIAMI and MyAMI (see Table 2), and (2) the equilibrium constants calculated here are fully consistent with the empirical equilibrium constants because we use MyAMI only to predict the effects of changes in seawater composition (see equation (S2) in the supporting information). For additional information on the model—and for model validation—the reader is referred to the supporting information of this study and to the original description of the MIAMI model by *Millero and Pierrot* [1998]. The source code of MyAMI, in the Python programming language, is also made available online (MyAMI source code available at https://github.com/MathisHain/MyAMI).

## 3. Results

### 3.1. Equilibrium Constants

Carbon cycle modeling, and in fact every quantitative treatment of the acid/base chemistry of seawater, has either ignored the sensitivities of the equilibrium constants to seawater major ion composition or relied on simple formulations that were developed to correct for these effects [e.g., *Ben-Yaakov and Goldhaber*, 1973; *Tyrrell and Zeebe*, 2004]. By comparing to MyAMI model output, we find these simple correction factors to be inadequate (Figure 2). As pointed out by *Roberts and Tripati* [2009], the *Tyrrell and Zeebe* [2004] correction for the calcite solubility product ($pK_{spC}$*) agrees poorly with the MIAMI model [*Millero and Pierrot*, 1998] when considering variations in both [$Ca^{2+}$] and [$Mg^{2+}$]. This is unsurprising because *Tyrrell and Zeebe* [2004] derive their correction based on an experimental data set where only [$Mg^{2+}$] is manipulated [*Mucci and Morse*, 1984], to which they fit a Mg/Ca-ratio dependence. Consequently, the *Tyrrell and Zeebe* [2004] formulation agrees rather well with the MyAMI model when only [$Mg^{2+}$] is changed at constant modern [$Ca^{2+}$] (gray shaded vertical bar in Figure 2), but it leads to substantial error when applied to seawater with modified [$Ca^{2+}$].

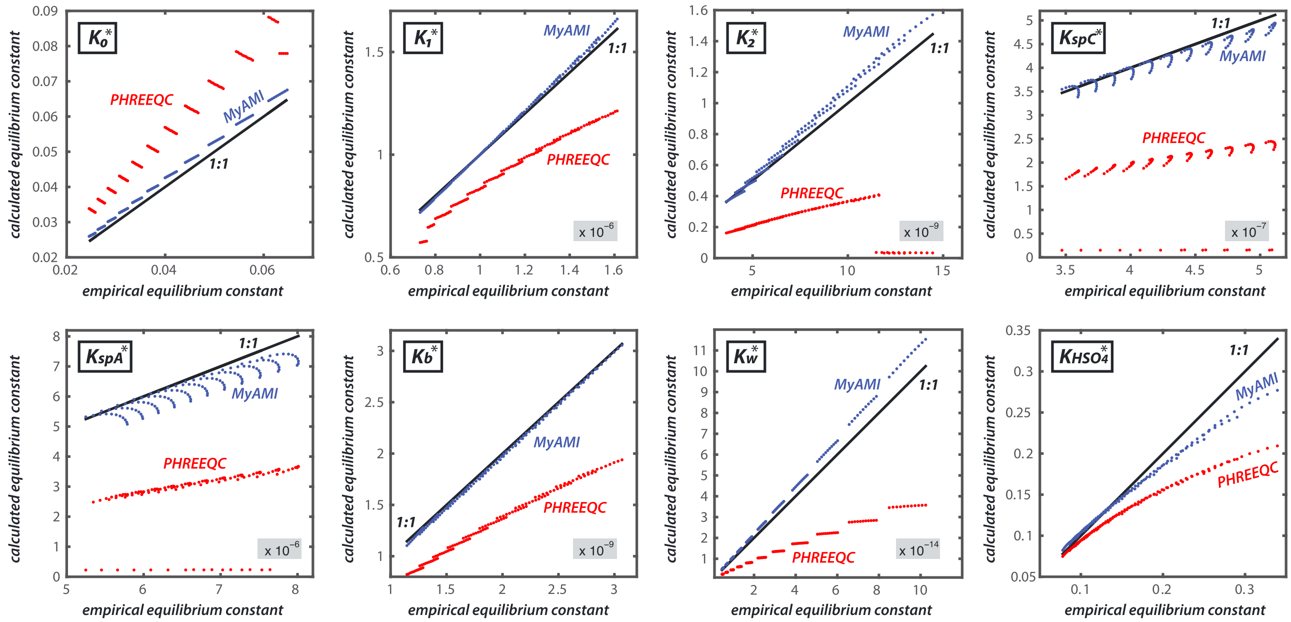


**Figure 3.** Assessment of model skill by comparison of predicted conditional equilibrium constants of MyAMI (blue; this study) and PHREEQC (red) [*Parkhurst*, 1995] against the empirical conditional equilibrium constants for modern seawater composition [*Weiss*, 1974; *Lueker et al.*, 2000; *Dickson et al.*, 1990a, 1990b; *Mucci*, 1983] in the range of 0–30°C and salinity of 30–40. Our MyAMI model closely tracks the "1:1" line target of perfect agreement with the empirical data. MIAMI model output (not shown) is very similar to MyAMI (see Figure S1). The equilibrium constants documented in this study are made to fully conform to empirical data by using MyAMI only to calculate the change of the equilibrium constants relative to modern seawater (according to supporting information equation (S2)).

**Table 2.** References for Thermodynamic Data Used in This Study[a,b,c,d,e]

| | $H^+$ | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | $MgOH^+$ |
|---|---|---|---|---|---|---|---|
| $OH^-$ | X | 20[f] | 11,12 | X | 15 | 10[g] | |
| $Cl^-$ | 18[f] | 1[f] | 1 | 2 | 1 | 11,13,14 | 15 |
| $HCO3^-$ | X | 4[f] | 7 | 10,16 | 15 | 10[g] | |
| $HSO4^-$ | X | 3[f] | 15 | 10[f] | 15 | 10[g] | |
| $B(OH)_4^-$ | X | 6[f] | 6[f] | 9[f] | 9 | 10[g] | |
| $CO_3^{2-}$ | X | 4[f] | 8 | X | X | X | |
| $SO_4^{2-}$ | X | 1[f] | 1 | 2 | 22[f] | 10[g] | |

[a]References are as follows: (1) *Møller* [1988], *Greenberg and Møller* [1989], (2) *Pabalan and Pitzer* [1987], (3) *Pierrot et al.* [1997], (4) *Peiper and Pitzer* [1982], (6) *Simonson et al.* [1988], (7) *Roy et al.* [1983], (8) *Simonson et al.* [1987a], (9) *Simonson et al.* [1987b], (10) *Millero and Pierrot* [1998], (11) *Pitzer and Mayorga* [1973], (12) *Criss and Millero* [1996], (13) *Silvester and Pitzer* [1978], (14) *Millero and Pierrot* [1998], referenced to *Criss and Millero* [1999]; (15) *Harvie et al.* [1984], (16) *Thurmond and Millero* [1982], (18) *Campbell et al.* [1993], (20) *Rai et al.* [2002], (21) *Pitzer et al.* [1985], *He and Morse* [1993], and (22) *Pitzer and Mayorga* [1974]; X denotes explicitly treated ion pairing or acid/base equilibria.

[b]References for cation-cation, anion-anion, cation-cation-anion, and anion-anion-cation Pitzer parameters are used as listed in Tables A10 and A11 of *Millero and Pierrot* [1998]; $\Theta Cl^-$-$CO_3^{2-}$ is corrected after *Peiper and Pitzer* [1982]; $\Theta OH^-$-$CO_3^{2-}$ = 0.1 after *Pitzer* [1991] and *Clegg et al.* [1994].

[c]Neutral species interaction parameters for $CO_2^{aq}$ and $H_3BO_3$ are taken from *He and Morse* [1993] and *Felmy and Weare* [1986].

[d]Activity coefficient for Ca-$CO_3^0$, Mg-$CO_3^0$, and Sr-$CO_3^0$ ion pairs is taken to be 1 following *Harvie et al.* [1984] and *He and Morse* [1993]; but see also *Millero and Schreiber* [1982].

[e]The empirical equilibrium constants are taken from ($K_0$*) *Weiss* [1974], ($K_1$* and $K_2$*) *Lueker et al.* [2000], ($K_B$*) *Dickson* [1990b], ($K_{HSO4}$*) *Dickson* [1990a], ($K_{spC}$*and $K_{spA}$*) *Mucci* [1983], and ($K_w$*) *Millero* [1995]. The thermodynamic equilibrium constants used to calculate conditional equilibrium constants are taken from ($K_0$ and $K_1$) *Plummer and Busenberg* [1982], ($K_2$) *Harned and Scholes* [1941] refit by *Millero* [1979], ($K_B$) *Owen* [1934], *Manov et al.* [1944] refit by *Millero* [1979], ($K_{HSO4}$) *Campbell et al.* [1993], ($K_{spC}$ and $K_{spA}$) *Mucci* [1983], and ($K_w$) *Harned and Owen* [1958] refit by *Millero* [1979]. All conditional constants are on the total pH scale calculated using $K_{HSO4}$* of *Dickson* [1990a].

[f]Different value or different reference than given in *Millero and Pierrot* [1998].

[g]Equated to $Ca^{2+}$ interaction by *Millero and Pierrot* [1998]; changes (*) carried over.

In carbon cycle models, the equilibrium constants are represented by functional forms that have been used to fit the empirical data sets for modern seawater [see *Dickson et al.*, 2007; *Millero*, 1995]:

$$\ln K_0^* = p_{0,0} + \frac{p_{0,1}*100}{T} + p_{0,2}*\ln\frac{T}{100} + S*\left(p_{0,3} + \frac{p_{0,4}*T}{100} + p_{0,5}*\left(\frac{T}{100}\right)^2\right) \quad (1a)$$

$$\log_{10}K_1^* = p_{1,0} + \frac{p_{1,1}}{T} + p_{1,2}*\ln T + p_{1,3}*S + p_{1,4}*S^2 \quad (1b)$$

$$\log_{10}K_2^* = p_{2,0} + \frac{p_{2,1}}{T} + p_{2,2}*\ln T + p_{2,3}*S + p_{2,4}*S^2 \quad (1c)$$

$$\begin{aligned}\ln K_B^* = p_{B,0} + p_{B,1}*\sqrt{S} + p_{B,2}*S + \frac{1}{T}\left(p_{B,3} + p_{B,4}*\sqrt{S} + p_{B,5}*S + p_{B,6}*S^{1.5} + p_{B,7}*S^2\right)\\ +\ln T\left(p_{B,8} + p_{B,9}*\sqrt{S} + p_{B,10}*S\right) + p_{B,11}*T*\sqrt{S}\end{aligned} \quad (1d)$$

$$\ln K_W^* = p_{W,0} + \frac{p_{W,1}}{T} + p_{W,2}*\ln T + \sqrt{S}\left(\frac{p_{W,3}}{T} + p_{W,4} + p_{W,5}*\ln T\right) + p_{W,6}*S \quad (1e)$$

$$\begin{aligned}\log_{10}K_{spC}^* = p_{spC,0} + p_{spC,1}*T + \frac{p_{spC,2}}{T} + p_{spC,3}*\log_{10}T + \sqrt{S}\left(p_{spC,4} + p_{spC,5}*T + \frac{p_{spC,6}}{T}\right)\\ + p_{spC,7}*S + p_{spC,8}S^{1.5}\end{aligned} \quad (1f)$$

$$\begin{aligned}\log_{10}K_{spA}^* = p_{spA,0} + p_{spA,1}*T + \frac{p_{spA,2}}{T} + p_{spA,3}*\log_{10}T + \sqrt{S}\left(p_{spA,4} + p_{spA,5}*T + \frac{p_{spA,6}}{T}\right)\\ + p_{spA,7}*S + p_{spA,8}S^{1.5}\end{aligned} \quad (1g)$$

$$\begin{aligned}\ln K_{HSO4}^* = p_{HSO4,0} + \frac{p_{HSO4,1}}{T} + p_{HSO4,2}*\ln T + \sqrt{I}\left(\frac{p_{HSO4,3}}{T} + p_{HSO4,4} + p_{HSO4,5}*\ln T\right)\\ + I\left(\frac{p_{HSO4,6}}{T} + p_{HSO4,7} + p_{HSO4,8}*\ln T\right) + \frac{p_{HSO4,9}}{T}*I^{1.5} + \frac{p_{HSO4,10}}{T}*I^2 + \ln(1 - 0.001005*S).\end{aligned} \quad (1h)$$

These general equations explicitly represent the dependencies to changes in temperature and salinity ($T$, $S$), whereas the dependence on seawater composition ($X$) is implicitly encoded into the various parameters. That is, the various parameters "$p$" can be determined so as to fit the general equations to output from the MyAMI model at any arbitrary seawater composition (see equation (S3) in the supporting information). For later reference, Table 3 shows the parameters $p$ for (a) modern seawater, (b) the Eocene seawater scenario, and (c) the Cretaceous scenario. A much more extensive list of tabulated parameter sets is provided in the supporting information (0 to 60 mM [$Ca^{2+}$] and [$Mg^{2+}$] range with 1 mM increments; Table S1).

### 3.2. Surface Ocean Chemistry in the Early Cenozoic

In the modern ocean, the well stratified surface water of the subtropical gyres is near equilibrium with respect to atmospheric $CO_2$ [*Takahashi et al.*, 2002] because of (a) a large surface area available for gas exchange, (b) a shallow mixed layer depth, which translates to a small volume of water to equilibrate, and (c) slow vertical exchange of water across the thermocline. These characteristics should also hold true for much of Earth history such that subtropical (low-latitude) surface water acid/base chemistry would be related to contemporaneous atmospheric $CO_2$ levels. To mathematically describe surface water chemistry, five parameters must be specified: temperature ($T$), salinity ($S$), major ion composition ($X$; at a nominal salinity of 35), and any combination of two additional parameters describing the state of seawater acid base chemistry (pH, $CO_2$, DIC, ALK, $\Omega$, etc.). That is, the unique relationship between pH, $CO_2$, DIC, ALK, and $\Omega$ systematically depends on, and changes with, $T$, $S$ and $X$.

Assuming equilibrium and without further approximation, the dependence of surface pH on atmospheric $CO_2$, surface calcite saturation $\Omega$, $T$, $S$, and $X$ is given by

$$\mathrm{pH} = \frac{1}{2}\left(\log\Omega - \log\left[Ca^{2+}\right] - \log(CO_2) + \left[pK_0^* + pK_1^* + pK_2^* - pK_{spC}^*\right]\right) \quad (2)$$

The aggregate "$pK^*$" term contains the entire $T$ and $S$ dependence, and it changes with seawater composition $X$. However, the aggregate $pK^*$ term is quite insensitive to [$Ca^{2+}$] and [$Mg^{2+}$] changes. The formation of complexes with divalent cations has a very large effect on the activity coefficient of carbonate ion [*Garrels and Thompson*, 1962] (Equation (S1) in the supporting information), but since the activity coefficient of carbonate ion is identical for $pK_2^*$ and $pK_{spC}^*$ this effect is canceled by subtracting $pK_{spC}^*$ from $pK_2^*$.

**Table 3.** Parameters Describing the Temperature and Salinity Dependence Conditional on Modern, Eocene Scenario, and Cretaceous Scenario Seawater Major Ion Composition According to Equations (1a) to (1h)[a]

| | p0 | p1 | p2 | p3 | p4 | p5 | p6 | p7 | p8 | p9 | p10 | p11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Modern: $[Ca^{2+}]$ = 10.2821 mM, $[Mg^{2+}]$ = 52.8171 mM* | | | | | | | | | | | | |
| $pK_0$* | −60.2409 | 93.4517 | 23.3585 | 0.023517 | −0.023656 | 0.0047036 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_1$* | 61.2172 | −3633.86 | −9.6777 | 0.011555 | −0.0001152 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_2$* | −25.929 | −471.78 | 3.16967 | 0.01781 | −0.0001122 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_B$* | 148.0248 | 137.1942 | 1.62142 | −8966.9 | −2890.53 | −77.942 | 1.728 | -0.0996 | −24.4344 | −25.085 | −0.2474 | 0.053105 |
| $pK_w$* | 148.9652 | −13847.26 | −23.6521 | 118.67 | −5.977 | 1.0495 | −0.01615 | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_{spC}$* | −171.9065 | −0.077993 | 2839.319 | 71.595 | −0.77712 | 0.0028426 | 178.34 | −0.07711 | 0.0041249 | - - - - | - - - - | - - - - |
| $pK_{spA}$* | −171.945 | −0.077993 | 2903.293 | 71.595 | −0.068393 | 0.0017276 | 88.135 | −0.10018 | 0.0059415 | - - - - | - - - - | - - - - |
| $pK_{SO4}$* | 141.328 | −4276.1 | −23.093 | −13856 | 324.57 | −47.986 | 35474 | −771.54 | 114.723 | −2698 | 1776 | - - - - |
| *Eocene Scenario (~50 Ma): $[Ca^{2+}]$ = 20 mM, $[Mg^{2+}]$ = 30 mM* | | | | | | | | | | | | |
| $pK_0$* | −59.10558297 | 91.85983392 | 22.80815968 | 0.026034049 | −0.025313942 | 0.004987136 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_1$* | 62.19335659 | −3669.526066 | -9.834540861 | 0.011193361 | −0.000113713 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_2$* | −26.71121142 | -437.8112533 | 3.287439691 | 0.017419883 | −0.000110534 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_B$* | 156.169978 | 138.6678081 | 1.744675879 | −9226.072384 | −2874.822309 | −82.05134674 | 1.444274205 | -0.09130297 | −25.71609713 | −25.43581085 | −0.264978916 | 0.054449827 |
| $pK_w$* | 146.6165292 | −13701.93677 | −23.34510121 | 105.5781367 | −5.777126033 | 1.023014734 | −0.016256003 | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_{spC}$* | −64.18088214 | −0.044574948 | 143.2440176 | 27.67482884 | −0.649495403 | 0.00263027 | 158.2903928 | −0.077072307 | 0.004120361 | - - - - | - - - - | - - - - |
| $pK_{spA}$* | −179.9975101 | −0.081280132 | 3057.503031 | 75.03748481 | −0.061276244 | 0.001715022 | 86.56805891 | −0.100247518 | 0.005942857 | - - - - | - - - - | - - - - |
| $pK_{SO4}$* | 143.2910799 | −4352.155483 | −23.38877839 | -13954.84693 | 326.3061964 | −48.24583211 | 35397.10448 | −771.2178916 | 114.6962928 | -2652.692412 | 1765.000598 | - - - - |
| *Cretaceous Scenario (~100 Ma): $[Ca^{2+}]$ = 40 mM, $[Mg^{2+}]$ = 32 mM* | | | | | | | | | | | | |
| $pK_0$* | −58.3877784 | 90.85340552 | 22.46019743 | 0.039823248 | −0.034752808 | 0.006578522 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_1$* | 67.18932711 | −3916.913791 | −10.54553663 | 0.011355982 | -0.00011562 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_2$* | −24.81329597 | −523.3786264 | 3.002902784 | 0.017068822 | −0.000108918 | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_B$* | 159.3008023 | 136.4242881 | 1.902713041 | −9404.24464 | −2782.038919 | −89.4841923 | 1.290414243 | −0.082801324 | −26.1662258 | -25.07932031 | -0.288321703 | 0.054177544 |
| $pK_w$* | 144.1332359 | −13676.54317 | −22.87294773 | 25.10849835 | −3.843156186 | 0.731748246 | -0.016375682 | - - - - | - - - - | - - - - | - - - - | - - - - |
| $pK_{spC}$* | 41.167495 | −0.012195259 | −2561.557454 | −15.09625568 | −0.443469509 | 0.002288422 | 129.8698493 | −0.078205182 | 0.004168981 | - - - - | - - - - | - - - - |
| $pK_{spA}$* | −168.5145238 | −0.076650722 | 2834.453071 | 70.13642768 | −0.067232499 | 0.001748572 | 89.2204672 | −0.101390116 | 0.006035644 | - - - - | - - - - | - - - - |
| $pK_{SO4}$* | 144.8263358 | −4407.614762 | −23.62233848 | −13844.49869 | 323.0478765 | -47.74074044 | 35412.66387 | −770.4184282 | 114.5696624 | −2689.876025 | 1774.755137 | - - - - |

[a]The model is constrained to match the empirical equilibrium constants for modern seawater according to equation (S2) in the supporting information.

  

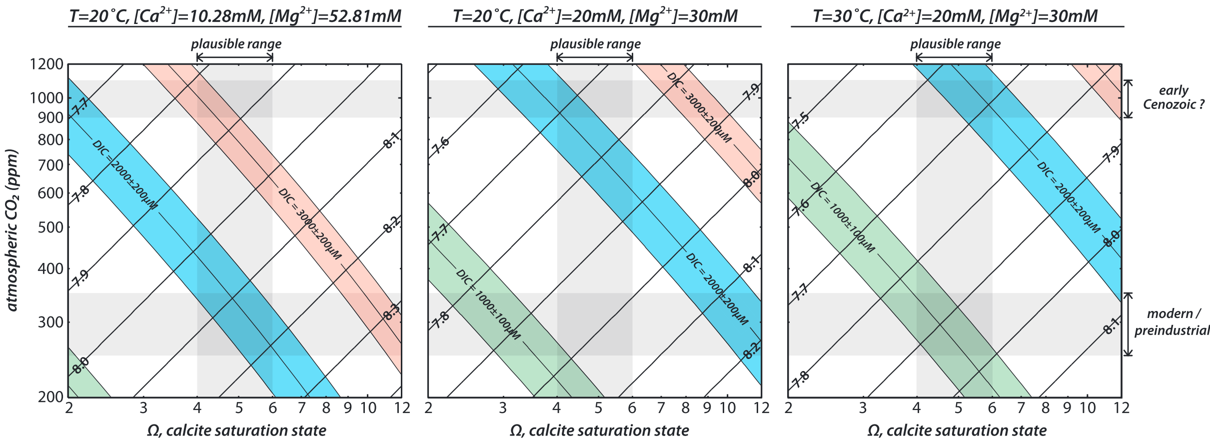


**Figure 4.** Thermodynamic Ω-$CO_2$-DIC-pH relationship for three cases of major ion composition and temperature that represent: (left) modern seawater composition at 20°C, (middle) scenario for Eocene seawater composition at 20°C, and (right) scenario for Eocene seawater composition at 30°C. Salinity (and ionic strength) is held constant at 35. Equilibrium constants are used according to equations (2) and (3). Blue, red, and green shading represents DIC ranges from 1800 to 2200 μM, 2800–3200 μM, and 900–1100 μM, respectively. Gray shading indicates modern and Eocene target $CO_2$ levels and the plausible rage of calcite Ω. The very mild curvature of the DIC contours results from the log(DIC/$HCO_3^-$) term in equation (2). Contours of ALK (not shown) would run almost parallel to DIC contours so as to yield: (1) DIC addition at constant ALK shifts the acid/base chemistry up and left in this plot (almost following DIC contours), and (2) ALK addition at constant DIC shifts the acid/base chemistry down and right in this plot (along DIC contours). Supporting information Figure S3 shows the same experiments but for the Cretaceous seawater scenario instead of the Eocene scenario.

Assuming equilibrium and without further approximation, the dependence of surface DIC on atmospheric $CO_2$, surface calcite saturation, $T$, $S$, and $X$ is given by

$$\log[DIC] = \frac{1}{2}\left(\log\Omega - \log\left[\mathrm{Ca}^{2+}\right] + \log\mathrm{CO}_2 - \left[pK_0^* + pK_1^* + pK_{\mathrm{spC}}^* - pK_2^*\right]\right) + \log\frac{[\mathrm{DIC}]}{\left[\mathrm{HCO}_3^-\right]}. \tag{3}$$

Note that in this expression for DIC, the aggregate $pK^*$ term is different from the expression for pH. However, the $pK^*$ term is again quite insensitive to [$Ca^{2+}$] and [$Mg^{2+}$] changes, which as above is due to the fact that $pK_{spC}^*$ and $pK_2^*$ are subtracted from each other so as to cancel the strong effect of the divalent metals calcium, magnesium, and strontium on the activity coefficient of carbonate ion. The last term is small because DIC ≈ $HCO_3^-$.

Using the above relationships that link $CO_2$, Ω, pH, and DIC, we consider three scenarios that illustrate the effects of seawater composition and temperature change (Figure 4), whereby the major ion change that we impose can be taken to represent early Cenozoic (Eocene) seawater (i.e., [$Ca^{2+}$] = 20 mM and [$Mg^{2+}$] = 30 mM; both for a nominal salinity of 35). Further, we pay particular attention to solutions of the acid/base chemistry where (a) atmospheric $CO_2$ is elevated to ~1000 ppm as has been proposed for the early Cenozoic [e.g., *Beerling and Royer*, 2011], and (b) the calcite saturation state Ω falls between 4 and 6, the long-term plausible range for the surface ocean since $CaCO_3$ burial came to be dominated by pelagic calcifying organisms during the mid-Mesozoic [*Ridgwell*, 2005]; for alternative argument that Ω was slightly lower prior to 40 million years ago, see *Demicco et al.* [2003].

In an ocean with modern major ion composition and temperature (Figure 4, left), there are two orthogonal ways to increase $CO_2$ toward the 1000 ppm target: (1) increase DIC at constant pH (roughly corresponding to an increase of DIC and ALK in a 1:1 ratio), which acts to increase Ω beyond the plausible range, and (2) decrease pH at constant DIC (i.e., a reduction in ALK), which acts to reduce Ω below plausible values. Of course, these two changes can be combined in a way that their opposing effects on Ω essentially cancel one another (yielding constant Ω of 4 to 6), and $CO_2$ reaches 1000 ppm due to a combination of greater DIC (>3000 μM) and lower pH (<7.95).

During the Eocene, [$Mg^{2+}$] was lower and [$Ca^{2+}$] was higher than in modern seawater (Figure 4, middle). As pointed out above, the strong effect of changes in divalent cation concentration essentially cancels in the aggregate $pK^*$ terms, such that the relationships among DIC, pH, Ω, and $CO_2$ are approximately constant in the face of changing seawater [$Mg^{2+}$]. The concentration of [$Ca^{2+}$], however, is a direct factor in the calculation of $CaCO_3$ saturation, and thus, it appears as a separate term in the relationships among DIC, pH, Ω, and $CO_2$ (equations (2) and (3)). This direct effect of calcium can be described in two equivalent ways (compare Figure 4, left and Figure 4, middle): (1) a given state of acid base chemistry (i.e., any combination of set pH, DIC, and $CO_2$) corresponds to a saturation state that changes proportionally with $[Ca^{2+}]$, and (2) a given coupled $CO_2$ and Ω target is achieved at progressively lower DIC and lower pH as $[Ca^{2+}]$ increases. If we consider explanations for elevated $CO_2$ during the Eocene, elevated $[Ca^{2+}]$ reduces the required DIC by lowering the pH. As for warming of subtropical surface waters during the Eocene (Figure 4, right), the most important consequences of warming are the reduction of $CO_2$ and $CaCO_3$ solubility (i.e., increases of $pK_0$* and $pK_{sp}$*), leading to two appropriate approximations: (1) warming raises $CO_2$ and Ω for any set DIC-pH combination, or (2) a given coupled $CO_2$ and Ω target is achieved at progressively higher pH and lower DIC as temperature increases.

Given the above considerations, how much error is incurred applying modern seawater equilibrium constants or the inaccurate simple correction factors that are in common use? To answer this question, it is helpful to consider equations (2) and (3) in the context of an Eocene global carbon cycle model that is spun-up to a given set level of $CO_2$ and Ω (e.g., via a constant $CO_2$ boundary condition and a steady state between riverine supply of dissolved $CaCO_3$ and seafloor $CaCO_3$ burial). Also, for this analysis we provisionally presume that our MyAMI-derived equilibrium constants are correct. First, if high Eocene $[Ca^{2+}]$ is not considered, the model will be massively wrong because $[Ca^{2+}]$ is a direct factor in determining pH and DIC. Assuming a scenario where $[Ca^{2+}]$ is doubled, simulated DIC will be √2 times higher and $[H^+]$ √2 times lower (pH 0.15 higher) than it should be. Second, given that the large changes of $pK_{spC}$* and $pK_2$* cancel each other the dominant change of the aggregate $pK$* term in equations (2) and (3) arises from $pK_1$*, which only changes modestly in our Eocene scenario (Figure 2). That is, if the carbon cycle model was using modern seawater equilibrium constants, the error in DIC and $[H^+]$ would be modest (about +2% and −5% for the Eocene and Cretaceous scenarios of Figure 2). However, in the most common case the carbon cycle model would be using the correction factors of *Ben-Yaakov and Goldhaber* [1973] and *Tyrrell and Zeebe* [2004], and thus the changes in $pK_{spC}$* and $pK_2$* do not cancel as they should. In this case, due to the flawed Mg/Ca-ratio assumption in the correction factor of $pK_{spC}$* alone, simulated DIC would be ~17% too low and $[H^+]$ 17% too high (pH ~0.07 too low) for our Eocene seawater scenario. The magnitude of the error incurred obviously depends on the exact scenario of seawater $[Ca^{2+}]$ and $[Mg^{2+}]$ that is used, with much worse bias (about 40% for DIC and $[H^+]$) implied by the Cretaceous scenario discussed in this study.

### 3.3. Chemical Buffering of Seawater

The *T-S-X*-Ω-$CO_2$ system described above (Figure 4) is fully determined, and it fully describes the buffering of ocean chemistry against changes in DIC and ALK. Buffer factors for pH, $CO_2$, Ω, or any other acid/base parameter are defined as the inverse of either absolute or fractional partial derivatives in DIC or ALK [e.g., *Egleston et al.*, 2010]. Here we determine the absolute differential changes both numerically (Figure 5) and by approximate analytical solution:

$$\frac{\delta\left[CO_3^{2-}\right]}{\delta(\mathrm{DIC})} \cong \mathrm{CPF} = -\left(1+\frac{B_T}{\left[CO_3^{2-}\right]}\left(\frac{[H^+]}{K_B^*}+2+\frac{K_B^*}{[H^+]}\right)^{-1}+\frac{[H^+]^2}{K_1^*K_2^*}+\frac{K_W^*}{[H^+]\left[CO_3^{2-}\right]}+\frac{[H^+]}{\left[CO_3^{2-}\right]}\right)^{-1} \tag{4a}$$

$$\frac{\delta\left[CO_3^{2-}\right]}{\delta(\mathrm{ALK})} \cong -\mathrm{CPF}\sim\left(1+\frac{\left[B(OH)_4^-\right]}{\left[CO_3^{2-}\right]}\right)^{-1}\sim\left(1+\frac{\gamma^T_{CO3}B_TK_B^*}{\left\{CO_3^{2-}\right\}[H^+]}\right)^{-1}=\left(1+\frac{B_TK_B^*}{\left[HCO_3^{2-}\right]K_2^*}\right)^{-1} \tag{4b}$$

$$\frac{\delta(\mathrm{pH})}{\delta(\mathrm{ALK})} \cong \frac{1}{\left[CO_3^{2-}\right]*\ln 10}*\mathrm{CPF} \Leftrightarrow \frac{\delta(H)}{\delta(\mathrm{ALK})} \cong \frac{-[H^+]}{\left[CO_3^{2-}\right]}*\mathrm{CPF}=\frac{-\left[HCO_3^{2-}\right]K_2^*}{\left[CO_3^{2-}\right]^2}*\mathrm{CPF} \tag{4c}$$

$$\frac{\delta(CO_2)}{\delta(\mathrm{DIC})} \cong \frac{[H^+]^2}{K_0^*K_1^*K_2^*}*\mathrm{CPF}=\frac{[H_2CO_3]}{K_0^*\left[CO_3^{2-}\right]}*\mathrm{CPF} \tag{4d}$$

$$\frac{\delta(\Omega)}{\delta(\mathrm{DIC})} \cong -\frac{[Ca^{2+}]}{K_{spC}^*}*\mathrm{CPF}. \tag{4e}$$

These above formulations describe the various aspects of seawater buffering: (equations (4a) and (4b)) the sensitivity of ${CO_3}^{2-}$ to incremental DIC and ALK change, (equation (4c)) the sensitivity of pH to incremental ALK

  

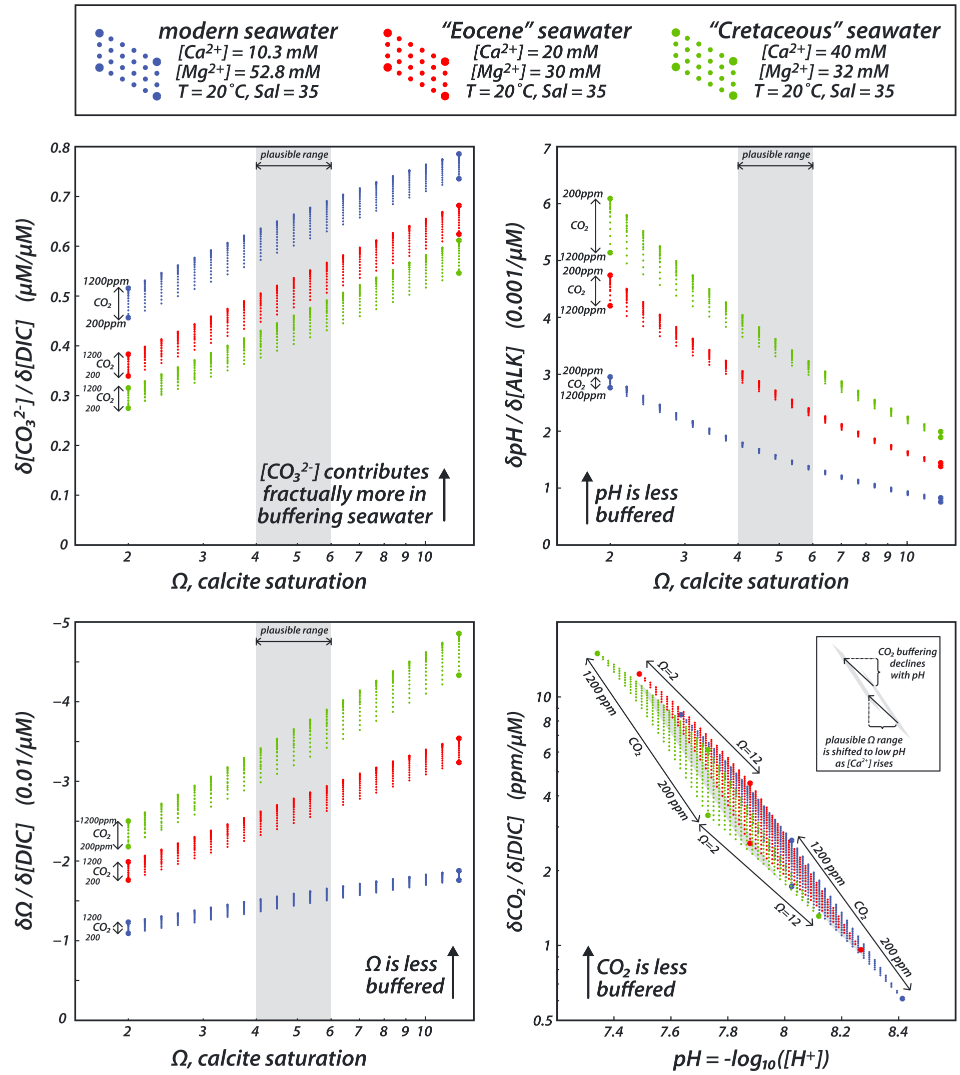


**Figure 5.** Sensitivity of $[CO_3^{2-}]$, pH, Ω, and $CO_2$ to incremental DIC and ALK change (δ/δDIC and δ/δDIC, respectively) under three cases: (blue) modern seawater major ion composition, (red) Eocene scenario major ion composition, and (green) Cretaceous scenario major ion composition. In all cases, salinity is 35 and $T$ = 20°C. The points of each color span the entire solution space of $CO_2$ = 200 ppm to 1200 ppm and Ω = 2 to 12. The sensitivity factors (i.e., inverse buffer factors) are numerically determined by perturbing DIC or ALK by 0.1 μM. Supporting information Figure S4 shows the same experiments but for both 20°C and 30°C, illustrating that buffering is only modestly affected by temperature (and verifying the accuracy of the approximate analytical solutions given by equation (4)).

change, (equation (4d)) the sensitivity of $CO_2$ to incremental DIC change, and (equation (4e)) the sensitivity of Ω to incremental DIC change. CPF, the "carbonate proton fraction," refers to the fraction of all proton transfers that is mediated by carbonate ion as opposed to the borate buffer system and the other minor contributors to seawater buffering. The approximations made in deriving these expressions are minimal, such that there is very good agreement with the numerical solutions (Figure S3). To demonstrate the effects of major ion change on seawater buffering, we consider three scenarios for seawater composition $X$ (Figure 5): (blue) modern $X$, (red) Eocene $X$, and (green) Cretaceous $X$; all at $S$ = 35 and $T$ = 20°C. As in Figure 4, all three cases correspond to the entire solution space spanned by Ω of 2 to 12 and $CO_2$ in the range 200 to 1200 ppm.

Our analysis reveals three principle factors that determine seawater buffering and the change of buffering in response to changing seawater $[Ca^{2+}]$ and $[Mg^{2+}]$: (1) calcium increase in the face of constant $CaCO_3$ saturation leads to a decline in buffering because it shifts the acid/base balance of seawater toward low $[CO_3^{2-}]$ and low pH, (2) buffering is greatest when pH is near $pK_1^*$, $pK_2^*$, and $pK_B^*$ and the conditional equilibrium constants respond to changes in seawater composition, and (3) a given perturbation of [$CO_3^{2-}$] causes a proportionally larger change in Ω as calcium increases. With these principles in mind we describe in detail below why the change in buffering of $CO_3^{2-}$, pH, Ω, and $CO_2$ behave differently, using modern, Eocene, and Cretaceous seawater scenarios for illustration.

Carbonate ion is the main proton acceptor acting to buffer seawater against incremental addition/removal of $CO_2$ (δDIC) and strong acid or base (δALK), but in modern surface water about one third of the proton transfer is buffered by the equilibrium between borate and boric acid [*Frankignoulle*, 1994; *Egleston et al.*, 2010], as well as a number of numerically less important chemical species ($H_2CO_3$ to $HCO_3^-$ equilibrium, $H^+$ to $OH^-$ equilibrium, etc.). Thus, the sensitivity of carbonate ion to incremental DIC and ALK change is equal to the "carbonate proton fraction" (CPF in equations (4a)–(4e)), which consequently is a factor in the buffering of any other chemical species in seawater. The CPF declines (carbonate ion is mediating less of the buffering) as the ratio of borate to carbonate ion increases, which could be due to (a) greater total boron $B_T$, (b) lower [$CO_3^{2-}$], or (c) higher pH at any given [$CO_3^{2-}$] (equation (4b)). As described above, we expect high [$Ca^{2+}$] during the Eocene and Cretaceous to drive substantially lower [$CO_3^{2-}$] (so as to maintain relatively constant Ω) such that the CPF should have been lower and [$CO_3^{2-}$] less sensitive to incremental DIC and ALK changes (Figure 5a). For a given $CO_2$, the shift toward lower [$CO_3^{2-}$] also causes a pH decline (i.e., Figure 4; equations (2) and (3)), which counteracts some of the CPF decline. Both these effects are caused by elevated calcium in the face of relatively constant Ω.

The CPF is also affected by complex formation between carbonate ion and the divalent cations: As the summed concentration of calcium, magnesium, and strontium that increases a greater fraction of [$CO_3^{2-}$] is complexed, the activity coefficient of carbonate ion declines (equation (S1c)), and $K_2$* rises (equation (S1a), Figure 2). Thus, a rise of total divalent cation (such as in our Cretaceous scenario) increases the CPF by reducing the fraction of proton transfer that is mediated by borate ion by shifting $pK_2$* down toward $pK_B$*. For the Cretaceous scenario, the reduction of [$CO_3^{2-}$] and pH in combination with the ~17% increase of $K_2$* increases the borate buffer term ~2.3-fold relative to the carbonate buffer term and thus reduces the CPF from modern ~66% to Cretaceous ~45% (Figure 5a; equations (4a) and (4b)). Overall, the decline of the CPF in both Eocene and Cretaceous scenarios implies that carbonate ion contributes fractionally less to seawater buffering (borate buffering is fractionally more important), making carbonate ion less sensitive to incremental DIC and ALK perturbation. This CPF decline, however, is related to a decline in the buffering action of carbonate ion rather than an increase in the buffering action of borate, hence leaving Eocene and Cretaceous seawater less well buffered overall.

The implied poor buffering of Eocene and Cretaceous seawater becomes clear when considering the sensitivities of [$H^+$] and pH to incremental change of DIC and ALK (Figure 5b; equation (4c)). An incremental change of carbonate ion leads to proportionally larger change of [$CO_3^{2-}$]/[$HCO_3^-$] and [$H^+$] if the initial [$CO_3^{2-}$] is lower, such as is implied for Eocene and Cretaceous seawater. Put differently, for a given combination of $CO_2$ and Ω, any increase of [$Ca^{2+}$] reduces [$CO_3^{2-}$] so as to shift pH down and away from $pK_2$* and $pK_B$*, thereby making seawater less well buffered. That is, even if an incremental change of DIC or ALK causes less absolute carbonate ion change at low pH, it still causes a greater fractional change of carbonate ion. Due to this partial cancelation between the CPF term and the [$H^+$]/[$CO_3^{2-}$] scaling factor, the shift in $pK_2$* due to ion pairing becomes a rather significant effect on the sensitivity of [$H^+$]. The lower than modern summed concentration of divalent cations in our Eocene scenario acts to raise $pK_2$* so as to further reduce the buffering of [$H^+$] by increasing the difference between pH and $pK_2$*. The reverse is true for Cretaceous scenario where summed divalent cation is greater and $pK_2$* is lower than modern.

The sensitivity of saturation state (Ω) is intimately related to the sensitivity of carbonate ion to incremental DIC and ALK change (equation (4e)), such that one might surmise that Ω buffering increases as CPF declines in the Eocene and Cretaceous scenario. However, as [$Ca^{2+}$] increases in these scenarios, a given incremental change of [$CO_3^{2-}$] causes a proportionally larger change in Ω. That is, the effect on Ω sensitivity from the ~20% decline in CPF for the Eocene scenario is overwhelmed by ~twofold greater [$Ca^{2+}$]. Moreover, the sensitivity of Ω also scales with the activity coefficient of carbonate ion (i.e., it scales with $1/K_{spC}$*), which rises by ~12% because the summed concentration of divalent cation is lower than modern in the Eocene scenario, such that Ω is about 1.65 times (e.g., 1.9 × calcium, 0.78 × CPF, and 1.12 × ion pairing) more sensitive

  

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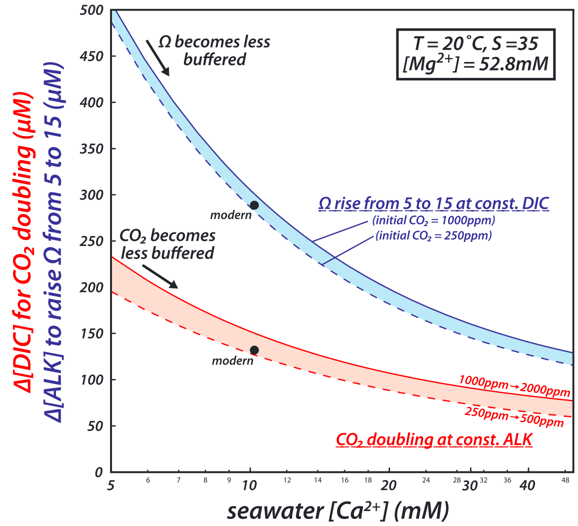


**Figure 6.** DIC and ALK change required to (red) double $CO_2$ and to (blue) raise Ω from 5 to 15 strongly decrease as seawater $[Ca^{2+}]$ concentration rises. The initial seawater is set to a $CO_2$ level of (dashed lines) 250 ppm or (solid lines) 1000 ppm, with Ω set to 5 in both cases.

to incremental DIC and ALK change. For the Cretaceous scenario the change is even more drastic with a 2.16 times increase in the sensitivity of Ω due to 3.8 × calcium, 0.67 × CPF, and 0.85 × ion pairing.

The buffering of $CO_2$ is strongly tied to both the carbonate ion to bicarbonate ion and the bicarbonate ion to carbonic acid equilibria. For this reason, the sensitivity of $CO_2$ is a function of the carbonic acid to carbonate ion ratio (equation (4d)). This dynamic can be described by two distinct relationships that amplify each other: (1) for a given $CO_2$ level $[H^+]$ increases and DIC decreases proportionally as $[CO_3^{2-}]$ declines, and (2) at a given $[CO_3^{2-}]$ concentration $[H^+]$ and DIC increase proportionally as $CO_2$ rises. For this reason, the sensitivity of $CO_2$ to incremental DIC and ALK change is very closely tied to $[H^+]$ while being essentially insensitive to DIC and with only secondary dependence on $[CO_3^{2-}]$, Ω, or $CO_2$.

This outcome for the buffering of $CO_2$ has implications for the effectiveness of carbon cycle perturbations to cause changes in atmospheric $CO_2$ and global climate for two related reasons. First, in a world with higher $CO_2$ levels, a given incremental perturbation of the carbon cycle causes a proportionally larger change in $CO_2$. And second, in a world with higher $[Ca^{2+}]$ (i.e., lower $[CO_3^{2-}]$) a given incremental perturbation of the carbon cycle causes a proportionally larger change in $CO_2$. Taking the ~3.5 × $CO_2$ (i.e., ~1000 ppm) and ~2 × $[Ca^{2+}]$ Eocene scenario as an example (assuming $\Omega = 5$ and $T = 20°C$), a 1 μM DIC addition causes 7 ppm $CO_2$ change (+0.7%), which is ~5 times greater (3.5 times for $CO_2$, 1.9 times for $[Ca^{2+}]$, and 0.78 times for the change of CPF) than the 1.4 ppm (+0.5%) caused by the same small carbon addition to modern surface water.

Concluding the treatment of seawater buffering, we note that the sensitivities derived above are valid only for small, incremental change of DIC and ALK; and estimating the magnitude of pH, Ω, or $CO_2$ change by simply multiplying the sensitivity by a large change of DIC or ALK leads to substantial error. Here we solve numerically the integral of the sensitivities to calculate (a) the amount of DIC that needs to be added in order to double $CO_2$, and (b) the amount of ALK that needs to be added to raise Ω to some set level (Figure 6). We find that these two quantities are a strong function of seawater $[Ca^{2+}]$: Seawater becomes less well buffered as calcium is increased (at $\Omega = 5$), and thus less DIC or ALK needs to be added to achieve any set change in seawater acid/base chemistry. As further discussed below, the two idealized experiments of Figure 6 are relevant in the context of "climate sensitivity" (i.e., equilibrium warming per $CO_2$ doubling likely in the range of 1.5–4.5 K per doubling; see section 10.8.2 in *Intergovernmental Panel on Climate Change* [2013] AR5) and as a driver for the evolution of calcifying organisms [e.g., *Stanley and Hardie*, 1999] and carbon concentration mechanisms [e.g., *Reinfelder*, 2011].

## 4. Discussion and Conclusion

### 4.1. Equilibrium Constants of Past Seawater

The use of empirically determined conditional equilibrium constants [*Millero*, 1995; *Dickson et al.*, 2007] associated with modern ocean major ion composition greatly simplifies calculations of seawater acid/base chemistry from field measurements and in carbon cycle models of the modern ocean because this approach implicitly accounts for "ion pairing" [*Garrels and Thompson*, 1962]. Currently available simple relationships to correct modern seawater conditional equilibrium constants for $[Ca^{2+}]$ and $[Mg^{2+}]$ changes [e.g., *Ben-Yaakov and Goldhaber*, 1973; *Tyrrell and Zeebe*, 2004] have proven inaccurate. The formulations of *Ben-Yaakov and Goldhaber* [1973] cause modest bias that could be acceptable under some circumstances. However, the $pK_{spC}$* correction factor derived by *Tyrrell and Zeebe* [2004] is based on a fundamentally flawed assumption (i.e., assumed Mg/Ca-ratio dependence) and insufficient thermodynamic data (only $Mg^{2+}$ is varied), and it should therefore be avoided [see also *Roberts and Tripati*, 2009]. To be clear, the criticism of *Tyrrell and Zeebe* [2004] is limited to their treatment of $pK_{spC}*$, and it does not relate to the main focus of that study.

The initial impetus for this study and our "MyAMI" model was the lack of adequate equilibrium constants for carbon cycle modeling of time periods when seawater composition was different than today. The general approach taken here is not new, but we are convinced that equilibrium constants for a wide range of seawater [$Mg^{2+}$] and [$Ca^{2+}$] are going to be a useful resource for the field. Hence, in the supporting information, we make the source code of MyAMI available (at https://github.com/MathisHain/MyAMI), and we provide pretabulated parameters that define the temperature and salinity dependences of the conditional equilibrium constants for [$Mg^{2+}$] and [$Ca^{2+}$] in the range 0–60 mM (Table S1). These equilibrium constants are processed with the goal to make them suitable for inclusion in carbon cycle models: (a) in existing model code, only parameters need to be changed while the algorithms can stay the same, and (b) at modern seawater composition, the MyAMI-derived equilibrium constants conform to the empirical data sets [*Millero*, 1995; *Dickson et al.*, 2007].

### 4.2. Early Cenozoic Acid/Base Chemistry

Beyond its utility for carbon cycle modeling, our assessment of the thermodynamics of seawater acid/base chemistry in the face of changes in seawater [$Ca^{2+}$] and [$Mg^{2+}$] more generally aids in the formulation of quantitative hypotheses for the state of carbon chemistry during any given interval of Earth history. In this context, we use the Eocene period as an example for how thermodynamic considerations can be used to weigh various observations against one another. Both our choice of Eocene seawater properties ([$Ca^{2+}$] = 20 mM, [$Mg^{2+}$] = 30 mM; 10°C warming; see Figure 4c) and a rough consensus of ~1000 ppm $CO_2$ in early Eocene [*Beerling and Royer*, 2011] bear significant uncertainty and need not be accepted. However, if these conditions are correct, only one free parameter remains to fully determine surface ocean acid/base chemistry. The above constraints force covariation among the three parameters Ω, DIC, and pH as follows. The remaining solution space is conveniently described by two end-member scenarios: (1) near-modern surface ocean Ω and DIC at a pH of ~7.65, or (2) Ω and DIC both substantially elevated above modern values at pH substantially higher than 7.65.

No methods exist to independently reconstruct surface Ω and DIC, and available pH reconstructions for the Eocene [*Pearson and Palmer*, 1999, 2000] are vigorously debated for their underlying assumptions [e.g., *Demicco et al.*, 2003] and systematic methodological uncertainties [*Pagani et al.*, 2005]. While keeping these caveats in mind, we note that reconstructed pH for the latest Paleocene and earliest Eocene ranges between 7.6 and 7.4, while reconstructed pH mostly falls between 7.8 and 8 for the later parts of the Eocene [*Pearson and Palmer*, 2000].

The methodology of pH reconstruction based on boron isotope measurements is being continuously improved. Together with the thermodynamic considerations presented here, there is the promise that the acid/base chemistry of Eocene surface waters can be constrained with confidence in the near future. Using Pitzer parameters of *Simonson et al.* [1988] for the ion interactions of orthoborate and the divalent cations (no boric acid interactions reported), we find the boric acid dissociation constant $pK_B*$, which is central to the boron isotope pH proxy, to be only weakly affected by changing [$Ca^{2+}$] and [$Mg^{2+}$], in agreement with earlier experimental results by *Hershey et al.* [1986].

### 4.3. Seawater Buffering

Our results demonstrate that—mainly due to elevated [$Ca^{2+}$] but also because of a lower than modern sum of divalent cations in the scenario—the Eocene ocean must have been less well buffered overall. The environmental and biological consequences of this change can be divided into those involving the buffering of $CO_2$ partial pressure and those involving the buffering of pH and Ω, as outlined below.

The buffering of $CO_2$ partial pressure against incremental change in DIC (and ALK) strongly depends on seawater pH, and to a lesser degree on the summed concentration of divalent cations that form complexes with carbonate ion (Figures 5b and S4; equation (4d)). Changes in ocean pH, both past and future, would then imply consequences for photosynthesizing marine organisms: in low-pH seawater, phytoplankton that rely on carbon concentrating mechanisms with active transport of DIC or ALK to improve photosynthetic efficiency [e.g., *Reinfelder*, 2011, and references therein] would have benefited from greater intracellular $CO_2$ increase per increment of transported chemical. Conversely, as atmospheric $CO_2$ declined over the Cenozoic and thus likely drove a greater need for carbon concentrating mechanisms, the secular pH rise would have necessitated greater DIC or ALK transport by carbon concentrating mechanisms to elevate phytoplankton-internal aqueous $CO_2$ by a given amount. This compounding of stressors was a likely driver of phytoplankton evolution toward more efficient carbon concentrating mechanisms.

The buffering of pH and Ω strongly depends on [$Ca^{2+}$] and Ω, as well as on the summed divalent cation concentrations (~[$Mg^{2+}$]+[$Ca^{2+}$]). That is, if [$Ca^{2+}$] was higher and Ω did not dramatically differ from its modern 4–6 range, then both Ω and pH must have been substantially less well buffered against DIC or ALK change during the Eocene (Figures 5c, 5d and S4; equations (4c) and (4e)). This finding suggests that the ocean's lysocline and calcite compensation depth (CCD) would have been more sensitive to DIC and ALK change. As a result, a given change in the global carbon cycle or the ocean's biological pump would have yielded more pronounced transient $CaCO_3$ dissolution/preservation events in the Eocene and thus shortened the timescale of imbalances in the ocean's alkalinity budget. Moreover, essentially all marine calcification is mediated or controlled by organisms that use evolved biochemical mechanisms to actively manipulate the acid/base chemistry and thus Ω at the site of calcification [e.g., *Lowenstam and Weiner*, 1989; *Gattuso et al.*, 1998; *Buitenhuis et al.*, 1999; *Iglesias-Rodriguez et al.*, 2008; *Ries et al.*, 2009; *de Nooijer et al.*, 2009; *Mackinder et al.*, 2010; *Gagnon et al.*, 2012]. In poorly buffered oceans of the past, Ω and pH are much more sensitive to incremental changes in DIC and ALK (Figure 5c, equations (4c) and (4e)), suggesting that metabolic expenditure of biologically controlled calcification should have been reduced. As a consequence, even organisms with less efficient mechanisms for increasing internal $CaCO_3$ saturation state may have been capable of hypercalcification in the poorly buffered, high-[$Ca^{2+}$] Cretaceous ocean (blue in Figure 6). Conversely, the secular increase in seawater buffering after the mid-Cretaceous would have required more DIC and/or ALK modification to reach a given level of internal $CaCO_3$ supersaturation. This effect probably contributed to the turnover and evolution of marine organisms since that time, including the Late Cretaceous decline of rudists and the early Cenozoic rise of corals as the main reef builders. This consideration is in addition to previously discussed effects of changing seawater Mg/Ca ratio as a direct mineralogical control on the evolution of calcifying organisms [*Stanley and Hardie*, 1998, 1999; *Ries,* 2005, 2006a, 2006b; *Ries et al.*, 2006; *Stanley et al.*, 2002, 2005, 2010; *Stanley*, 2006].

Finally, the poor buffering of pre-Neogene seawater to small, incremental DIC and ALK change discussed above also translates to much larger sensitivity of pH, $CO_2$, and Ω to large-scale changes in the carbon cycle, such as geologic carbon release. Focusing on the sensitivity of $CO_2$, less carbon needs to be added to Eocene seawater in order to double its $CO_2$ from 1000 to 2000 ppm than is required to double $CO_2$ from 250 to 500 ppm under modern seawater composition (Figure 6). This finding effectively reduces the amount of geologic carbon release needed to explain the large magnitude of global warming during the Paleocene-Eocene Thermal Maximum (PETM) [e.g., *Dickens et al.*, 1995; *Pagani et al.*, 2006; *Zeebe*, 2013]. And yet, the argument by *Zeebe et al.* [2009] that a pulse of 3000 PgC is insufficient to explain the magnitude of $CO_2$ increase and warming still holds because they already implicitly include poor seawater buffering. It therefore appears that at least some of the carbon originated from sources other than the limited methane reservoir [e.g., *Higgins and Schrag*, 2006]. Any such geologic carbon addition would also cause greater transient shoaling of the CCD under high [$Ca^{2+}$] with low Ω buffering (Figures 5d and 6). Beyond the PETM, the same amplified response of atmospheric $CO_2$ and the ocean interior's calcite saturation depth would also have applied to changes in the ocean's biological pump and other aspects of the ocean/atmosphere carbon cycle. This high sensitivity of deep ocean saturation state may help to explain the dramatic swings in lysocline depth that have been reconstructed for the early to mid-Cenozoic [*Pälike et al.*, 2012].

Poor seawater buffering and its consequences are even more extreme in the mid-Cretaceous, when seawater [$Ca^{2+}$] was ~4 times its modern value. By the same token, seawater [$Ca^{2+}$] today appears to be at the lowest concentration it has been in the last 100 million years, likely giving rise to the most strongly buffered seawater. In this context, we need to take careful account of changing seawater composition and buffering when comparing anthropogenic carbon release to geologic events.

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