

A model of Phanerozoic cycles of carbon and calcium in the global ocean: Evaluation and constraints on ocean chemistry and input fluxes

Robert E. Locklair*, Abraham Lerman

Department of Geological Sciences, Northwestern University, Evanston, IL 60208, USA

Received 23 March 2004; received in revised form 16 December 2004; accepted 27 December 2004

Abstract

The relationships between the global carbon cycle and paleo-climates on short and long time scales have been based on studies of accumulation rate of the two main components of the sedimentary carbon reservoir, organic carbon and carbonate carbon. Variations in the rate and proportion of carbonate burial through Phanerozoic time have been attributed to the effects of tectonics on eustasy, atmospheric CO₂ concentration, MOR (Mid-Ocean Ridge) hydrothermal flux, and weathering and riverine flux.

This study addresses the history of variations in the state of the surface ocean and its degree of saturation with respect to calcite and aragonite, based on a geochemical model that considers the Phanerozoic atmospheric P_{CO_2} and surface ocean temperature reconstructions as the main forcings on the system. The results show that, using near-present-day values of ocean salinity and alkalinity, the Early Paleozoic and Middle Mesozoic oceans are calculated to be undersaturated (or nearly undersaturated) with respect to CaCO₃. For the near-present-day values of supersaturation ($\Omega = \text{ICP}/K_{\text{sp}}$) of 3–5 with respect to calcite, paleo-alkalinity of ocean water would have been up to 2.5 times greater than at present, although the pH values of surface ocean water would have been somewhat lower than the present values. This alkalinity factor is consistent with a higher calcium concentration (up to $\times 2.5$) due to increased circulation at ocean spreading-zones and also higher salinity (up to $\times 1.5$) attributed by other authors to segments of the geologic past. Our model results indicate that although P_{CO_2} was a contributing factor to shifts between calcite and aragonite saturation of seawater, additional changes in alkalinity were needed to maintain supersaturation at the level of 3–5, comparable to the present. Continental weathering of crystalline and older carbonate rocks, in addition to MOR (Mid-Ocean Ridge) circulation, was likely an important mechanism for maintaining supersaturation of surface ocean water, particularly during times of increased carbonate storage.

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Keywords: Phanerozoic; Calcium carbonate; Carbonate minerals saturation; Carbon cycle; Alkalinity

* Corresponding author. Fax: +1 847 491 8060.

E-mail address: locklair@earth.northwestern.edu (R.E. Locklair).

1. Introduction

Natural perturbations of the long-term carbon cycle and atmospheric CO₂ reservoir size have been suggested to impact global climate (e.g., Crowley and Berner, 2001). Variations in atmospheric CO₂ are likely linked to CO₂ variations within the oceanic reservoir because of its much greater carbon mass and relatively rapid exchange of CO₂ with the atmosphere. In the Earth surface environment, carbon exchange between atmospheric, biotic, soil, and oceanic reservoirs is generally rapid on a geologic time scale, with characteristic times from years to thousands of years, and it is referred to as the exogenic or short-term carbon cycle (e.g., Berner, 1999). The long-term carbon cycle, with characteristic times of 10⁸–10⁹, years involves accumulation of oceanic sediments, their partial subduction and partial incorporation in the continental crust, volcanic and metamorphic degassing, continental uplift, erosion and chemical weathering (e.g., Rankama and Sahama, 1950).

The oceans are the largest short-term carbon cycle reservoir where mineral CaCO₃ and biologically produced organic matter form, that are the main sources of carbon to the sedimentary reservoir for long-term storage. Therefore, the oceanic reservoir of carbon and environmental conditions in that reservoir are important components of long-term carbon cycling.

The relationships between the global carbon cycle and paleo-climates on short and long time scales have largely been based on studies of accumulation rates of the two main components of the sedimentary carbon reservoir, organic carbon and carbonate carbon (Berner and Canfield, 1989; Wilkinson and Walker, 1989; Mackenzie and Morse, 1992; Bosscher and Schlager, 1993; Hayes et al., 1999; Walker et al., 2002). Variations in the rate and proportion of carbonate burial through Phanerozoic time have been variably attributed to the influence of eustasy, atmospheric CO₂ concentration, mid-ocean ridge (MOR) hydrothermal flux, and weathering and riverine flux (Mackenzie and Pigott, 1981; Sandberg, 1985; Hardie, 1996). However, the relative importance of these processes to carbon cycling, possible changes in surface ocean chemistry, and paleo-climate is not fully understood.

For example, either the dynamics of MOR circulation, and corresponding changes in Mg/Ca ratios (Stanley and Hardie, 1998) or atmospheric CO₂ concentrations and associated changes in marine carbonate chemistry (Sandberg, 1985) were postulated as drivers of oscillations in preferential preservation of aragonite or calcite in sediments. These oscillations are due to the different solubilities of the two minerals: $K_{sp}(\text{calcite})=10^{-6.37}$ and $K_{sp}(\text{aragonite})=10^{-6.19}$ at the salinity of 35, 25 °C, and $P=1$ bar; at the same salinity, but at 5000 m depth where $P \approx 510$ bar and the temperature is 1.5 °C, the two minerals are more soluble although the difference between their solubilities is essentially the same, $K_{sp}(\text{calcite})=10^{-5.93}$ and $K_{sp}(\text{aragonite})=10^{-5.76}$. The difference in the degree of saturation at ocean surface conditions is $\Omega_{\text{calcite}} \approx 1.5\Omega_{\text{aragonite}}$, due to the higher solubility of aragonite. Such oscillations are noted in the record of inorganic precipitates of CaCO₃ in ooids and cements (Sandberg, 1985) are interpreted as reflecting changes in ocean chemistry or environmental conditions in calcification and depositional settings. As a better understanding of the input and burial fluxes of carbon and calcium within the oceanic reservoir would help to constrain their relative importance to the changes in the long-term carbon cycle, this study addresses the following specific questions:

- What would be the saturation state (Ω) of calcite and aragonite in Phanerozoic surface waters at equilibrium with reconstructed P_{CO_2} concentrations and temperatures?
- What other major parameters of the oceanic carbon cycle have likely changed through time and can such changes be constrained?
- Are resulting saturation states consistent with the hypothesis of P_{CO_2} as a driver of calcitic–aragonitic oscillations in the marine record?
- What input fluxes of C and Ca were needed to maintain organic carbon and carbonate burial rates through the Phanerozoic?

2. Background relationships

The chemical relationships essential to our analysis are summarized below. The solubility of CO₂ and its

apparent dissociation constants in surface ocean water are:

$$[\text{H}_2\text{CO}_3^*] = K_0 P_{\text{CO}_2} \quad (1)$$

$$[\text{HCO}_3^-] = P_{\text{CO}_2} K_0 K_1 / [\text{H}^+] \quad (2)$$

$$[\text{CO}_3^{2-}] = P_{\text{CO}_2} K_0 K_1 K_2 / [\text{H}^+]^2 \quad (3)$$

K_0 , K_1 , and K_2 are functions of temperature and salinity (Zeebe and Wolf-Gladrow, 2001) and H_2CO_3^* represents both $\text{CO}_{2(\text{aq})}$ and carbonic acid, concentrations are in [mol/kg], and the H^+ -ion concentration in relation to the pH is on the pH total scale (Zeebe and Wolf-Gladrow, 2001). The sum concentration of dissolved carbonate species is total dissolved inorganic carbon (DIC):

$$[\text{DIC}] = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (4)$$

Total alkalinity is the electric charge balance in solution between the ionic concentrations of H^+ -independent cations and H^+ -independent anions, and it is equal to the charge–concentration balance of the H^+ -dependent species:

$$[\text{A}_T] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] = A_C + A_B + A_W \quad (5a)$$

where A_C is carbonate alkalinity, A_B is borate alkalinity (the borate anion concentration), and A_W is water alkalinity or the difference between the OH^- and H^+ -ion concentrations. At atmospheric CO_2 concentration of 280 ppmv and temperature between 5°C and 15 °C, carbonate alkalinity accounts for 96–97% of total alkalinity and borate alkalinity is 4–3% of the total. Total alkalinity as a function of P_{CO_2} and pH is:

$$[\text{A}_T] = (K_0 K_1 P_{\text{CO}_2} / [\text{H}^+]) + (2K_0 K_1 K_2 P_{\text{CO}_2} / [\text{H}^+]^2) + K_W / [\text{H}^+] + [\text{DIB}] / (1 + [\text{H}^+] / K_B) - [\text{H}^+] \quad (5b)$$

DIB is dissolved inorganic boron and K_W and K_B are the apparent dissociation constants of water and boric acid, respectively. In simpler terms, alkalinity is a conservative quantity that does not change with temperature, and it is equivalent to the amount of acid that can be neutralized by a solution. Total alkalinity is not affected by changes in internal P_{CO_2}

or atmospheric CO_2 concentration at equilibrium with seawater. However, DIC, the pH, and $\text{B}(\text{OH})_4^-$ concentration as a fraction of total dissolved boron all change with changing P_{CO_2} .

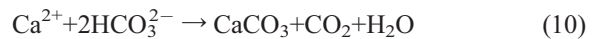
Rivers bring both a dissolved and particulate flux of carbon to surface ocean water. The dissolved flux of inorganic carbon is sourced by oxidation of organic matter, Eq. (6), dissolution of carbonate minerals, Eq. (7), and hydrolysis of silicate minerals, Eq. (8):



Alteration of oceanic crust at mid-ocean ridges is comparable to reaction Eq. (8). Primary production consumes CO_2 in the photic zone through photosynthesis:



Much of the organic matter is oxidized (Eq. (6)) in shallow water, but some is vertically transported to the deep ocean, to be, in part, returned in dissolved form by upwelling and, in part, buried in sediment. Numerous groups of marine biota are also prominent producers of biogenic calcium carbonate (Lowenstam and Weiner, 1989):



To maintain the alkalinity of ocean water, supply of dissolved ionic constituents must be balanced by their removal, as shown in Eqs. (7)–(10). Precipitation of calcite generates dissolved CO_2 , Eq. (10), and biological production of organic matter consumes CO_2 , Eq. (9). At the time scales of the last 10^4 – 10^2 years, since the Last Glacial Maximum 18,000 yr b.p. to the end of pre-industrial time about 300 yr ago, net storage of CaCO_3 and C_{org} in the coastal and open ocean sediments was responsible for significant fluxes of CO_2 from surface ocean to the atmosphere (Lerman and Mackenzie, 2004). However, at geologically longer time scales, the sea-to-air CO_2 transfer must have been balanced by its uptake in other reservoirs of the global carbon cycle, without which the fluctua-

tions in atmospheric CO₂ concentration would have been unreasonably large.

The saturation state of the carbonate minerals in surface water can be expressed as the ratio (Ω) of ion concentration product (ICP) to the solubility product (K_{sp}) (Mucci, 1983; Zeebe and Wolf-Gladrow, 2001):

$$\Omega = \text{ICP}/K_{sp} \quad (11)$$

The ICP for calcite and aragonite is the product of calcium and carbonate total ion concentrations in solution. The K_{sp} values for these minerals are the product of total calcium and carbonate ion concentrations in seawater that is saturated with the particular mineral. At the specific conditions of temperature and salinity, Ω values greater than 1 represent supersaturation and $\Omega < 1$ undersaturation with respect to these minerals.

3. Model parameters

The effects of temperature and atmospheric carbon dioxide concentration on equilibrium constants and surface water pH are important, as ancient ocean composition (the carbonate system in particular) in the Phanerozoic was argued to have been different from modern ocean composition. The evidence for varied Phanerozoic seawater chemistry has been derived from several types of studies: carbonate mineralogy and abundance patterns (Mackenzie and Pigott, 1981; Sandberg, 1985; Mackenzie and Morse, 1992; Stanley and Hardie, 1998), evaporite and fluid inclusion compositions (Hardie, 1996; Holland et al., 1996; Kovalevich et al., 1998; Lowenstein et al., 2001; Horita et al., 2002), variation in marine isotopic records (Pearson and Palmer, 1999; Veizer et al., 1999; De La Rocha and DePaolo, 2000), and various models of marine systems (Wallmann, 2001; Zeebe, 2001; Demicco et al., 2003; Hansen and Wallmann, 2003). If models of atmospheric carbon dioxide (e.g., Berner and Kothavala, 2001) provide a reasonable estimate of Phanerozoic surface ocean CO₂ through its solubility following Henry's Law, Eq. (1), then portions of the Phanerozoic, when atmospheric P_{CO_2} might have been up to 30 times that of pre-industrial values, are

also likely to record changes in marine carbonate chemistry. In order to evaluate and constrain changes in Phanerozoic surface ocean chemistry at time scales of 10⁷–10⁸ years and quantify transport fluxes of C and Ca with respect to this reservoir, the following data were used: (1) shallow, tropical marine temperatures reconstructions (Veizer et al., 1999; Wallmann, 2001, 2004); (2) modeled atmospheric CO₂ concentrations (Berner and Kothavala, 2001); and (3) estimates of the sedimentary burial rates of organic carbon (Berner and Canfield, 1989) and carbonate (Wilkinson and Walker, 1989; Mackenzie and Morse, 1992; Berner, pers. comm., 2004). The carbon dioxide and temperature data sets, also shown in Fig. 1A, were used to evaluate oceanic carbonate chemistry. The equations discussed in the previous section address oceanic equilibrium with respect to atmospheric CO₂ in the geologic past. The sediment organic carbon and carbonate data are shown in Fig. 1B. The equilibrium constants for each reaction were calculated for given temperatures and modern values of salinity (35 psu or practical salinity units on the UNESCO salinity scale, close to 35 g/kg) using the equations of Mucci (1983) and Zeebe and Wolf-Gladrow (2001).

4. Results

For the Phanerozoic, values of the pH, DIC, and the carbonate species, as shown in Fig. 2, were calculated, using the temperature (Wallmann, 2001, 2004) and P_{CO_2} (Berner and Kothavala, 2001) reconstructions for the Phanerozoic, in conjunction with assumed present day alkalinity, salinity, and DIB for the entire time period. The results of the pH and [CO₃²⁻] are similar to those reported by Tyrrell and Zeebe (2004), who calculated these values from estimates of CaCO₃ saturation state over the past 100 million years, whereas our results aim to calculate saturation states of calcite and aragonite from the aforementioned parameters. Our results indicate that the ocean would have been undersaturated with respect to calcite and aragonite over long periods of time in the Paleozoic and nearly reach undersaturation in the Mesozoic (Fig. 2D), assuming present-day alkalinity. With respect to calcite, this computed undersaturation occurs about 160 million

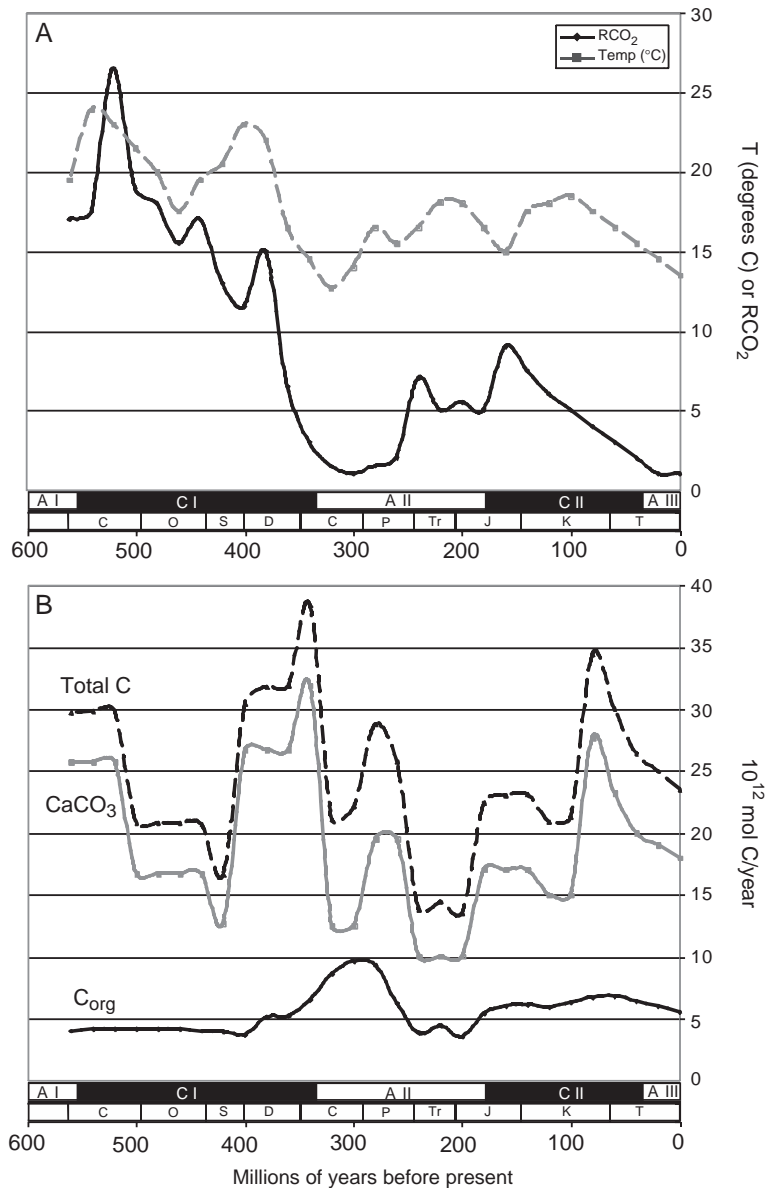


Fig. 1. Reconstructions of Phanerozoic P_{CO_2} , shallow sea temperatures, and carbon burial fluxes in relation to oscillations in calcitic, labeled C, and aragonitic, labeled A, seas, following Stanley and Hardie (1998). (A) Modeled atmospheric CO_2 concentrations are expressed relative to the 300 ppmv Holocene value (RCO_2 ; Berner and Kothavala, 2001) and shallow sea temperatures, derived from oxygen isotopes in biogenic carbonate, are in degrees Celsius (Wallmann, 2004). (B) Reconstructions of organic carbon (C_{org} ; including coal; Berner and Canfield, 1989) and carbonate (Mackenzie and Morse, 1992) burial rates.

years ago in the Mesozoic Era (Jurassic) and 560–380 million years ago in the Paleozoic, from the Cambrian to the Late Devonian. The duration of undersaturation with respect to aragonite is similar, though slightly longer, as aragonite is more soluble

under surface ocean conditions; undersaturation occurs from Jurassic to Early Cretaceous (160–120 million years ago) and from Cambrian to Devonian (560–380 million years ago). The range of the Ω values shows that during these periods the degree of

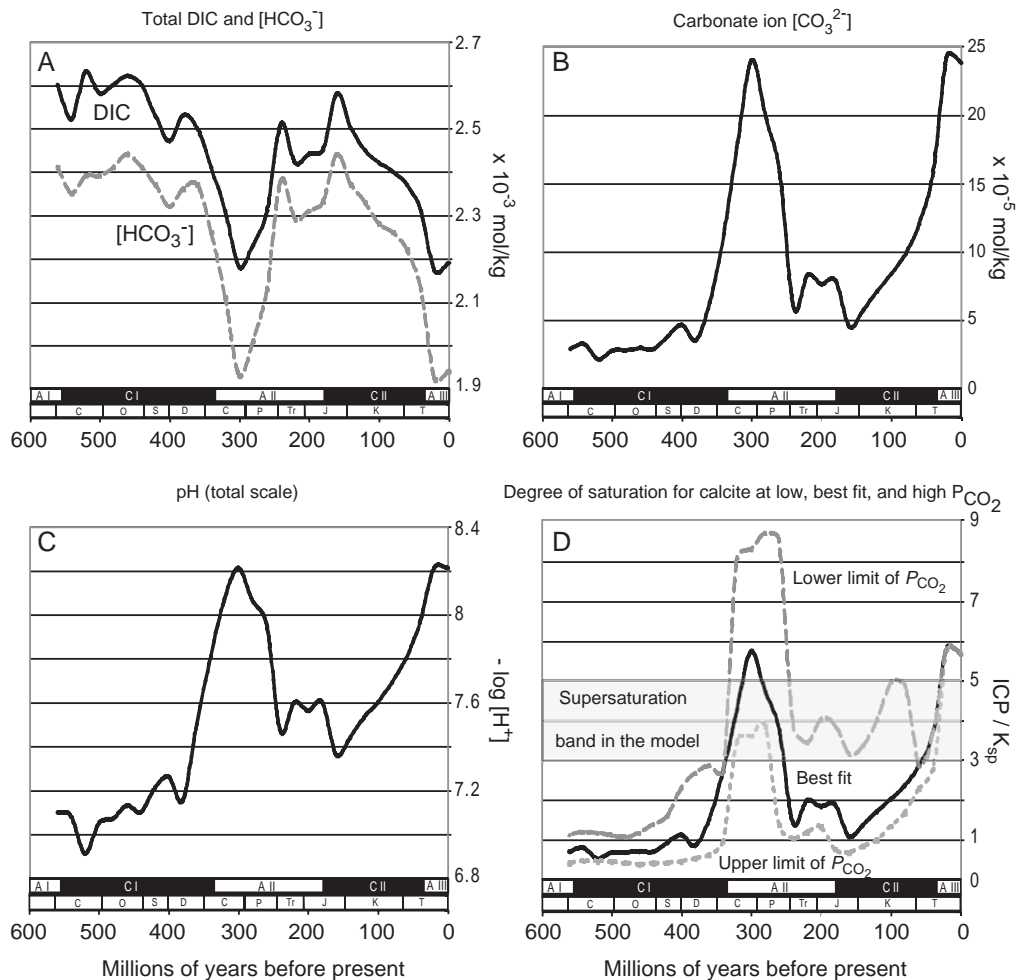


Fig. 2. Modeled components of the oceanic carbonate system as a function of P_{CO_2} and surface ocean temperatures at constant alkalinity. (A) Total dissolved inorganic carbon and bicarbonate concentrations. (B) Carbonate ion concentration. (C) pH as the negative logarithm of hydrogen ion concentration on the total scale. (D) Degree of saturation (Ω) values for calcite based on constant Ca^{2+} -ion concentration (modern) and the carbonate ion concentration in (B). Values below 1 indicate undersaturation. The highlighted band represents near modern saturation values that are referred to in the text and Fig. 3. The three model runs are from the best fit P_{CO_2} values from Berner and Kothavala (2001) and their upper and lower limits through the Phanerozoic.

saturation was considerably lower than in the Recent and it roughly corresponds to time intervals when primary inorganic carbonate sediments and cements are calcitic, and calcite secreting organisms flourished in comparison to aragonite secretors (Sandberg, 1985; Stanley and Hardie, 1998). Results of undersaturation for both calcite and aragonite are difficult to reconcile with the occurrence of massive deposits of limestone in these geologic periods (Sandberg, 1985). Although the rate of CaCO_3 deposition, as

shown in Fig. 1, might have varied by a factor of about 3, between 10 and 30×10^{12} mol C/yr during most of the Phanerozoic, the high and low depositional periods do not coincide with the high and low degrees of supersaturation with respect to calcite, as computed in Fig. 2. The effect of P_{CO_2} on the degree of saturation of ocean water is considerably greater than the effect of temperature because of the large range and the high values of P_{CO_2} estimated for the Early Paleozoic (Fig. 1).

5. Discussion

The result in the preceding section, showing undersaturation of surface ocean water with respect to calcite at the given forcings of P_{CO_2} and temperature at constant alkalinity, leads to the following question: what would be the alkalinity of surface ocean water if the degree of supersaturation with respect to calcite were always in a band between $\Omega \approx 3$ and 5 (Fig. 2D), at the P_{CO_2} and temperature values as used in the preceding computation and shown in Fig. 1? The conservative range of supersaturation between 3 and 5 is representative of the Tertiary and close to the modern value of about 5.5–6. The Tertiary is characterized by relatively strong mechanical erosion of the continents and deposition of CaCO_3 formed to a large extent by planktonic and benthonic oceanic organisms, and coral reefs and possibly calcareous algae on continental shelves. This environment is likely to be different from the earlier geologic periods when other calcium-carbonate-secreting organisms, occupying different ecological

niches, were abundant in the ocean or when the origin of the limestones might have been weighted differently between inorganic and biogenic modes. Despite these uncertainties, the range of supersaturation between 3 and 5 is at least as defensible as any other range for the past and the assumption of a constant band of Ω may be consistent with a relatively long Ca^{2+} residence time in the ocean ($\sim 10^6$ years; from data in Broecker and Peng, 1982; Drever, 1988).

For this range of supersaturation, using the same value of P_{CO_2} and temperature, as well as the modern value of $[\text{Ca}^{2+}]$ in ocean water, alkalinity was computed, Eq. (5b). The results, shown in Fig. 3, indicate that alkalinity would have to be greater by a factor of 2.5–3.5 at certain geologic periods, if the degree of supersaturation with respect to calcite were at a level of 3–5. This alkalinity factor is consistent with a higher calcium concentration, up to $\times 2.5$ due to increased MOR circulation, as estimated by Hardie (1996), and higher salinity, up to $\times 1.5$ (Hay and Wold, 1997). Such variation in alkalinity, however, may be due to dynamics of continental weathering

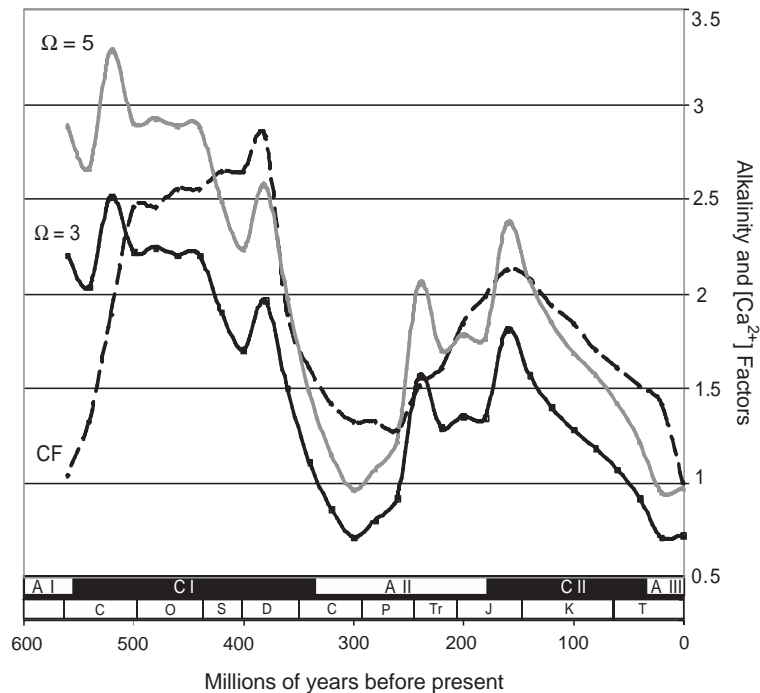


Fig. 3. Modeled alkalinity factors (normalized to the modern value= 2.41×10^{-3} mol-equivalent/kg) for maintaining calcite supersaturation of $\Omega=3$ and 5 with input conditions of temperature (Wallmann, 2004) and atmospheric CO_2 (Bernier and Kothavala, 2001). Dashed line shows the Phanerozoic calcium ion concentration factor (CF; relative to present) of Horita et al. (2002).

and riverine transport more than to interaction between ocean water and mid-ocean ridge system, if the latter contributed less alkalinity to the ocean than weathering, as in the present. Alternatively, increases in Ca^{2+} ion flux and concentration may be called upon (e.g., by a concentration factor up to ~ 2.5 ; [Hardie, 1996](#); [Horita et al., 2002](#)) in conjunction with the same input parameters of P_{CO_2} and temperature, in order to achieve modeled supersaturation of calcite during these times. Incorporation of such Ca^{2+} factors ([Fig. 3](#)) in our model of aqueous carbonate species through the Phanerozoic does, of course, result in higher degrees of saturation for the previously described undersaturated periods (Early Paleozoic and Middle Mesozoic, [Fig. 2D](#)), but many of the values are still below 3 ([Fig. 4](#)), lower than the near-present-day value. This indicates that neither atmospheric carbon dioxide nor seawater calcium concentrations are likely to have been sole drivers of observed calcite–aragonite oscillations in the Phanerozoic sedimentary record, at least under the input conditions of temperature ([Wallmann, 2004](#)) that are used in this model. Other geochemical studies of

ancient marine waters assume constant temperature ([Pearson and Palmer, 2000](#); [Demicco et al., 2003](#)).

On time scales of $>10^6$ years, burial fluxes of both C and Ca must be matched by cumulative input fluxes or else oceanic reservoirs would have become depleted with respect to these elements, which are largely dominated by riverine (weathering) and hydrothermal fluxes on such long time scales ([Berner, 1999](#)). Present-day and last 25-million-year average fluxes of calcium to the world's oceans have been attributed primarily to riverine sources ($\sim 72\%$; hydrothermal reactions and cation exchange $\sim 28\%$) and 93–96% of the marine bicarbonate is supplied from rivers. For these two periods, riverine inputs of Ca account for 57–81% of CaCO_3 removal into sediments, respectively ([Berner and Berner, 1996](#)). However, on longer time scales, the restored burial rates of carbonate ([Mackenzie and Morse, 1992](#); [Berner, pers. comm., 2004](#)) and organic carbon ([Berner and Canfield, 1989](#)), as shown in [Fig. 1](#), should be balanced by similar input fluxes of similar magnitude.

Changes in alkalinity of the paleo-oceans that are needed, as calculated here, to maintain surface ocean

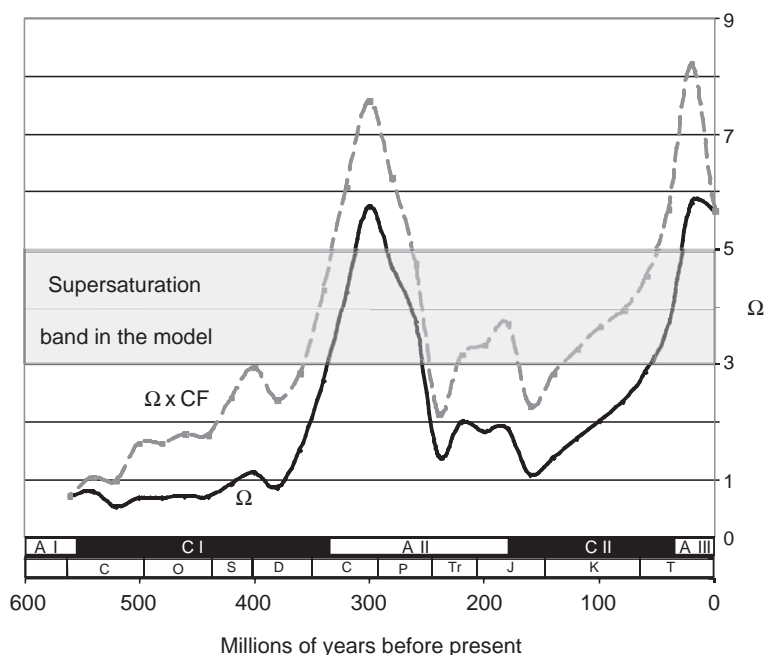


Fig. 4. Calculated saturation value of calcite at constant alkalinity and modern $[\text{Ca}^{2+}]$ ([Fig. 3D](#), best fit) and saturation value multiplied by estimated Phanerozoic $[\text{Ca}^{2+}]$ factor (CF) of [Horita et al. \(2002\)](#). Note that either curve falls below the supersaturation band for long periods of time.

supersaturation with respect to calcite at a factor of $\Omega=3-5$ (Fig. 4) could have been produced by very small changes, about 0.4%, in each of the major cations' concentrations in ocean water relative to the present composition, without considering any changes in Cl^- and SO_4^{2-} (present-day values: $\text{Na}^+=0.470$, $\text{K}^+=0.010$, $\text{Ca}^{2+}=0.010$, and $\text{Mg}^{2+}=0.053$ mol/kg). The present-day sum of the four major cation-equivalent concentrations is 0.6060 mol-equivalent/kg and an increase of the individual concentrations by about 0.4% increases the sum to 0.6084 mol-equivalent/kg, which makes alkalinity greater by 2.4×10^{-3} than the present-day value of 2.41×10^{-3} mol-equivalent/kg, or greater by a factor of 2. Although the calculation of a slight increase in cationic concentrations needed to maintain charge balance with increased alkalinity is simplistic, it helps demonstrate the point that alkalinity changes remain a potentially important mechanism for sustaining calcium carbonate supersaturation through the Phanerozoic. We recognize that studies of evaporite sequences (e.g., Horita et al., 2002; Demicco et al., 2003) have documented changes in Phanerozoic cation concentrations of seawater indicating that concentrations of some species have changed significantly (e.g., Mg^{2+} and Ca^{2+} may have varied by a factor of 2–6 relative to the modern), whereas others, such as K^+ , have not (Horita et al., 2002). Modeled saturation states of calcite at constant alkalinity and calcium ion concentration are compared to model results with elevated $[\text{Ca}^{2+}]$, following Phanerozoic values of Horita et al. (2002). Incorporation of such calcium factors effectively raises the degree of saturation of calcite throughout the Phanerozoic, but fails, in some intervals, to raise these values to a range near that of the modern and suggests that other changes are requisite, such as alkalinity.

If increased surface ocean alkalinity were a product of enhanced weathering and runoff then, presumably, there would have been a correlative increase in riverine transport of major ionic species. This increase is small relative to the baseline of average cation and anion concentrations in modern river water (e.g., Meybeck, 1979; Drever, 1988; Gaillardet et al., 1999). Phanerozoic burial rates of C and Ca, as estimated by other authors, are tabulated in Table 1 (Bernier and Canfield, 1989 for organic carbon; Mackenzie and Morse, 1992, and Bernier,

pers. comm., 2004, for carbonate). Estimates of Ca sequestered in evaporite deposits are not included here, as such output fluxes are 1–5 orders of magnitude smaller than that of Ca in carbonate. Burial fluxes of Ca in evaporites were determined from the total mass of evaporites reported by period for the post-Triassic in Hay and Wold (1997) and the proportion of Ca in evaporites presented in Bernier and Bernier (1987). In conjunction with a model of Phanerozoic riverine discharge (Tardy et al., 1989; Table 1), necessary riverine composition to maintain supersaturation of calcite and replenish Ca lost to sedimentation and burial (reconstructed net burial flux) is shown in Table 1. The calculated results in the table are based on the assumption that the oceanic carbon reservoir is replenished with carbon, dominantly bicarbonate from runoff, to compensate for carbon (both organic and carbonate forms) that is delivered to storage in sediments. This mass of carbon is taken as representing dissolved inorganic carbon (DIC) supplied by rivers. The DIC/Ca ratio of input flux needed to maintain conditions of supersaturation and carbon storage is lower (1.1–1.4) than that of typical modern river systems (2.31–2.55; Table 1, column 9) or of the pre-industrial input of carbon and the estimated Ca concentration that would have matched the CaCO_3 sediment storage (1.81). However, if the mole ratios of carbon to calcium in rivers have remained at a global average of 1.8 through Phanerozoic time then, in conjunction with estimates of total carbon burial rates, the rate of Ca delivery by rivers would be smaller than the computed rate needed to match the CaCO_3 burial rate as given in Table 1 (column 10). The difference between the two Ca concentrations in rivers gives a deficiency of Ca in riverine input relative to the modern DIC/Ca ratios. This computed deficiency suggests that a significant proportion of Ca, 30–40%, would be needed from another source, such as hydrothermal circulation, to maintain carbonate supersaturation and burial rate. The computed DIC/Ca ratio in river input that is needed to match the CaCO_3 and C_{org} burial rates (Table 1, column 9) may be underestimated because the formation and net storage of CaCO_3 in sediments generate CO_2 and, in a counter process, CO_2 is taken in by the production of organic matter. The net result may be emission of CO_2 from the surface ocean to the

Table 1
Estimates of global runoff, carbon burial, and computed input fluxes of C and Ca needed to balance burial and computed supply by rivers at time intervals of 20 million years

Time Ma	River flow (runoff) ^a 10 ¹⁶ kg/yr	C _{org} burial rate ^b 10 ¹³ mol/yr	CaCO ₃ burial rate ^c 10 ¹³ mol/yr	CaCO ₃ burial rate ^d 10 ¹³ mol/yr	C _{org} +HCO ₃ ⁻ in rivers ^e 10 ⁻⁴ mol/kg	Input Ca matching CaCO ₃ burial ^f 10 ¹³ mol/yr	Ca conc. in rivers ^g 10 ⁻⁴ mol/kg	DIC/Ca in input ^h	Ca deficiency in rivers ⁱ 10 ⁻⁴ mol/kg	Percent Ca in CaCO ₃ supplied by rivers ^j
0	4.0	0.5	1.8	2.1	6.5	2.1	5.3	1.24	1.7	68
20	4.1	0.6	1.9	2.3	6.9	2.3	5.5	1.25	1.7	69
40	4.9	0.6	2.0	3.2	7.6	3.2	6.5	1.18	2.3	65
60	5.2	0.6	2.3	3.7	8.2	3.7	7.1	1.16	2.6	64
80	5.2	0.5	2.8	2.8	6.4	2.8	5.4	1.19	1.8	66
100	5.0	0.5	1.5	3.4	7.8	3.4	6.8	1.15	2.5	63
120	4.7	0.5	1.5	3.4	8.2	3.4	7.2	1.15	2.6	64
140	4.3	0.5	1.7	3.3	8.9	3.3	7.8	1.15	2.8	64
160	4.0	0.5	1.7	3.5	9.9	3.5	8.6	1.14	3.2	63
180	3.9	0.4	1.7	3.5	10.2	3.5	9.1	1.13	3.4	62
200	4.1	0.3	1.0	3.9	10.3	3.9	9.5	1.08	3.8	60
220	4.4	0.4	1.0	3.4	8.7	3.4	7.7	1.12	2.9	62
240	4.5	0.3	1.0	3.3	7.9	3.3	7.3	1.08	3.0	59
260	4.1	0.4	2.0	2.1	6.0	2.1	5.1	1.18	1.8	65
280	4.3	0.4	2.0	1.9	5.2	1.9	4.4	1.19	1.5	66
300	4.3	0.4	1.3	2.0	5.5	2.0	4.6	1.19	1.6	65
320	4.7	0.3	1.3	1.9	4.8	1.9	4.0	1.18	1.4	65
340	4.9	0.5	3.2	3.0	7.1	3.0	6.2	1.15	2.2	64
360	4.9	0.5	2.7	3.3	7.8	3.3	6.7	1.16	2.4	64
380	5.0	0.5	2.7	3.7	8.5	3.7	7.4	1.14	2.8	63
400	5.5	0.4	2.7	3.4	6.9	3.4	6.2	1.11	2.4	61
420	5.5	0.4	1.3	3.3	6.8	3.3	6.0	1.12	2.3	62
440	5.8	0.4	1.7	3.6	6.9	3.6	6.2	1.11	2.4	61
460	5.8	0.4	1.7	2.8	5.6	2.8	4.8	1.15	1.8	63
480	5.8	0.4	1.7	2.7	5.4	2.7	4.7	1.15	1.7	64

500	6.2	0.4	1.7	3.0	5.5	3.0	4.8	1.14	1.8	63
520	6.3	0.4	2.6	3.5	6.2	3.5	5.5	1.12	2.1	62
540	6.3	0.4	2.6	2.2	4.1	2.2	3.5	1.19	1.2	66
560	6.3	0.4	2.6	0.9	2.0	0.9	1.4	1.44	0.3	80
Present(pre-industrial)	3.74 ^k	0.8 ^l		3.2 ^l	10.7 ^{e,m}	3.2	3.34 ⁿ	2.43±0.12 ⁿ		
					15.5 ^o		8.56 ^{g,m}	1.81 ^p		57 to 81 ^q

Note that the concentration of carbon in present day runoff varies due to uncertainties of runoff rate and carbon burial rate.

^a Estimated global runoff rate for the Phanerozoic (Tardy et al., 1989).

^b Estimated organic carbon burial rate (excluding coal) for the Phanerozoic (Bernier and Canfield, 1989).

^c Reconstructed carbonate burial rate for the Phanerozoic (Mackenzie and Morse, 1992).

^d Reconstructed carbonate burial rate for the Phanerozoic (Bernier, pers. comm., 2004).

^e Calculated concentration of C in rivers to match burial [(column 3+5)/column 2].

^f Input of Ca needed to match burial of CaCO₃.

^g Calculated [Ca²⁺] of rivers, assuming no other sources for deposition (column 7/column 2).

^h Mole ratio of buried C (sum of columns 3 and 5) and Ca (column 5).

ⁱ Calculated deficit of Ca in rivers, assuming no other source of Ca to the ocean and pre-industrial DIC/Ca ratio of 1.81.

^j Percentage of Ca supplied by rivers.

^k Meybeck (1979), Drever (1988).

^l Milliman (1993), Mackenzie et al. (2004), Lerman and Mackenzie (2004).

^m (Column 3+5)/Column 2=10.7×10⁻⁴ mol C/kg; Column 5/Column 2=8.56×10⁻⁴ mol C/kg.

ⁿ Drever (1988), Bernier and Bernier (1987).

^o DIC 32×10¹² and DOC reactive 26×10¹² mol C/yr in pre-industrial river flow (Ver et al., 1999).

^p Column 6/Column 8=1.81.

^q Bernier and Bernier (1996), Ca in river input as a fraction of CaCO₃ sediment storage.

atmosphere. Because of this CO_2 loss, input of carbon to the surface ocean must be slightly greater than the mass of carbon removed into sediments or, otherwise, there would be a long-term depletion of carbon from the oceanic reservoir. These estimates do not support the hydrothermal source of Ca as a lead driver for changes in the degree of carbonate saturation through Phanerozoic time. The calculation places an upper limit of Ca contribution from hydrothermal circulation at spreading zones at roughly 30–40% of estimated carbonate burial rates. Modern riverine values and ratios of DIC/Ca vary between drainage basins and they depend on source lithology, with typical average values: crystalline rock=2.46; volcanic rock=3.69; sedimentary rock=2.19 (Berner and Berner, 1987).

Some uncertainties in the forcing and input data used in this paper should be mentioned. First, the marine surface temperatures of Wallmann (2001, 2004) are, as the author points out, derived from $\delta^{18}\text{O}_{\text{PDB}}$ values of biogenic carbonate that are not well constrained, bathymetrically or latitudinally. The reported values are thus likely to reflect near-bottom shallow-ocean temperatures at low latitudes. The lower temperature values of the Middle Mesozoic should also be noted. Second, hypothesized variations in seafloor spreading rate through time, specifically over the last 180 million years, have been called into question (Rowley, 2002) with significant implications for the estimated input of Ca from hydrothermal circulation, and atmospheric and oceanic concentrations of carbon dioxide and carbonate species. Finally, calculations of paleo-accumulation rates and storage of inorganic and organic carbon through time are also subject to uncertainties. Preserved volumes of ancient sediments and their geochemical signatures provide some evidence for carbon storage and accumulation histories, but, nevertheless, we compare our model results with the results of other models. Certainly, more primary data are needed to improve this and other models. Despite these uncertainties, the model in this paper, although certainly simplistic given the complexities of the system, attempts to arrive at gross carbonate chemistry of Phanerozoic surface oceans based on equilibration of these waters with respect to paleo- P_{CO_2} , surface water temperatures, and riverine input from land as reported in the literature.

6. Conclusions

The model of surface ocean chemistry and input fluxes presented in this paper is based on two forcings, for which there is a fair degree of confidence (temperature, P_{CO_2}). Less well-known parameters, such as salinity, are kept at their present value in the model. The results indicate that: (1) surface waters equilibrated with atmospheric P_{CO_2} , as reconstructed by Berner and Kothavala (2001), and at reconstructed temperatures (Wallmann, 2004), are calculated as undersaturated with respect to calcite and aragonite for portions of the Paleozoic and Mesozoic, assuming constant alkalinity; (2) elevated alkalinities during modeled periods of undersaturation would maintain supersaturation of ocean water with respect to calcite without modification of the two external forcings; (3) changes in either hydrothermal circulation rate or atmospheric carbon dioxide concentration are unlikely to have forced observed calcite–aragonite oscillations unilaterally; in light of our results and other studies, both mechanisms likely played a role; and (4) within the uncertainties of ancient carbon weathering and burial fluxes, the necessary fluxes of C and Ca needed to maintain supersaturation and burial rates can be reconstructed. However, continental weathering and supply of Ca may be an underappreciated mechanism for satisfying the oceanic conditions of carbonate deposition.

The periods when the computed alkalinity had to be higher than at present are roughly coincident with other investigators' periods of calculated higher Ca^{2+} -ion concentration in ocean water (Stanley and Hardie, 1998), salinity (Hay and Wold, 1997), and continental runoff to the oceans (Tardy et al., 1989). Salinity changes, though difficult to reconstruct for the past, are potentially important because of their effect on the solubility of gases and carbonate equilibria in ocean water. Other authors have also reported oceanic models (e.g., Pearson and Palmer, 2000; Zeebe, 2001) that call upon alkalinity changes for portions of the Phanerozoic. Although variations in either P_{CO_2} or seawater $[\text{Ca}^{2+}]$, specifically MOR-derived, would have had a significant impact on carbonate saturation states, our results do not support either one as an exclusive forcing factor. A more integrated explanation of Phanerozoic calcite–aragonite oscil-

lations that includes variability in $[Ca^{2-}]$ and total alkalinity via both riverine and hydrothermal flux dynamics that is correlative and consistent with changes in atmospheric carbon dioxide partial pressures is favored. Continental weathering of crystalline and older carbonate rocks was an important mechanism for maintaining supersaturation of surface ocean water, particularly during times of increased carbonate storage, possibly more important than MOR circulation. Such variations in ocean chemistry and input fluxes that reflect the computed degree of saturation with respect to the $CaCO_3$ minerals depend on the reconstructed values of temperature and P_{CO_2} in our model input data.

The rates of $CaCO_3$ burial in sediments, as reported by other investigators, do not clearly correlate with the computed higher values of ocean-water alkalinity that were needed to maintain supersaturation with respect to calcite. Possibly, the carbonate burial rates were at least to some extent dependent on the abundance of $CaCO_3$ -secreting marine organisms or, more speculatively, alkalinity is somewhat decoupled from nutrient availability and the links within the food chain. Alternatively, a more vigorous hydrologic cycle could have supplied the balancing Ca and also delivered more (compared to the present) bicarbonate to the oceans through elevated rates of chemical weathering, which is consistent with hypotheses of enhanced weathering with high atmospheric CO_2 concentrations.

Acknowledgements

This work was supported by NSF grants OAR-0002889 and EAR-02-23509, and the Arthur L. Howland Fund of the Department of Geological Sciences, Northwestern University. We thank Robert A. Berner (Yale University) and Klaus Wallmann (Leibniz-Institut für Meereswissenschaften, Universität Kiel) whose critical reviews helped improve the paper, Fred T. Mackenzie (University of Hawaii) and Bruce H. Wilkinson (University of Michigan) for reviews and helpful comments on an earlier version of this manuscript, Richard E. Zeebe (University of Hawaii) for making available a paper in press, and Robert Berner for making available unpublished data. [LW]

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