

How I (almost) stopped being afraid of geochemistry and learned to spell **AlKaLiNiTY**

Learning the basics of glacial CO₂ biogeochemistry

working notes, Eli Tziperman

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1 Introduction

Tutorial notes for myself on basic glacial CO₂ geochemistry. The model formulation follows Toggweiler (1999). This is complemented by the Matlab box model `box_geochem.m`. Perhaps this would be useful to others interested in the subject, but having no chemistry background whatsoever, like myself. . .

2 Outline

Here is a brief outline of the various dependencies between the biogeochemical quantities that we need to deal with to calculate the atmospheric carbon dioxide concentration, CO₂(g). The atmospheric CO₂ concentration depends on the concentration of carbon dioxide dissolved in sea water CO₂(aq),

$$\text{CO}_2(\text{g}) = F_1(\text{CO}_2(\text{aq}), T, S).$$

The concentration of dissolved CO₂, in turn, depends on the concentration of the rest of the carbonate system ions (H₂CO₃, HCO₃⁻, CO₃²⁻, OH⁻, H⁺). The distribution of carbon among these ions depends on the “alkalinity” (*Alk*) which is a quantity having to do with the concentration of charged ions (belonging to weak acids, more below) in the ocean and which will be useful when writing the charge conservation for the ocean, and on the “total CO₂” (ΣCO₂, or *C_T*) which is the sum of all dissolved inorganic carbonate ions. Both terms are defined more precisely below. So the following equation represents this dependence which includes the entire carbonate system (some 6-8 equations) which needs to be solved for the dissolved CO₂ as will be described in detail below. In the meanwhile we write symbolically,

$$\text{CO}_2(\text{aq}) = F_2(\text{Alk}, \Sigma\text{CO}_2).$$

While we still have not defined alkalinity and total CO₂ precisely, we need equations for them. The charge distribution in the ocean varies due to chemical reactions that combine ions into neutral molecules. In particular, this happens when living organisms perform photosynthesis or grow their shells and form biological “particles” which eventually sink to the deep ocean and dissolve there. The Alkalinity also varies due to advection and diffusion between different water masses that have different alkalinities, and due to other inputs from rivers etc. So we write symbolically at this stage,

$$\begin{aligned} \frac{d}{dt} \text{Alk} &= \text{advection+diffusion} + r[\text{alk/particles}] \text{ Particle Flux} \\ &+ \text{river input+bottom sediment+volume changes.} \end{aligned}$$

Similarly, the total CO₂ in the ocean varies for similar reasons,

$$\begin{aligned} \frac{d}{dt} \Sigma\text{CO}_2 &= \text{advection+diffusion} + r[\Sigma\text{CO}_2/\text{particles}] \text{ Particle Flux} \\ &+ \text{river input+bottom sediment+volume changes.} \end{aligned}$$

To evaluate the biological productivity of those particles and their effects on total CO₂ and alkalinity which appears in the above equation as particle flux, we also need to know the concentration of the nutrients which are used by the plankton to produce particles. We therefore add an equation for a representative nutrient, [PO₄], which is again affected by the production of particles and by advection and diffusion,

$$\begin{aligned} \frac{d}{dt}PO_4 &= \text{advection+diffusion} + r[PO_4/particles] \times \text{Particle Flux} \\ &+ \text{river input+bottom sediment+volume changes} \end{aligned}$$

To close the system, we need expressions for the sinking biological particle flux as function of the biological productivity (also called export production), and for the export production as function of other known factors. These will be given below.

To calculate the atmospheric CO₂(g), integrate in time the prognostic ($\frac{d}{dt}$) equations for the alkalinity, total CO₂ and nutrient. At each time, solve for the dissolved CO₂(aq) in ocean water from the known alkalinity and total CO₂ by solving the carbonate system equations. Given the dissolved CO₂, calculate the atmospheric CO₂(g) and proceed to the next time step. That's all there's to it...

3 Definitions

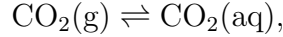
Here are some elementary definitions of things mentioned in these notes.

1. $P_{CO_2}^{atmos}$: atmospheric CO₂
2. $P_{CO_2}^{ocean}$: pressure of gas phase CO₂ that would be in equilibrium with dissolved CO₂ in the ocean.
3. T, S : temperature and salinity
4. $pH = -\log_{10}[H^+]$; $[H^+]$ in *mol/liter*.
5. Redfield ratio: $P : N : C = 1 : 16 : 122$ in organic matter in the ocean. Also define $R_{P:C} = 1 : 122$ and $R_{P:N} = 1 : 16$
6. Rain ratio: ratio of organic to inorganic carbon atoms extracted from the ΣCO_2 pool per PO₄ molecule that sinks as particulate matter to the deep ocean.
7. Calcification: rate of **net** CaCO₃ deposition in mols/(liter×sec); (calcification by corals and Forams, or minus rate of dissolution).
8. Respiration: rate of oxidation of organic material (normally by bacteria in sediments or deep water) turning organic matter and oxygen back into CO₂.

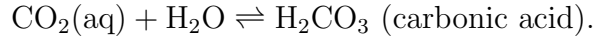
9. Rate of export production EP is the number of $[\text{PO}_4]$ molecules per unit time per unit area falling as particulate organic matter (fecal pellets and dead plankton) from the surface to the deep ocean. Number of molecules of Carbon and Nitrogen can be calculated from that using the Redfield ratio).

4 The carbonate system

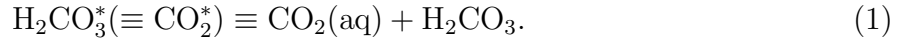
Our objective is to find the relation between atmospheric CO_2 , dissolved CO_2 , CO_3^{2-} , ocean pH and other related variables. We start by introducing the relevant chemical reactions that are part of the ocean carbonate system. Carbon dioxide is soluble in water, and its dissolution occurs in two steps. First, “Henry’s law” states that atmospheric $\text{CO}_2(\text{g})$ concentration is in equilibrium with dissolved $\text{CO}_2(\text{aq})$,



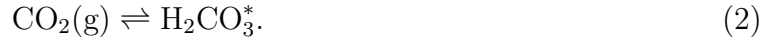
and then, its reaction with water is given by,



Because it is difficult to distinguish between $\text{CO}_2(\text{aq})$ and H_2CO_3 , they are treated together as a single variable defined as,



In terms of this variable, Henry’s law is,



Now, carbonic acid is a weak diprotic acid (diprotic acids are able to release two protons),



Finally, water dissociation is given by,



In order to solve the carbonate system for the six unknowns: $\text{CO}_2(\text{g})$, H_2CO_3^* , HCO_3^- , CO_3^{2-} , OH^- , H^+ , we so far have only four equations: (2), (3), (4) and (5). We therefore need to specify two more constraints. One is mass conservation for the total number of carbon ions, expressed via a quantity known as total Dissolved Inorganic Carbon (DIC), also referred to as total CO_2 and denoted ΣCO_2 or C_T , which is conserved in the above reactions. The other constraint is the charge balance (conservation of electric charge), that again must be conserved in the above reactions, and is expressed via a parameter called

“alkalinity”, *Alk*. C_T and *Alk* are both measurable quantities for which one can write conservation equations affected by various sources and sinks, as well as by the movement and mixing of water masses. Once DIC and alkalinity are specified at a given location in the ocean, the carbonate system is completely determined (that is, there are the same number of unknowns and equations) and the concentrations of the different ions can be calculated. Consider these two constraints in some detail now.

Total CO₂ The total number of micromoles carbon atoms per liter ($\mu MC/l$) is given by the sum of the different species of the carbonate system,

$$\begin{aligned} \text{DIC} \equiv \Sigma \text{CO}_2 \equiv C_T &= [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\ &\approx [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \end{aligned}$$

where the partition of carbon among the species appearing on the first line in the ocean, in percents, is correspondingly, 1%, 90%, 10% (this partition is a strong function of pH), hence the approximation in the second line.

Alkalinity The concept of alkalinity (measured in $\mu Eqv/l$) arises when one considers the charge balance of seawater. The net charge needs to be zero, which, when we take into account the major ions in the ocean, means that,

$$\begin{aligned} 0 &= ([\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]) \\ &\quad - ([\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{Cl}^-] \\ &\quad + 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HBO}_3^-]). \end{aligned} \tag{6}$$

Now, we are interested in how some of these ion concentrations change with pH, CO₂ and other factors. For this purpose, it is useful to differentiate between strong bases and acids whose concentration does not change with pH, and weaker ones that do change. For example, when NaCl dissolves in seawater, it separates completely into Na⁺ and Cl⁻ regardless of the pH. However, in the dissociation of the weak acid HCO₃⁻, $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$, the concentrations of the ions on the RHS and LHS of this equilibrium vary with pH. Alkalinity is a measure of the charge balance due to these weak acids and bases. It is defined as the sum of negative ions that belong to weak acids that change their dissociation with the ocean pH, minus the sum of positive ions that originate from weak acids. Separating the charge balance (6), into the parts due to the weak acids and bases (first line) and strong ones (second and third lines), we have,

$$\begin{aligned} 0 &= ([\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{HBO}_3^-]) \\ &\quad + ([\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] \\ &\quad - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-]). \end{aligned}$$

Defining the alkalinity to be the negative of the first line, we have

$$\begin{aligned}
Alk &\equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HBO}_3^-] - [\text{H}^+] \\
&= [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] \\
&\quad - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-].
\end{aligned} \tag{7}$$

Clearly the pH and alkalinity affect each other. This occurs directly as $[\text{H}^+]$ appears in the expression for alkalinity. But also indirectly, as when the pH changes, it affects some of the equilibria in the carbonate system and thus changes the concentration of ions that determine the alkalinity. Finally, note that the concentration of $[\text{H}^+]$ is very small (for seawater, pH=8.2, implying $[\text{H}^+] \approx 10^{-8}$ mole = 10^{-2} μ mole, while HCO_3^- in the ocean is measured in thousands of μ mole), and so are the concentrations of other ions, so that the alkalinity may be approximated by the carbonate alkalinity alone as defined in the first line below, and then further approximated as shown in the second line,

$$\begin{aligned}
Alk_C &\equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \\
&\approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}].
\end{aligned} \tag{8}$$

4.1 Carbonate system equations

To perform calculations, we write the carbonate system as the following set of equations using the equilibrium constants, based on the above reactions. The six unknowns are,

$$[\text{CO}_2(g)], [\text{H}_2\text{CO}_3^*], [\text{OH}^-], [\text{H}^+], [\text{HCO}_3^-], [\text{CO}_3^{2-}], \tag{9}$$

where we remember that

$$\text{H}_2\text{CO}_3^*(\equiv \text{CO}_2^*) \equiv \text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3, \tag{10}$$

and the first four equations are,

$$K_H \equiv K_0(T, S, P) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(g)]} \tag{11}$$

$$K_1(T, S, P) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \tag{12}$$

$$K_2(T, S, P) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \tag{13}$$

$$K_w(T, S, P) = [\text{H}^+][\text{OH}^-]. \tag{14}$$

For typical values of these reaction coefficients on the LHS, which depend on temperature T , salinity S and pressure P , see section 4.2. To close the system, we need two more equations, the definitions of alkalinity and total CO_2 ,

$$Alk = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \tag{15}$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*]. \tag{16}$$

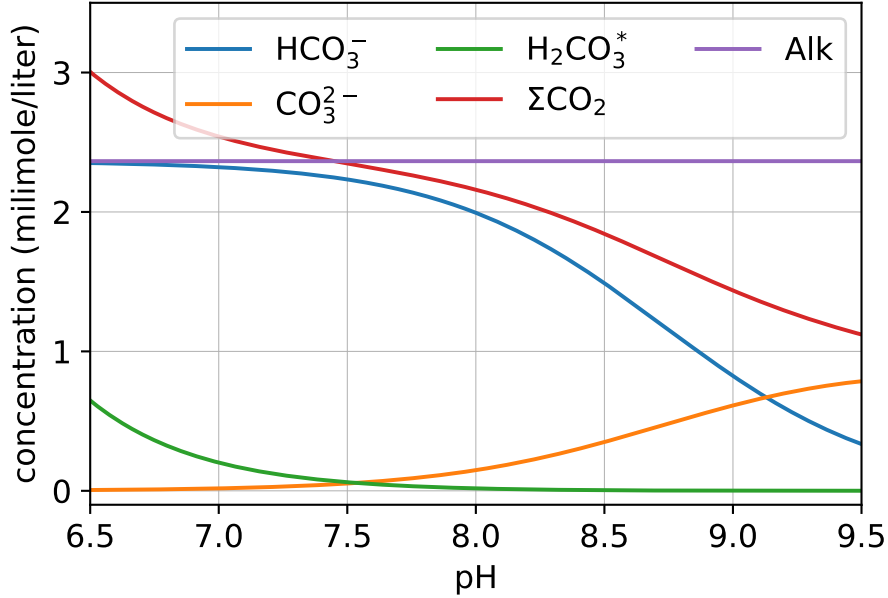


Figure 1: The solution of the carbonate system, showing the concentration of carbonate species as function of pH, for a fixed alkalinity.

Given the values of Alk , C_T , K_H , K_1 , K_2 and K_w , we can use the six carbonate system equations (11, 12, 13, 14), and the definitions of alkalinity and total CO_2 (15, 16), to solve for the six unknowns (9). This is a nonlinear system of equations, and it may be solved iteratively. Note that instead of specifying Alk and C_T , we could have specified any two of the carbonate system variables, such as $CO_2(g)$ and Alk , or C_T and pH.

The solution of the carbonate system as function of pH, for a constant alkalinity, is shown in Figure 1. As a reminder, the current average surface ocean pH is about 8.1. Note that the carbonate ion (orange line), whose concentration controls the dissolution of calcium carbonate via the saturation state $\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}$, decreases significantly for lower pH values, while the concentration of the bicarbonate ion (blue) increases. This solution provides the information regarding the response of the carbonate system as function of pH required for us to calculate the ocean response to increased CO_2 . In particular, the solution for pH and the carbonate ion as function of CO_2 is shown in Figure 2, showing a significant reduction of the carbonate ion concentration as the atmospheric CO_2 increases. An even better understanding of the system can be developed by considering an approximate set of carbonate system equations that can be solved directly, as we do in the next section.

4.2 Approximate solution of the carbonate system

Consider an approximate solution to the carbonate system that allows us to better understand the response of the system to increased atmospheric CO_2 in a future global warming scenario, or removal of DIC by the ocean biology as part of the glacial-interglacial variability.

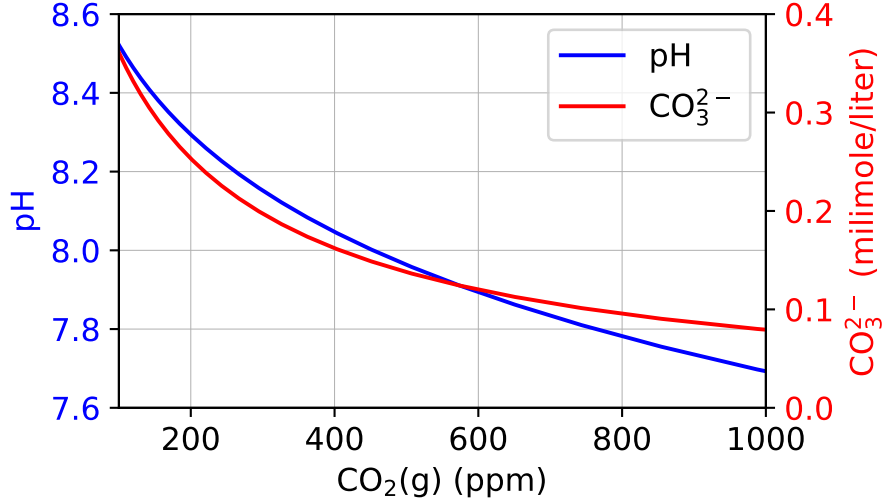


Figure 2: The solution of the carbonate system, showing the ocean pH (blue) and the carbonate ion CO_3^{2-} concentration (red) as function of atmospheric CO_2 .

The approximation used here is valid only at pH values around 8, and for small perturbations to the DIC, and is consistent with the ocean pH values at present or those that are anticipated in the coming decades. For this pH range we may assume,

$$[\text{HCO}_3^-], [\text{CO}_3^{2-}] \gg [\text{H}^+], [\text{OH}^-], [\text{H}_2\text{CO}_3^*].$$

The ions on the left are measured in hundreds to thousands of micromoles per liter (Figure 1). The smallness of $[\text{H}_2\text{CO}_3^*]$ may be deduced from Figure 1 (see green line near pH= 8). That $[\text{H}^+]$ is small is clear from the pH level which implies that $[\text{H}^+] \sim 10^{-8}$ mole/l. That $[\text{OH}^-]$ is small is similarly deduced from the water dissociation equation (14) and the fact that $K_w \sim 2 \times 10^{-14}$.

With this approximation, let the carbonate system unknowns be the values of the five concentrations $[\text{CO}_2(\text{g})]$, $[\text{H}_2\text{CO}_3^*]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and $[\text{H}^+]$. With a total of five unknown ($[\text{OH}^-]$ is not calculated, nor needed now), we need five equations (the one for water dissociation is not needed),

$$\begin{aligned}
 K_H &= \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}, \\
 K_1 &= \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]}, \\
 K_2 &= \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}, \\
 \text{Alk}_C &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}], \\
 C_T &= [\text{HCO}_3^-] + [\text{CO}_3^{2-}].
 \end{aligned} \tag{17}$$

The last two equations give,

$$[\text{HCO}_3^-] = 2C_T - \text{Alk}_C, \quad (18)$$

$$[\text{CO}_3^{2-}] = \text{Alk}_C - C_T. \quad (19)$$

Using the K_2 equation,

$$[\text{H}^+] = K_2 \frac{2C_T - \text{Alk}_C}{\text{Alk}_C - C_T}, \quad (20)$$

next, using the K_1 equation,

$$[\text{H}_2\text{CO}_3^*] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 (\text{Alk}_C - C_T)},$$

which, using Henry's law, gives

$$[\text{CO}_2(\text{g})] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 K_H (\text{Alk}_C - C_T)}. \quad (21)$$

We have now solved for all unknowns in terms of the reaction constants, and the specified total CO_2 and alkalinity. Given their definitions, total CO_2 is smaller than alkalinity (see last two lines in eqn. 17), $\text{Alk}_C > C_T$. The last equation therefore makes it clear that if the carbonate alkalinity increases, the atmospheric CO_2 decreases. To calculate numerical values of the solution, use the following typical values $\text{Alk} = 2350 \mu\text{mol/l}$, $C_T = 2075 \mu\text{mol/l}$, and the following constants that are derived for a temperature and salinity of $T = 15^\circ\text{C}$ and $S = 35 \text{ ppt}$, and at a depth of 0 m: $K_H = 0.0375 \text{ mol/atm}$, $K_1 = 1.15 \cdot 10^{-6} \text{ mol/l}$, $K_2 = 7.43 \cdot 10^{-10} \text{ mol/l}$, $K_w = 2.37 \cdot 10^{-14} (\text{mol/l})^2$, and the calcite and aragonite solubility constants are $K_{sp,c} = 4.31 \cdot 10^{-7} (\text{mol/l})^2$ and $K_{sp,a} = 6.72 \cdot 10^{-7} (\text{mol/l})^2$, correspondingly.

4.3 Response to increased atmospheric CO_2 concentration

If the atmospheric CO_2 is increased, so would the ocean reservoir of total CO_2 due to Henry's Law. Consider therefore that the DIC increases by 1 unit. Yet the alkalinity does not change in this case, as no ions related to weak acids are added to the ocean. The approximate solution of the previous subsection then allows us to calculate the pH response,

$$\begin{aligned} \Delta C_T &= \mathbf{1} \uparrow, & \Delta \text{Alk}_C &= \mathbf{0} \\ [\text{H}^+] &= K_2 \frac{2C_T - \text{Alk}_C + \mathbf{2}}{\text{Alk}_C - C_T - \mathbf{1}} \uparrow \Rightarrow \text{pH} \downarrow \\ [\text{CO}_3^{2-}] &= \text{Alk}_C - C_T - \mathbf{1} \downarrow, \end{aligned}$$

indicating that the pH should drop, and the ocean should become more acidic, as expected. The decrease in the concentration of the carbonate ion CO_3^{2-} means that the reaction of dissolution of calcium carbonate,



will be driven toward its right hand side and therefore lead to more dissolution (or less deposition) of calcium carbonate, moving upward the transition zone between the dissolving deep ocean and the upper ocean. This is also seen by writing this reaction as $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$ where K_{sp} is the solubility product of a specific CaCO_3 mineral phase (e.g., aragonite or calcite). Reduction in the carbonate ion would lead to calcium carbonate dissolution to keep the product unchanged as required in equilibrium between the solid phase calcium carbonate and its ions.

4.4 Response to warming

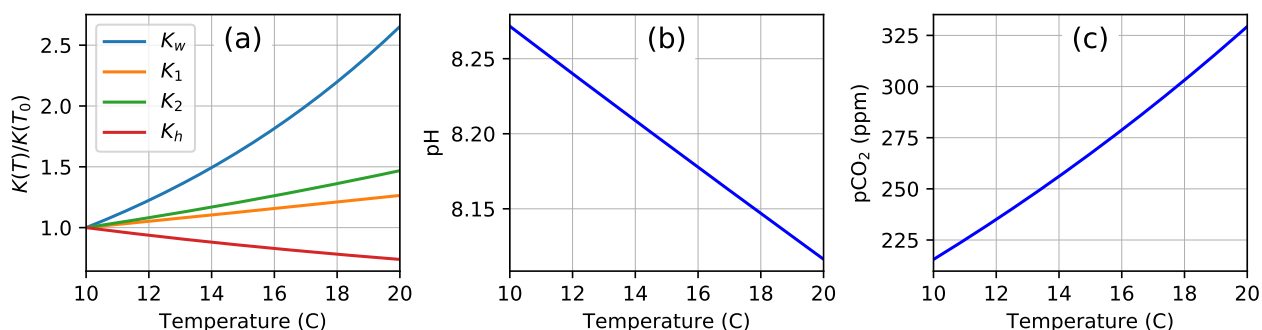


Figure 3: Response of the carbonate system to warming, showing quantities as function of the ocean temperature, when the DIC and alkalinity are assumed fixed. (a) Reaction constants normalized by their values at 10°C. (b) pH. (c) Atmospheric partial pressure of CO_2 , denoted pCO_2 .

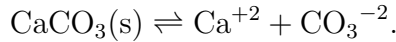
So far the ocean has been absorbing a significant fraction of the anthropogenic CO_2 emission, leading to the observed acidification, yet also to a reduction in the greenhouse effect and warming that would have been experienced otherwise. However, a warming of the ocean would lead to changes in the solubility of CO_2 in sea water, such that as the warming intensifies, some dissolved CO_2 will be released to the atmosphere, further amplifying the greenhouse warming. During the last glacial maximum 21,000 years ago, for example, the ocean temperature was colder by a few degrees, and the CO_2 concentration was 180 ppm, about a hundred ppm less than its preindustrial value of 280 ppm. About a third of this drop in CO_2 can be attributed to the cooler glacial ocean temperatures, an effect which is referred to as the “solubility pump”.

This effect is demonstrated in Figure 3, where the pH, atmospheric CO_2 and reaction constants are shown as function of temperature, in a scenario assuming constant total CO_2 and alkalinity. The dependence of the reaction constants on temperature leads to the changes seen to ocean pH and to the atmospheric CO_2 with temperature, showing increasing atmospheric CO_2 with warming, as expected. The figure suggests that a few degrees warming can lead to an atmospheric CO_2 increase of a few tens of ppm.

The approximate solution to the carbonate system discussed in section 4.2 reproduces the magnitude of the changes to the pH and $p\text{CO}_2$ with temperature (albeit with a non-negligible constant bias, not shown), and can provide further insight into this effect. Eqn (20) suggests that the pH changes as function of temperature mostly due to the variation of K_2 with temperature, while eqn (21) indicates that K_1 , K_2 and K_h all play a role, rather than, say, only Henry's law constant responsible for the direct dissolution of CO_2 in sea water. Note that in the fraction appearing in the solution for the atmospheric CO_2 concentration, K_2/K_1K_H , Henry's constant K_H decreases with temperature, while the other two increase. The ratio overall increases, leading to the increase in atmospheric CO_2 with warming.

4.5 Understanding the response to increased alkalinity and CaCO_3 dissolution

We can use the above approximate system and its solution to gain some insight into changes in the carbonate system in response to several major processes: photosynthesis, calcium carbonate dissolution, and the addition of CO_2 . Thus we are interested in the interaction of seawater with solid $\text{CaCO}_3(\text{s})$. There are two crystalline forms of calcium carbonate, calcite and aragonite. Calcite is the more stable and more common of the two. The dissolution/precipitation reaction is given by,



We can now discuss two specific perturbations to the carbonate system that are relevant in the glacial cycle context.

- Response to the dissolution of calcium carbonate CaCO_3 into calcium Ca^{2+} and carbonate CO_3^{2-} ions ($\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$, or, equivalently, $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$): This adds two units of alkalinity and one of C_T (DIC) due to the carbonate ion. The approximate solution of the previous subsection allows us to calculate the response as follows,

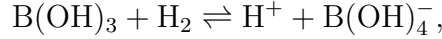
$$\begin{aligned} \Delta C_T &= 1 \uparrow, \quad \Delta \text{Alk}_C = 2 \uparrow \\ [\text{H}^+] &= K_2 \frac{2C_T - \text{Alk}_C + \mathbf{0}}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \Rightarrow pH \uparrow \\ [\text{CO}_2(\text{g})] &= \frac{K_2}{K_1K_H} \frac{(2C_T - \text{Alk}_C + \mathbf{0})^2}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \end{aligned}$$

- Response to Photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$, which removes one unit of C_T and does not change the alkalinity,

$$\begin{aligned} \Delta C_T &= -1 \downarrow, \quad \Delta \text{Alk}_C = 0 \\ [\text{H}^+] &= K_2 \frac{2C_T - \text{Alk}_C - \mathbf{2}}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \Rightarrow pH \uparrow \\ [\text{CO}_2(\text{g})] &= \frac{K_2}{K_1K_H} \frac{(2C_T - \text{Alk}_C - \mathbf{2})^2}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \end{aligned}$$

5 Accounting for Borate alkalinity

Often, when higher accuracy is desired, one does not neglect the contribution of Borate to ocean alkalinity, and then the carbonate system needs to also include the reaction,



which may be written as a first additional equation to the carbonate system,

$$K_B = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}. \quad (23)$$

The alkalinity is then,

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

The addition of Borate requires that we specify (or calculate via an advection-diffusion equation) the total Borate, serving as one more equation,

$$B_T = [\text{B(OH)}_4^-] + [\text{B(OH)}_3],$$

so that we have two more equations in order to solve for the two additional unknowns,

$$[\text{B(OH)}_3], [\text{B(OH)}_4^-]. \quad (24)$$

6 The Toggweiler (1999) 3-box glacial CO₂ model: qualitative analysis

Let T be the mass flux from the low latitude surface box to the high latitude box, which then sinks to the deep box and returns to the low latitude box deep box. Upward flux of nutrients to the low-latitude surface box, $T \times PO_{4,d}$, measured in moles of phosphate, is used by the biology to produce particulate organic matter that contributes to the downward carbon particulate flux. We assume that the upwelling nutrient flux is completely utilized by the biology because there is no lack of micronutrients (iron) or sunlight for photosynthesis. The downward carbon particulate flux (in moles of carbon) is then,

$$P_l = r_{c:p} \times T \times PO_{4,d}. \quad (25)$$

The deep box Dissolve Inorganic Carbon budget is then (note that in Toggweiler's paper $\text{TCO}_2 \equiv \sum \text{CO}_2 \equiv \text{DIC}$),

$$\frac{d}{dt}(\Sigma \text{CO}_{2d}) = (f_{hd} + T)(\Sigma \text{CO}_{2h} - \Sigma \text{CO}_{2d}) + (P_l + P_h) \quad (26)$$

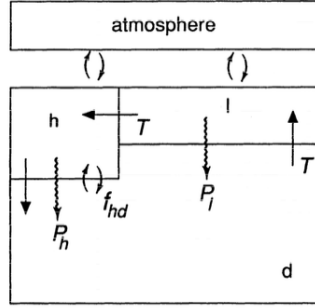


Figure 1. Schematic diagram of the three-box model of Sarmiento and Toggweiler [1984] and Siegenthaler and Wenk [1984].

Figure 4: From Toggweiler (1999). The model discussed in section 6 below is based on section 2 in that paper, where the direction of T is as shown in this picture. The direction is then reversed in section 3 in Toggweiler’s paper.

assume steady state and substitute P_l ,

$$\Sigma\text{CO}_{2d} - \Sigma\text{CO}_{2h} = r_{c:p} \frac{T \times \text{PO}_{4d}}{f_{hd} + T} + \frac{P_h}{f_{hd} + T}. \quad (27)$$

Neglecting the small P_h

$$\Sigma\text{CO}_{2d} - \Sigma\text{CO}_{2h} = r_{c:p} \text{PO}_{4d} \frac{T}{f_{hd} + T}. \quad (28)$$

Now, $\Sigma\text{CO}_{2d} - \Sigma\text{CO}_{2h}$, the deep CO_2 minus the high latitude total CO_2 , is the amount of CO_2 trapped in the deep ocean by the biological pump, without which the ocean will be mixed and have a uniform CO_2 concentration. When it is large, atmospheric CO_2 is small, and vice versa. The reason is that the combined total DIC in the deep and surface ocean is constant, ignoring interaction with sediments, so a large difference between the two means smaller surface values. To see this, let the sum of the surface (s) and deep (d) values of the DIC be $s + d = A = \text{constant}$, while the difference is $d - s = B > 0$. Therefore $s = (A - B)/2$, so that if the difference B decreases, the surface value s increases. Remember that the surface value determines the atmospheric concentration as well.

Equation (28) therefore provides intuition as to how mixing and circulation affect atmospheric CO_2 , e.g., as the mixing between the high latitude surface and the deep ocean decreases, so does the surface value, so that we can write

$$f_{hd} \downarrow \Rightarrow \text{CO}_{2(g)} \downarrow. \quad (29)$$

One expects the mixing to be weaker in glacial times due to increased stratification then, as the surface temperature near Antarctica (h box) is as cold as today, but the deeper water being supplied by the NADW should be colder in glacial times (Gildor et al., 2002).

The above follows previous work (Siegenthaler and Wenk, 1984; Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984), and while this also explains the lower glacial CO₂, it turns out the predictions of such a model are inconsistent with some proxy records. To see why, consider the phosphate budget of the high latitude box,

$$\frac{d}{dt}(PO_{4h}) = T(PO_{4l} - PO_{4h}) + f_{hd}(PO_{4d} - PO_{4h}) - P_h \frac{1}{r_{c:p}}. \quad (30)$$

at steady state, neglecting P_h and letting $PO_{4l} = 0$ because surface nutrients at low latitude are efficiently utilized by the biology,

$$PO_{4h} = PO_{4d} \frac{f_{hd}}{f_{hd} + T}. \quad (31)$$

Therefore, if the factor $T/(f_{hd} + T)$ increases (as f_{hd} decreases) for CO_{2(g)} to decrease, this predicts that PO_{4h} should decrease as well, but proxy observations do not show a change in high latitude nutrients during the LGM.

Reversing the circulation: Toggweiler (1999) tries next to reverse the direction for the circulation T , to have upwelling in the Southern Ocean representing NADW getting into the surface water rather than AABW sinking from the high latitude surface box. The phosphate budget for the high latitude box is given by,

$$\frac{d}{dt}(PO_{4h}) = T(PO_{4d} - PO_{4h}) + f_{hd}(PO_{4d} - PO_{4h}) - P_h \frac{1}{r_{c:p}}. \quad (32)$$

Assume a steady state and neglect the small export flux from the high latitude box, P_h , to get $PO_{4h} = PO_{4d}$. The result is therefore that the high latitude phosphate is equal to the deep one, and there is no dependence on the mixing and transport, eliminating the discrepancy with the observations.

7 Numerical solution of the Toggweiler (1999) 3-box model

The dissociation coefficients needed to solve the carbonate system above are known functions of the temperature and salinity, but we need advection-diffusion eqns for the alkalinity and total carbon. The source/ sink terms in these equations are also affected by the concentration of nutrients, which requires another advection diffusion equation. Finally, we need an equation for the total Borate which also affects the alkalinity and is required for solving the carbonate system. Fortunately, the Borate turns out to be simply related to the salinity.

Begin with an advection-diffusion equation for the total CO₂ in the surface water, which is affected by the fall of soft tissue (at the rate of $R_{P:C}^{-1} \times EP$) and calcite shells (at the rate

of $Rain \times EP$), as well as by air-sea exchange of CO_2 ,

$$\begin{aligned}\frac{\partial \Sigma CO_2}{\partial t} &= -\nabla(\mathbf{u} \Sigma CO_2) + \kappa \nabla^2 \Sigma CO_2 + S_{\Sigma CO_2}^{surface} \\ S_{\Sigma CO_2}^{surface} &= -R_{P:C}^{-1} \times EP - Rain \times EP \\ &+ PV \times ([CO_2(atm)] - [CO_2(aq)])\end{aligned}\quad (33)$$

where at depth the source/ sink term is

$$S_{\Sigma CO_2}^{deep} = +R_{P:C}^{-1} \times EP + Rain \times EP.$$

Next, we form an advection-diffusion equation for the alkalinity. The production of calcite shells involves the reaction $Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$ which involves the elimination of two negative charges per each calcium carbonate molecule that is formed. The rate of change of Alkalinity due to the production of calcite shells is therefore $2 \times EP \times Rain$. At the same time, the production of organic matter via the reaction $H^+ + NO_3^- \rightleftharpoons HNO_3$ and its export to the deep water reduces the concentration of $[H^+]$ and therefore increases the alkalinity at a rate of $R_{P:N}^{-1} \times EP$.

$$\begin{aligned}\frac{\partial Alk}{\partial t} &= \nabla(\mathbf{u} Alk) + \kappa \nabla^2 Alk + S_{Alk}^{surface} \\ S_{Alk}^{surface} &= -2 \times EP \times Rain + R_{P:N}^{-1} \times EP \\ S_{Alk}^{deep} &= +2 \times EP \times Rain - R_{P:N}^{-1} \times EP\end{aligned}\quad (34)$$

If the borate contribution to the alkalinity is not neglected (because we want to bring into account the effects of salinity changes, for example), then we need an equation for the total Borate, which is simply linearly proportional to the salinity: the salinity is composed of many constituents, borate being one of them.

$$B_T(mmol/l) = 1.212 \cdot 10^{-05} \times S \times \rho_{sea-water} \quad (35)$$

where $\rho_{sea-water}$ is in mks, S is the salinity in PSU, and total Borate is given in $mmol/l$, so another factor is needed to convert to $\mu mol/l$. Finally, an advection-diffusion equation for the surface Phosphate is derived by noting that the export production also reduces the phosphate concentration in the upper ocean and increases it in the deep ocean, so that

$$\begin{aligned}\frac{\partial PO_4}{\partial t} &= -\nabla(\mathbf{u} PO_4) + \kappa \nabla^2 PO_4 + S_{PO_4}^{surface} \\ S_{PO_4}^{surface} &= -EP \\ S_{PO_4}^{deep} &= EP\end{aligned}\quad (36)$$

Now, the rate of export production EP which is the number of $[PO_4]$ molecules per unit time per unit area falling as particles from the surface to the deep ocean is parameterized as follows (similar to Maier-Reimer, 1993),

$$EP = rL_f[PO_4] \frac{[PO_4]}{h + [PO_4]} \quad (37)$$

As mentioned above, the units of EP are $\mu\text{mol } PO_4$ molecules per m^2 per second. Alternatively, one could measure EP in units of gram carbon per m^2 per year. To translate between the two units,

$$\begin{aligned} \frac{gr\ C}{m^2 yr} &= \frac{\mu\text{mol } PO_4}{m^2 sec} \times (R_{P:C}^{-1} + Rain) \left(\equiv \frac{\mu\text{mol } C}{\mu\text{mol } PO_4} \right) \times \frac{gr\ C}{\mu\text{mol } C} \times \frac{sec}{yr} \\ &= \frac{\mu\text{mol } PO_4}{m^2 sec} \times (122 + Rain) \times (12.011 \times 10^{-6}) \times (365 \times 86400) \end{aligned}$$

From <http://imars.marine.usf.edu/cariaco/ief.html>: carbon flux at 275 m is on average 5.6% of integrated primary production. This decreased to 5.1% at 455 m , to 2.8% at 930 m , and to 1.7% at 1,225 m . On p. 265 of Pilson (1998), the net primary production map shows values of 30-125 $gr\ C\ m^2 yr^{-1}$ in most open ocean areas, with a global total of some 27 Gt per year. A typical value for local export production at 455 m would therefore be 1.5-6 $gr\ C\ m^2 yr^{-1}$, and the global export production at 455 m would therefore be some 1.3 Gt per year. Another note on units (see also Matlab program): because export production is in units of $\mu\text{mol } cm^{-2} sec^{-1}$ and Alk, PO_4, C_T in units of $\mu\text{mol}/liter$, rather than $\mu\text{mol}/cm^2$, one needs to multiply EP by 1000 (cm^3 per liter) before it is used as a source term.

Now, some of this export production is in the form of inorganic shells and some is composed of soft organic material. To figure out the effect of export production on the alkalinity and total CO_2 , we need to know the portions of carbon atoms falling as soft and hard tissue, termed the Rain ratio, and parameterized as follows (Maier-Reimer, 1993),

$$Rain = 61 / \{1 + \exp[0.1(10 - T)]\} \quad (38)$$

where T is the surface temperature. This expression is actually the number of Carbon atoms within Calcium Carbonate molecules in the export production, per PO_4 molecules. This expression therefore gives an upper limit of 0.5 for the rain ratio.

Results. Finally, set the vertical diffusion coefficient in the high latitude box (parameter `k_v_highlat` in the enclosed Matlab program) to 200 cm^2/sec and then to 1 cm^2/sec , to see how the atmospheric CO_2 varies roughly as in Toggweiler (1999).

A Iterative solution of the carbonate system

The full carbonate system equations are highly nonlinear, and may be solved by an iteration method. Start by defining

$$a \equiv \frac{1}{[H^+]}, \quad (39)$$

so that from (14) we immediately have

$$[OH^-] = aK_w. \quad (40)$$

Using (12) we find

$$[HCO_3^-] = aK_1[H_2CO_3^*]. \quad (41)$$

Similarly, from (13) we have $[HCO_3^-] = [CO_3^{-2}]/(aK_2)$ so that from these last two equations we find $aK_1[H_2CO_3^*] = [CO_3^{-2}]/(aK_2)$, or simply

$$[CO_3^{-2}] = a^2K_1K_2[H_2CO_3^*] \quad (42)$$

Combining (41), (13) into the definition of total CO_2 (16) we have $\Sigma CO_2 \equiv C_T = (aK_1 + a^2K_1K_2 + 1)[H_2CO_3^*]$ so that we can finally solve for the followings in terms of the total CO_2 and $a = 1/[H^+]$,

$$\begin{aligned} [H_2CO_3^*] &= \frac{1}{aK_1 + a^2K_1K_2 + 1} C_T \\ [CO_3^{-2}] &= \frac{a^2K_1K_2}{aK_1 + a^2K_1K_2 + 1} C_T \\ [HCO_3^-] &= \frac{aK_1}{aK_1 + a^2K_1K_2 + 1} C_T \end{aligned} \quad (43)$$

Next, consider the Borate system, where we use (23) and (35) to solve for the Borate ion concentration $[B(OH)_4^-]$ in terms of total Borate,

$$[B(OH)_4^-] = \frac{aK_B}{1 + aK_B} B_T. \quad (44)$$

So, now substitute (43), (40) and (44) into the definition of Alkalinity (15) to obtain a closed equation for $a = 1/[H^+]$ in terms of total CO_2 and Alkalinity,

$$\begin{aligned} Alk &= \frac{aK_1\Sigma CO_2}{1 + aK_1 + a^2K_1K_2} + \frac{2a^2K_1K_2\Sigma CO_2}{1 + aK_1 + a^2K_1K_2} \\ &+ \frac{aK_B B_T}{1 + aK_B} + aK_w - \frac{1}{a}. \end{aligned} \quad (45)$$

This is a bit messy, and needs to be solved iteratively as follows. First, neglect in (15) the Borate alkalinity and the contributions of $[H^+]$ and $[OH^-]$, so that we approximate the

alkalinity by the carbonate alkalinity Alk_C only,

$$\begin{aligned}
Alk_C &= [HCO_3^-] + 2[CO_3^{2-}] \\
&= Alk - ([OH^-] - [H^+] + [B(OH)_4^-]) \\
&= Alk - \left(\frac{aK_B B_T}{1 + aK_B} + aK_w - \frac{1}{a} \right)
\end{aligned} \tag{46}$$

In this case, we have $Alk_C = (aK_1 + 2a^2K_1K_2)\Sigma CO_2 / (1 + aK_1 + a^2K_1K_2)$ or equivalently $((2 - \gamma)K_1K_2a^2 + (1 - \gamma)K_1a - \gamma = 0)$, where

$$\gamma \equiv Alk_C / C_T, \tag{47}$$

so that we can write the zeroth order approximation to a_0 as

$$a \approx \frac{-(1 - \gamma)K_1 + \sqrt{(1 - \gamma)^2K_1^2 + 4(2 - \gamma)K_1K_2\gamma}}{2(2 - \gamma)K_1K_2} \tag{48}$$

where the solution of the quadratic equation for a with the minus sign (in the \pm term) drops out because in the ocean $\gamma \approx 1.1$ (Table 1) so this solution results in an unphysical negative concentration of $[H^+]$.

The next approximation for a is obtained by using the last equation of (46) to correct Alk_C and then recalculate γ in (47) and solve (48) for a_1 . By iterating the three equations (48), (46) and (47) this approximation may be made to converge to the accurate solution.

B Variables, units, typical values

The typical numbers for all of the variables mentioned above are given in Table 1, both for the modern ocean and for the LGM.

variable	name	units	now		LGM	
			srfc	deep	srfc	deep
$[CO_2(g)]$	pCO_2	ppt	270	-	↓80	-
$[H_2CO_3^*]$	carbonic acid	$\mu mol/kg$	$10\%C_T$	-	-	-
$[OH^-]$	hydroxyl	$\mu mol/kg$	1 (pH8.2)	-	-	-
$[H^+]$	acidity (pH)	$\mu mol/kg$	0.01 (pH8.2)	-	↓0.5?	-
$[HCO_3^-]$	bi-carbonate	$\mu mol/kg$	$90\%C_T$	-	-	-
$[CO_3^{2-}]$	carbonate	$\mu mol/kg$	$1\%C_T$	-	-	-
$[B(OH)_3]$	Borate	$\mu mol/kg$	$75\%B_T$	-	-	-
$[B(OH)_4^-]$	Borate ion	$\mu mol/kg$	$3\%Alk; 25\%B_T$	-	-	-
Alk	Alkalinity	$\mu eq/kg$	2300	2400	↓200	=
$\sum CO_2; C_T$	total carbon	$\mu mol/kg$	2000	2300	-	-
PO_4	phosphate	$\mu mol/kg$.2-1.4	2.1	.2-.6	2.2
B_T	total Borate	$\mu mol/kg$	400	-	-	-

Table 1: Symbols, names and typical values of biogeochemical variables (Regarding $[H^+]$ and $[OH^-]$: we have $[H^+] \times [OH^-] \approx 10^{-14}$; if $pH = 8$, then $[H^+] = 10^{-8} = 0.01 \mu mole/lt$ and therefore $[OH^-] = 10^{-6} = 1 \mu mole/lt$).

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