

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

Learning the basics of glacial CO₂ biogeochemistry

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7/28, 2002, updated 9/2009, 1/2011, 4/2013, last edited Monday 8th April,
2019, 14:32

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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, $\text{CO}_2(\text{g})$. The atmospheric CO_2 concentration depends on the concentration of carbon dioxide dissolved in sea water $\text{CO}_2(\text{aq})$,

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

The concentration of dissolved CO_2 , in turn, depends on the concentration of the rest of the carbonate system ions (H_2CO_3 , HCO_3^- , CO_3^{2-} , 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 CO_2 ” (ΣCO_2 , 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 CO_2 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 CO_2 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,

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

Similarly, the total CO_2 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 CO_2 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, $[\text{PO}_4]$, which is again affected by the production of particles and by advection and diffusion,

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

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 $\text{CO}_2(\text{g})$, integrate in time the prognostic ($\frac{d}{dt}$) equations for the alkalinity, total CO_2 and nutrient. At each time, solve for the dissolved $\text{CO}_2(\text{aq})$ in ocean water from the known alkalinity and total CO_2 by solving the carbonate system equations. Given the dissolved CO_2 , calculate the atmospheric $\text{CO}_2(\text{g})$ 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. $P_{\text{CO}_2}^{\text{atmos}}$: atmospheric CO_2
2. $P_{\text{CO}_2}^{\text{ocean}}$: pressure of gas phase CO_2 that would be in equilibrium with dissolved CO_2 the ocean.
3. T, S : temperature and salinity
4. $\text{pH} = -\log_{10}[\text{H}^+]$; $[\text{H}^+]$ in *mol/liter*.
5. Alkalinity (measured in $\mu \text{Eqv/l}$): the concept of Alkalinity arises when one does the charge balance of seawater. The net charge needs to be zero, which means that

$$0 = ([\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]) - ([\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HBO}_3^-]) \quad (1)$$

Now, we are interested in how some of these ion concentrations change with the pH 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, if one dissolves NaCl in seawater, it separates completely into Na^+ and Cl^- regardless of the pH. However, the equilibrium $\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$ on the other, does depend strongly on the pH, which means that the concentrations of the ions on the rhs and lhs of this equilibrium vary with the 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. Separating the charge balance (1), into the parts due to the weak acids and bases (first line) and strong ones (second), we have

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

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

$$\begin{aligned} Alk &\equiv ([HCO_3^-] + 2[CO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] + [HBO_3^-] - [H^+]) \\ &= ([Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] - [Cl^-]) \end{aligned} \quad (2)$$

Clearly the pH and alkalinity affect each other. This occurs directly as $[H^+]$ appears in the expression for alkalinity. But also indirectly, as when the pH is changed, it would affect some of the equilibria in the carbonate system (discussed below) and thus change the concentration of several ions that affect the alkalinity. Finally, note that the concentration $[H^+]$ is negligible (for seawater, pH=8.2, implying $[H^+] \approx 10^{-8}$ mole = 10^{-2} μ mole, while HCO_3^- in the ocean is measured in thousands of micro mole), and so are some of the other ions, so that to a good approximation the alkalinity may be approximated by the carbonate alkalinity alone,

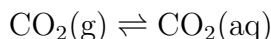
$$Alk_C \approx [HCO_3^-] + 2[CO_3^{2-}].$$

6. $\Sigma CO_2 \equiv C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$: total CO_2 , where the distribution in the ocean, in percents, of the three components is, correspondingly, 1%,90%,10% (this distribution is a strong function of pH). Measured in micromole carbon per liter ($\mu MC/l$).
7. Redfield ratio: $P : N : C = 1 : 16 : 122$ in organic matter in the ocean. Also define $R_{P:C} = 1 : 122$ and $R_{P:N} = 1 : 16$
8. Rain ratio: ratio of organic to inorganic carbon atoms extracted from the ΣCO_2 pool per PO_4 molecule that sinks as particulate matter to the deep ocean.
9. Calcification: rate of **net** $CaCO_3$ deposition in mols/(liter \times sec); (calcification by corals and Forams, or minus rate of dissolution).
10. Respiration: rate of oxidation of organic material (normally by bacteria in sediments or deep water) turning organic matter and oxygen back into CO_2 .
11. Rate of export production EP is the number of $[PO_4]$ 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).

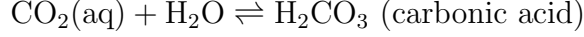
4 The carbonate system

Our objective is to calculate dissolved CO_2 from alkalinity, total CO_2 , temperature and salinity. We start with introducing the various relevant quantities and chemical reactions.

Carbon dioxide is soluble in water, and its dissolution occurs in two steps. First, Henry's law,



and then its reaction with water,



Because it is difficult to distinguish between $\text{CO}_2(\text{aq})$ and H_2CO_3 , they are treated together and we define

$$\text{H}_2\text{CO}_3^*(\equiv \text{CO}_2^*) \equiv \text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3. \quad (3)$$

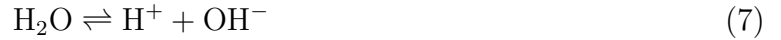
In terms of this variable, Henry's law is

$$\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^* \quad (4)$$

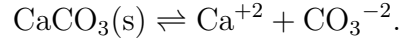
Now, carbonic acid is a weak diprotic acid (diprotic acids are able to release two protons),



The equilibrium constants for seawater are functions of temperature, pressure and salinity. Water dissociation is given by,



Our particular interest here is 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,



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: [(4), (5), (6), (7)]. We therefore need to specify two more constraints. One is mass conservation for total inorganic carbon which cannot change via the above reactions. As the inorganic carbon switches between the different carbonate ions, their sum must be equal to the total inorganic carbon,

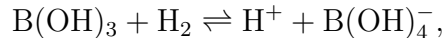
$$\Sigma\text{CO}_2 \equiv C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{-2}] \quad (8)$$

The other constraint is a charge balance specified via the alkalinity parameter,

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{-2}] + [\text{OH}^-] - [\text{H}^+] + (\text{small terms}) \quad (9)$$

ΣCO_2 and Alk are measurable quantities for which we will write conservation (advection-diffusion) equations. Once they are specified, the system is completely determined (same number of unknowns and equations).

If we don't neglect Borate, then we also need to include the reaction,



specify via an advection-diffusion equation the total Borate

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

and make the alkalinity be

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

This increases the number of equations and unknowns by two each.

4.1 Carbonate system equations

To create a specific model, we need to write the carbonate system as the following set of equations using the equilibrium constants. The six unknowns are

$$[\text{CO}_2(g)], [\text{H}_2\text{CO}_3^*], [\text{OH}^-], [\text{H}^+], [\text{HCO}_3^-], [\text{CO}_3^{2-}] \quad (10)$$

where we remember that

$$\text{H}_2\text{CO}_3^*(\equiv \text{CO}_2^*) \equiv \text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3 \quad (11)$$

Now, if Borate contribution to Alkalinity is not neglected, then we have two more unknowns

$$[\text{B}(\text{OH})_3], [\text{B}(\text{OH})_4^-] \quad (12)$$

and the first four equations are

$$K_0(T, S, P) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(g)]} \quad (13)$$

$$K_1(T, S, P) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \quad (14)$$

$$K_2(T, S, P) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (15)$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (16)$$

For typical values of these coefficients, see section 4.2. If Borate is not neglected, we also need

$$K_B = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]}, \quad (17)$$

To close the system, we need three more equations, which are the definitions of alkalinity, total CO_2 and total Borate,

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B}(\text{OH})_4^-] \quad (18)$$

$$\Sigma\text{CO}_2 \equiv C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*] \quad (19)$$

$$B_T = [\text{B}(\text{OH})_4^-] + [\text{B}(\text{OH})_3] \quad (20)$$

Assuming we know $\text{Alk}, \Sigma\text{CO}_2, B_T, K_0, K_1, K_2, K_w, K_B$, we can use the eight equations composed of the carbonate system equations (13, 14, 15, 16), the borate system equation (17), and the definitions of alkalinity, total CO_2 and total borate (18, 19, 20) to solve for the eight unknowns (10) and (12). This is a nonlinear system of equations, so it needs to be solved iteratively, as described below.

4.2 Approximate solution of the carbonate system

Consider an approximate solution to the carbonate system. The approximation used here for DIC is valid only at pH values around 8, and for small perturbations to the DIC. The assumptions that go into this solution are consistent with the pH in the present-day ocean. These assumptions include,

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

Let the unknowns be the values of the concentrations $[\text{CO}_2(\text{g})]$, $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $[\text{H}^+]$. With a total of five unknown ($[\text{OH}^-]$ is not calculated and not needed), we need five equations (water dissociation not needed),

$$\begin{aligned} K_H &= \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}, \\ K_1 &= \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]}, \\ K_2 &= \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}, \\ C_T &= [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \\ \text{Alk}_C &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \end{aligned} \tag{21}$$

The last three equations give,

$$[\text{HCO}_3^-] = 2C_T - \text{Alk}_C, \tag{22}$$

$$[\text{CO}_3^{2-}] = \text{Alk}_C - C_T, \tag{23}$$

Using the K_2 equation,

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

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

$$[\text{CO}_2(\text{g})] = \frac{K_2}{K_1 K_H} \frac{(2C_T - \text{Alk}_C)^2}{\text{Alk}_C - C_T}. \tag{24}$$

Given that $\text{Alk}_C > C_T$, the last equation makes it clear that if the carbonate alkalinity increases, the atmospheric CO_2 decreases. To see the numerical values, use typical values $\text{Alk} = 2350 \mu\text{mol/l}$, $C_T = 2075 \mu\text{mol/l}$, $K_H = 2.84 \cdot 10^{-2} \text{ mol/atm}$, $K_1 = 1.4 \cdot 10^{-6} \text{ mol/l}$, $K_2 = 1.2 \cdot 10^{-9} \text{ mol/l}$.

4.3 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 .

- 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,

$$\begin{aligned}\Delta C_T &= 1 \uparrow, & \Delta \text{Alk}_C &= 2 \uparrow \\ [\text{H}^+] &= K_2 \frac{2C_T - \text{Alk}_C + \mathbf{0}}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \Rightarrow pH \uparrow \\ [\text{CO}_2(\text{g})] &= \frac{K_2}{K_1 K_H} \frac{(2C_T - \text{Alk}_C + \mathbf{0})^2}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow\end{aligned}$$

- 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,

$$\begin{aligned}\Delta C_T &= -1 \downarrow, & \Delta \text{Alk}_C &= 0 \\ [\text{H}^+] &= K_2 \frac{2C_T - \text{Alk}_C - \mathbf{2}}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow \Rightarrow pH \uparrow \\ [\text{CO}_2(\text{g})] &= \frac{K_2}{K_1 K_H} \frac{(2C_T - \text{Alk}_C - \mathbf{2})^2}{\text{Alk}_C - C_T + \mathbf{1}} \downarrow\end{aligned}$$

5 The Toggweiler (1999) 3-box glacial CO_2 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 by moles of phosphate, is used by the biology to produce particulate organic matter that contributes to the downward carbon particulate flux. The carbon particulate downward flux (in moles of carbon) is then,

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

The deep box CO_2 budget is then (note that in Toggweiler's paper $\text{TCO}_2 \equiv \sum \text{CO}_2 \equiv \text{DIC}$),

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

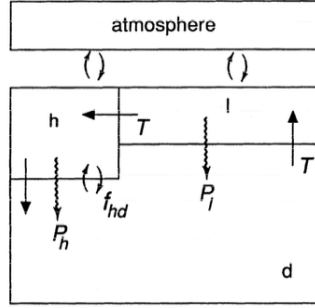


Figure 1. Schematic diagram of the three-box model of Sarmiento and Toggweiler [1984] and Siegenthaler and Wenk [1984].

Figure 1: From Toggweiler (1999). The model discussed in section 5 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 ,

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

Neglecting the small P_h

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

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 total CO_2 in deep and surface ocean is constant, ignoring interaction with sediments, so 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.

6 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),

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

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 (16) we immediately have

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

Using (14) we find

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

Similarly, from (15) 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), (15) into the definition of total CO_2 (19) 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 (17) 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 (18) 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 (18) 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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