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12.740 Paleoceanography  
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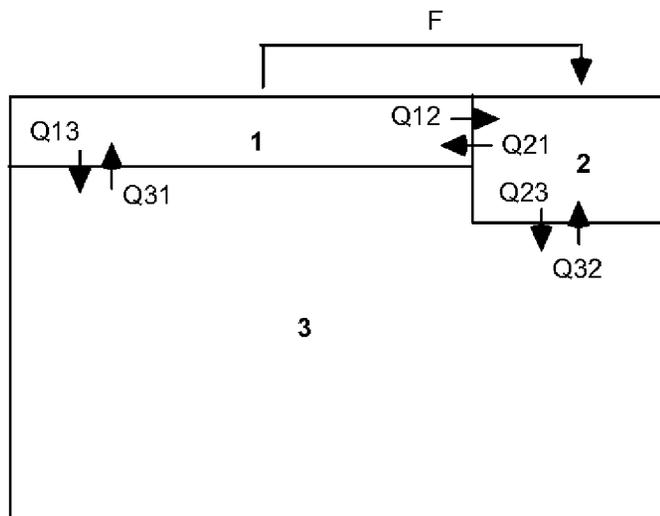
INTRODUCTION TO OCEAN CARBON SYSTEM BOX MODELS:  
THE TOGGWEILER-SARMIENTO 3-BOX MODEL  
Spring, 2006

A 3-box model is the simplest model that illustrates most of the principles involved in construction of ocean carbon system chemical models. The model presented below is based most closely on that by Toggweiler and Sarmiento (1985), but is not exactly the same (changes have been made to simplify the presentation while retaining most of the functionality). Toggweiler and Sarmiento didn't compute their model in matrix form - they worked out the algebraic equations. However, it is much simpler to set up a model in this matrix form once you get used to it - it took me a couple of days to set up most of this model, half of which was spent in getting the units correct! Getting the units consistent at the outset is worth the effort; it will save a lot of debugging later.

After the basic model is set up, two scenarios are illustrated. The first scenario is a "pre-industrial atmosphere" scenario where  $p\text{CO}_2 = 280$  ppmV and the ocean carbon system is adjusted to be consistent with observations on the modern ocean (corrected for fossil fuel  $\text{CO}_2$  uptake, etc.). The second scenario is a hypothetical "glacial" scenario where some changes between glacial and interglacial times are driven by observation (e.g. atmospheric  $\text{CO}_2$  was  $\sim 200$  ppmV) and others were made as assumptions. The salinity of the ocean increased due to the withdrawal of water into continental glaciers (and the average concentrations of phosphorus, alkalinity and dissolved carbon dioxide increased proportionately, while the mass of the ocean decreased). A transfer of carbon to the ocean from oxidized continental carbon was assumed (estimated from mean oceanic  $\delta^{13}\text{C}$ ) and this extra  $\text{CO}_2$  was "neutralized" by stoichiometric dissolution of  $\text{CaCO}_3$ . Warm surface T decreased from  $21.5^\circ\text{C}$  to  $20^\circ\text{C}$ . Cold surface T decreases from  $2.5^\circ\text{C}$  to  $2.0^\circ\text{C}$  (somewhere between the realm of observation and hypothesis).

**SALINITY:**

Although it is of only minor relevance to the carbon system, the salinity distribution provides the easiest illustration of the model equations. The processes include mixing between boxes, and a transfer of water from low latitudes to high latitudes through the atmosphere. Underlying this salt balance is the water balance, where water fluxes in and out of each box must balance.



Consider the steady-state salinity mass balance for the high latitude box 2:

$$+Q_{12} S_1 - Q_{21} S_2 - Q_{23} S_2 + Q_{32} S_3 = 0$$

which can be slightly rewritten to:

$$+Q_{12} S_1 + (-Q_{21} - Q_{23}) S_2 + Q_{32} S_3 = 0$$

which can be expressed as a vector equation:

$$\begin{vmatrix} +Q_{12} & (-Q_{21} - Q_{23}) & +Q_{32} \end{vmatrix} \begin{vmatrix} S_1 \\ S_2 \\ S_3 \end{vmatrix}$$

$$\begin{vmatrix} S_2 \\ S_3 \end{vmatrix} = 0$$

Writing the equation for box 2 and the overall mass balance equation in this form, and collecting them together into a matrix equation: the matrix formula describing this system of simultaneous equations is:

$$\begin{array}{ccc|ccc} \mathbf{A} & & & \mathbf{x} & = & \mathbf{b} \\ \hline \begin{vmatrix} -Q_{12}-Q_{13} & +Q_{21} & +Q_{31} \end{vmatrix} & & & \begin{vmatrix} S_1 \\ S_2 \\ S_3 \end{vmatrix} & & \begin{vmatrix} 0 \\ 0 \\ S_{tot} \end{vmatrix} \\ \hline \begin{vmatrix} +Q_{12} & -Q_{21}-Q_{23} & +Q_{32} \end{vmatrix} & & & & & \\ \hline \begin{vmatrix} +V_1 & +V_2 & +V_3 \end{vmatrix} & & & & & \end{array}$$

The first two equations describe the mass balances for boxes 1 and 2, and the third equation is the salt mass balance for the system as a whole (an equation for box 3 is not necessary since it is a linear combination of the equations for boxes 1 and 2). Note that the atmosphere is assumed to have no salt and as no significant reservoir of water.

discussion of units: water fluxes in the ocean are typically expressed as "Sverdrups",  $10^6 \text{ m}^3/\text{sec}$ . However, concentrations of chemicals are typically expressed in units of moles/kg. To keep the units consistent, we multiply water fluxes by the density of seawater,  $1027 \text{ kg/m}^3$ . This conversion factor is an approximation, because the density of seawater depends slightly on temperature, salinity, and pressure, which must be taken into account for very precise applications.

Also note that the average salinity of the ocean is tied to the mass of the ocean - changes in mean salinity are created by withdrawing water from the ocean into massive continental glaciers. Any model which assumes a change in mean ocean salinity has

to include an inversely proportional change in the mass of the ocean, which will impact the concentrations of other dissolved chemicals.

Another point to note is that our choice of the water fluxes and system volume as the master variables in "A" is a contextual choice; they could have been included as variables. In our case, the fluxes and volumes are chosen as master variables because they apply to all constituents - hence, once "A" is set up, it applies to all of the subsystems.

## PHOSPHORUS:



$$\begin{array}{c}
 \mathbf{A} \qquad \qquad \qquad \mathbf{x} \qquad = \qquad \mathbf{b} \\
 \left| \begin{array}{ccc} -Q_{12} - Q_{13} & +Q_{21} & +Q_{31} \\ +Q_{12} & -Q_{21} - Q_{23} & +Q_{32} \\ +V_1 & +V_2 & +V_3 \end{array} \right| \left| \begin{array}{c} P_1 \\ P_2 \\ P_3 \end{array} \right| = \left| \begin{array}{c} F_{p1} \\ F_{p2} \\ P_{tot} \end{array} \right|
 \end{array}$$

$F_{p1}$  and  $F_{p2}$  are the fluxes of particulate biogenic phosphorus from boxes 1 and 2 into box 3, where they quantitatively decompose back into dissolved form ("regeneration"). The mass balance is:

$$\text{Advective Fluxes} + \text{Particle Fluxes} = 0 \quad (\text{for each box.})$$

The sign of the particle flux in the  $\mathbf{b}$  matrix for boxes 1 & 2 is positive because it has been moved from the left side of the equation to the right; e.g., the P equation for box one is:

$$+Q_{12} P_1 - Q_{21} P_2 - Q_{23} P_2 + Q_{32} P_3 - F_{p1} = 0$$

The particle flux is the negative term (at the end of the left hand side of the equation) switches sign when you move it to the right hand ("zero") side of the equation:

$$+Q_{12} P_1 - Q_{21} P_2 - Q_{23} P_2 + Q_{32} P_3 = F_{p1}$$

How do we derive the biological particle fluxes? Rather than model the biological system explicitly, we simply take observations (or hypotheses) of the phosphorus distribution in the ocean to constrain  $P_1$ ,  $P_2$ , and  $P_{tot}$ . (which sets  $P_3$  from the mass balance). The equation is used to calculate  $F_{p1}$  and  $F_{p2}$  ( $Ax=b$ ). Low-latitude surface water P is depleted to low concentrations by efficient biological uptake (in other words, P is the model "limiting nutrient"), and high-latitude surface water P is taken as a master variable to be explored. Note that it cannot be varied completely arbitrarily; some values might imply an upward flux of particles! Also, Although the ocean phosphorus concentration is not mechanistically dependent on salinity, a withdrawal of water from the ocean (resulting in higher salinity) will increase the mean dissolved phosphorus concentration.

## ALKALINITY:

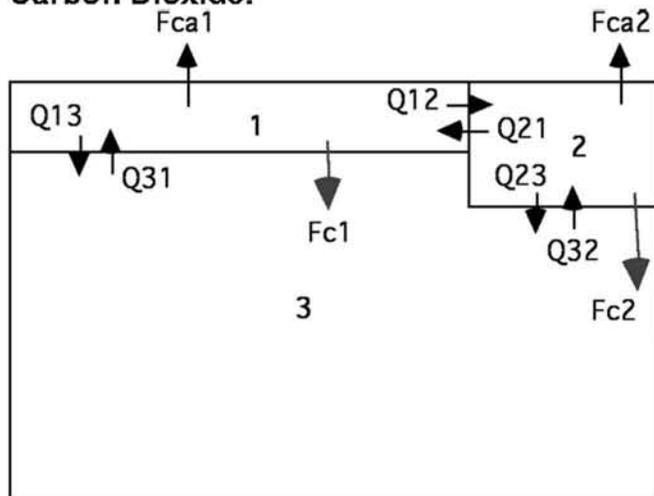


$$\begin{array}{c}
 \mathbf{A} \qquad \qquad \qquad \mathbf{x} \qquad = \qquad \mathbf{b} \\
 \left| \begin{array}{ccc} -Q_{12}-Q_{13} & +Q_{21} & +Q_{31} \\ +Q_{12} & -Q_{21}-Q_{23} & +Q_{32} \\ +V_1 & +V_2 & +V_3 \end{array} \right| \quad \left| \begin{array}{c} A_1 \\ A_2 \\ A_3 \end{array} \right| \quad \left| \begin{array}{c} f_{a1}F_{p1} \\ f_{a2}F_{p2} \\ A_{tot} \end{array} \right|
 \end{array}$$

The alkalinity model is similar to the phosphorus model, except that the alkalinities are not fixed by observation or hypothesis but instead calculated after fixing the "Redfield" ratio particulate Alk/P ratios for the low- and high-latitude boxes. Note that alkalinity flux is mainly governed by the effect of calcium carbonate precipitation and dissolution and to a lesser extent by the oxidation/reduction of protein ammonia from nitrate. Alkalinity is also not transported/stored by the atmosphere!

Alkalinity is added to the ocean dominantly by the flux of  $\text{CaCO}_3$  (limestone) dissolved on the continents and transported by rivers. It is removed from the ocean dominantly by the sedimentation of  $\text{CaCO}_3$ . In considering changes to the carbon system over time, we require that the input of  $\text{CaCO}_3$  and the output balance (over time scales of 5-10 kyr). In simple models such as this, this balance is often maintained by assuming that the deep carbonate ion concentration is constant.

## Carbon Dioxide:

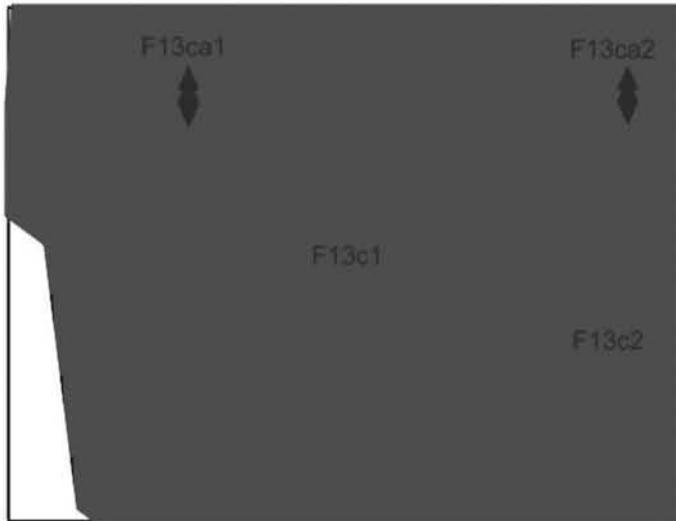


$$\begin{array}{c}
 \left| \begin{array}{ccc|c|c}
 -Q_{12}-Q_{13} & +Q_{21} & +Q_{31} & C_1 & f_{c1}F_{p1} + F_{ca1} \\
 +Q_{12} & -Q_{21}-Q_{23} & +Q_{32} & C_2 & f_{c2}F_{p2} + F_{ca2} \\
 +V_1 & +V_2 & +V_3 & C_3 & C_{tot} - P_{CO_2} M_{atm}
 \end{array} \right. \\
 \mathbf{A} \qquad \qquad \qquad \mathbf{x} = \mathbf{b}
 \end{array}$$

The  $CO_2$  model is similar to the alkalinity model, except that  $CO_2$  is transported through the atmosphere and the atmosphere is a significant reservoir. The introduction of the atmosphere as a reservoir would best be handled by adding a fourth box (this is how it is implemented in the Excel spreadsheet; it makes the extension to C13 and C14 much easier). However, to stick to our simple 3-box formulation for this tutorial, we handle this issue simply by removing the carbon dioxide content of the atmosphere from the total contained in the ocean system (bottom term of **b**).

The particulate carbon flux is affected both by calcium carbonate formation/dissolution and organic matter formation/degradation. The fluxes of carbon dioxide between the ocean and atmosphere ( $F_{ca1}$  and  $F_{ca2}$ ) are shown as both going into the atmosphere for the sake of consistent notation; at steady-state these will be equal to each other in magnitude but of opposite signs. Because  $p_{CO_2}$  and hence gas exchange fluxes are non-linear functions of **Alk** and  **$CO_2$** , it is necessary to solve this system by iteration; we guess atmospheric  $p_{CO_2}$  and air-sea fluxes, solve the linear system, and then modify the guesses iteratively until the system converges. Note also that because we are comparing fluxes calculated per unit of volume transfer (fluxes between ocean boxes) and fluxes calculated per unit of surface area (gas exchange as a function of the partial pressure difference between the ocean and atmosphere), it is especially important to make the units consistent.

## Carbon 13:



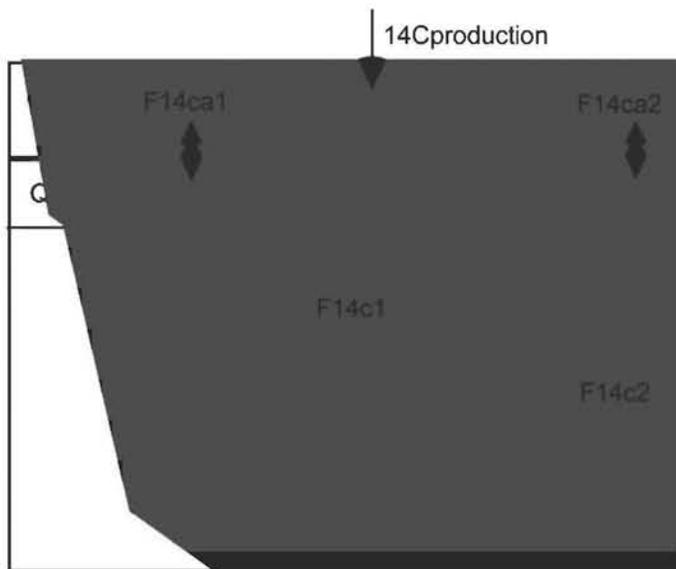
$$\begin{array}{c}
 \begin{array}{cccc|ccc}
 -Q_{12} - Q_{13} - g_1 & +Q_{21} & +Q_{31} & +g_{a1} & C_1 & & f_{13c1}F_{p1} \\
 +Q_{12} & -Q_{21} - Q_{23} - g_2 & +Q_{32} & +g_{a2} & C_2 & & f_{13c2}F_{p2} \\
 +Q_{13} & +Q_{23} & -Q_{31} - Q_{32} & 0 & C_3 & & -f_{13c1}F_{p1} - f_{13c2}F_{p2} \\
 +V_1 & +V_2 & +V_3 & M_{atm} & p^{13}C_a & & ^{13}C_{tot}
 \end{array} \\
 \mathbf{A} & & \mathbf{x} & = & \mathbf{b}
 \end{array}$$

For  $^{13}\text{C}$ , we are better off abandoning our pretense of a 3-box model and finally adding in the atmosphere as a fourth box. The main reason for doing this is that the carbon isotope ratio of gases entering each of the ocean boxes is different from that leaving each box.

The equations are then set up as mass balances for each ocean box (no longer linearly dependent because of the fluxes into the atmosphere) and total mass balance for the system. Note that the gas exchange fluxes can now be expressed as part of the flux matrix A (because we can take the difference between the atmosphere and ocean  $p\text{CO}_2$ ). The terms  $g_1$  and  $g_2$  are the proportionality constants that convert the total  $\text{CO}_2$  in the warm and cold boxes into the  $^{13}\text{C}$  flux out of those boxes into the atmosphere (they are the product of the  $^{13}\text{C}$  piston velocity, the fraction of the dissolved  $\text{CO}_2$  that exists as gaseous dissolved  $\text{CO}_2$ , the area of the ocean box, and the kinetic discrimination against  $^{13}\text{C}$ ).  $g_{a1}$  and  $g_{a2}$  are the proportionality constants that convert the atmospheric  $p\text{CO}_2$  into  $^{13}\text{C}$  fluxes into the warm and cold ocean boxes (the product of the  $^{13}\text{C}$  piston velocity, the solubility constant for aqueous  $^{13}\text{CO}_2$ , the area of the ocean boxes, and the kinetic discrimination against  $^{13}\text{C}$ ).

Note that one difference in obtaining the solution to  $^{13}\text{C}$  compared to total C is that the pH is not a function of  $^{13}\text{C}$  (which has already been determined by the total carbon dioxide solution). Hence, the fraction of  $^{13}\text{C}$  that exists in each of the aqueous species is fixed according to the pH and equilibrium constants (note that the equilibrium constants for  $^{13}\text{C}$  have to be modified from those for  $^{12}\text{C}$  by the equilibrium isotope fractionations). Also, because the fraction of aqueous dissolved  $^{13}\text{CO}_2$  is fixed, we do not have to iterate to get a solution; the system is simply solved as  $x=A^{-1}b$ .

## Carbon 14:



$$\begin{array}{cccc|cc|c}
 -Q_{12}-Q_{13}-g_1-\lambda & +Q_{21} & +Q_{31} & +g_{a1} & | & | & {}^{14}\text{C}_1 & | & f_{14c1}F_{p1} & | \\
 +Q_{12} & -Q_{21}-Q_{23}-g_2-\lambda & +Q_{32} & +g_{a2} & | & | & {}^{14}\text{C}_2 & | & f_{14c2}F_{p2} & | \\
 +Q_{13} & +Q_{23} & -Q_{31}-Q_{32}-\lambda & 0 & | & | & {}^{14}\text{C}_3 & | & -f_{14c1}F_{p1}- & | \\
 & & & & & & & & f_{14c2}F_{p2} & | \\
 +g_1 & +g_2 & 0 & -g_{a1}-g_{a2}-\lambda M_{\text{atm}} & | & | & p^{14}\text{C}_a & | & {}^{14}\text{C}_{\text{production}} & | \\
 \mathbf{A} & & & & & & \mathbf{x} & = & \mathbf{b} & 
 \end{array}$$

The  $^{14}\text{C}$  model is almost the same as the  $^{13}\text{C}$  model. Two changes are very minor: (1) converting the equilibrium and gas exchange constants to the  $^{14}\text{C}$  values from the  $^{13}\text{C}$  values, and (2) adding a radioactive decay term to each box ( $-\lambda C$ ). The biggest change is in the 4th equation for mass balance. Because  $^{14}\text{C}$  is radioactive, it is not conserved and its total inventory on earth can change as cosmic ray production increases. This factor could be handled in different ways; in this version we simply require that the total  $^{14}\text{C}$  flux across the air/sea boundary is equal to the amount produced by cosmic rays (less the small amount which decayed while in the atmosphere).

## Reference:

Toggweiler R., and Sarmiento J. L. (1985) Glacial to interglacial changes in atmospheric carbon dioxide: the critical role of ocean surface water in high latitudes. In *The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations Archaen to Present* (ed. E. A. S. a. W. S. Broecker), Vol. 32, pp. 163-184. Am. Geophys. Union.