

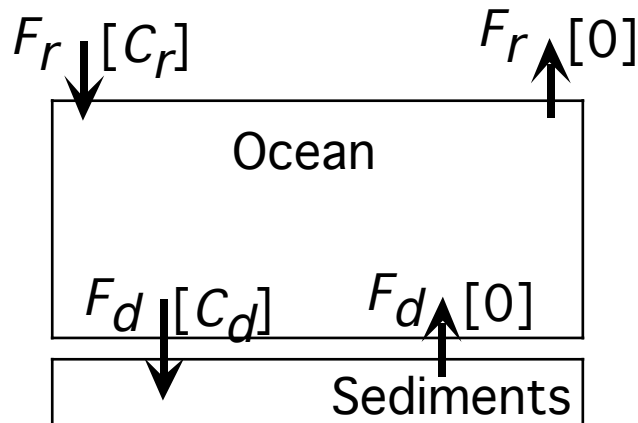
### 1. Binary Mixing

You measure the following trace-element ratios in a suite of basalt glasses:

Ti/Zr	Sm/Yb
140.85	0.84
65.19	0.99
50.95	1.23
50.40	1.36
49.47	1.28
51.28	1.31
49.94	1.38
54.13	1.13
53.98	1.11
62.16	0.98

- Plot the data in ratio-ratio space. Compute the best-fitting hyperbola using some appropriate least-squares calculation.
- Assume the data represent additive binary mixing of two end members, A and B. Let A be the one with the lower Ti/Zr ratio. Knowing only the given data, what is the possible range of Ti/Zr ratio for end member A? What constraint can you place on the Ti/Zr ratio of end member B?
- Likewise, what are the possible ranges for the Sm/Yb ratios of the end members?
- Which end member has the larger Zr/Yb ratio? Given only this data, can you fit a unique value for the curvature parameter  $r = (Zr/Yb)_A / (Zr/Yb)_B$ ?

### 2. A One-Box Model Ocean



Let us use a simple box model to analyze Mg/Ca ratios measured in stratigraphic sequences of oceanic carbonate sediments. Here is the setup:

- There is a constant flux of river water into the oceans,  $F_r$ , carrying Mg and Ca in concentrations  $[Mg]_r$  (variable) and  $[Ca]_r$  (constant). The river flux of water is balanced by an evaporation flux  $F_r$  with zero concentrations of Mg and Ca.
- The concentrations of Mg and Ca in the ocean water, assumed well-mixed, are  $[Mg]_d$  and  $[Ca]_d$  (d for deep water). We model sedimentation by imagining that a flux  $F_d$  of deep ocean water enters the sediment box carrying Mg and Ca and an equal water flux returns to the ocean totally stripped of these elements (note the volume of the oceans is constant, since inputs of water are  $F_r + F_d$  and outputs are  $F_r + F_d$ ).
- Let us say  $[Ca]_d$  is in steady state and is equal to  $10^{-3}$  "Balta units"/m<sup>3</sup> (The Balta unit is chosen so that CaCO<sub>3</sub> sediment has a Ca concentration of 1 Balta/m<sup>3</sup>, just for convenience).
- Take the area of the oceans to be  $3.6 \times 10^8$  km<sup>2</sup> and the average depth 5 km.

a. You examine a lot of magnetic reversals and fossil ages and you learn that in the sediment column, the sedimentation rate is  $10^{-3}$  m/yr. This sediment is almost pure CaCO<sub>3</sub>. Calculate the flux of water through the sedimentation process,  $F_d$  in m<sup>3</sup>/yr. What is the residence time  $\tau_d$  of an element like Ca or Mg in this ocean?

b. Let us say river water has a constant  $[Ca]_r = 10^{-4}$  Balta/m<sup>3</sup>. Recall that  $[Ca]_d$  is in steady state, and calculate the river water flux  $F_r$ . What is the residence time of H<sub>2</sub>O in this ocean?

c. Write an equation for evolution of  $[Mg]_d$  as a function of time. We are going to allow  $[Mg]_r(t)$  to be an arbitrary function of time, so do not assume it is constant. Now, since  $[Ca]_d$  is a constant and since the Mg/Ca ratio of the sediment being deposited at any time is equal to  $[Mg]_d/[Ca]_d$ , go ahead and convert this to an equation for the evolution of sediment Mg/Ca.

d. *A forward calculation.* Either by numerical or symbolic integration of your ODE for Mg/Ca, plot the Mg/Ca ratio of the sediments for the case  $[Mg]_r = 10^{-8}(1 + \sin[10\pi t/\tau_d])$ , starting from  $[Mg]_d = 10^{-7}$  at  $t = 0$ .

e. Repeat part (d) for the forcing function  $[Mg]_r = 10^{-8}(1 + \sin[0.1\pi t/\tau_d])$ .

f. Describe and interpret the difference between your answers to parts (d) and (e); note that the oscillation in river composition is of the same magnitude in both cases, only the frequency is different.

### 3. How practical are Practical Salinity Units?

In lecture it was pointed out that it is difficult (inaccurate and slow) to measure salinity in absolute units (mg of dissolved salts per kg of water). Instead one uses conductivity of the water, expressed in psu (practical salinity units), which are calibrated so that for seawater the values are about equal. That is, seawater with 35 mg total salts per kg H<sub>2</sub>O has a conductivity of 35 psu. One problem is that this calibration only works for a particular composition of the ions in solution. Let's see how this works:

Consider a pure NaCl solution with 35 mg of NaCl per kg of H<sub>2</sub>O, and define its conductivity to be 35 ipsu (impractical salinity units, since this is not quite the same calibration as the official one for seawater). Now, to first order, the conductivity of an ionic solution is proportional to a sum over all ions of *molar* concentration times *charge* squared:

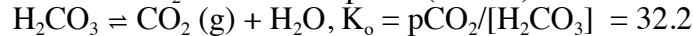
$$\text{conductivity} \propto \sum_i z_i^2 c_i$$

- a. Estimate the conductivity in ipsu of a solution of 35 mg of  $\text{CaCl}_2$  per kg  $\text{H}_2\text{O}$ .
- b. Estimate salinity (mg per kg of  $\text{H}_2\text{O}$ ) for a  $\text{MgSO}_4$  solution with conductivity 35 ipsu.

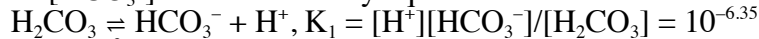
#### 4. Seawater chemistry and uptake of atmospheric $\text{CO}_2$

In lecture we saw a plot of the speciation ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) of inorganic carbon in seawater as a function of pH. Let's use the principles behind that diagram to determine what the ocean will do if we raise atmospheric  $\text{CO}_2$  and it dissolves in the ocean. This is a key issue in the study of global warming...how much  $\text{CO}_2$  can the ocean store, and what are we doing to ocean chemistry by burning fossil fuels? We're going to do this at  $25^\circ\text{C}$  and assume ideal solution, so the numbers do not quite match the figure from lecture.

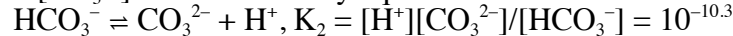
The concentration  $[\text{H}_2\text{CO}_3]$  (in mol/kg) in surface water is determined by equilibrium with the partial pressure of  $\text{CO}_2$  in the atmosphere (in bars):



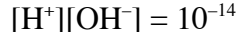
The concentration  $[\text{HCO}_3^-]$  is determined by equilibrium with carbonic acid:



The concentration  $[\text{CO}_3^{2-}]$  is determined by equilibrium with bicarbonate ion:



The hydrogen and hydroxide ion concentrations must satisfy the dissociation of water:



And, finally, we toss in enough  $\text{Ca}^{2+}$  to satisfy net charge balance (note, the following is NOT a balanced chemical reaction; it is an equation stating the condition of charge neutrality for the solution):



a. For a pre-industrial atmospheric  $p\text{CO}_2 = 3 \times 10^{-4}$  and an oceanic  $\text{pH} = -\log([\text{H}^+]) = 8$ , calculate the concentrations of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{Ca}^{2+}$ . Which is the major inorganic carbon species at this pH? Also calculate total dissolved  $\Sigma\text{CO}_2 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ .

b. The solubility product  $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$  for calcite is  $10^{-8.35}$ ; is this solution saturated, oversaturated, or undersaturated with respect to calcite precipitation? To be in equilibrium both with calcite and with atmospheric  $\text{CO}_2$ , would the solution need to be more acidic (i.e., lower pH) or more alkaline (i.e., higher pH)?

c. Now let us increase  $p\text{CO}_2$  to  $4 \times 10^{-4}$ , (which it will reach in a few years), keeping the pH constant at 8 (implicitly, then, adjusting  $[\text{Ca}^{2+}]$  to maintain charge balance). By what factor does  $\Sigma\text{CO}_2$  increase? Define the C storage capability of the ocean as  $d(\Sigma\text{CO}_2)/d(p\text{CO}_2)$  and calculate it for this exercise.

d. However, what really happens as atmospheric  $p\text{CO}_2$  changes is that we hold  $[\text{Ca}^{2+}]$  constant and let pH and the concentrations of the inorganic C species adjust to reach a new equilibrium. Find this new equilibrium, and determine the concentrations of all the species, the pH, and  $\Sigma\text{CO}_2$ . Does the acidification of seawater increase or decrease the C storage capability of the shallow ocean?