Ge 101
Problem Set 5
Due December 5, 2012 (in person or electronically)

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

a. Plot the data in ratio-ratio space. Compute the best-fitting hyperbola using some appropriate least-squares calculation. Life is simple here because, without stated errors, you can use unweighted least-squares fitting and, without outliers, you shouldn't need robust statistical methods.

b. 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?

c. Likewise, what are the possible ranges for the Sm/Yb ratios of the end members?

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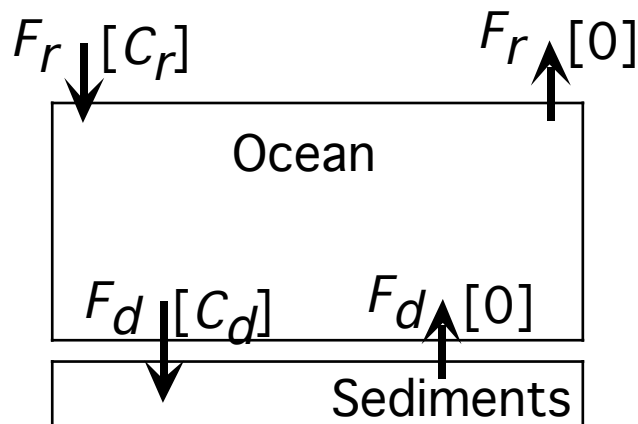
Let us use a simple box model to analyze Mg/Ca ratios measured in stratigraphic sequences of oceanic carbonate sediments. Here is the setup:

• 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} Thomas/m^3 (The Thomas unit is chosen so that CaCO$_3$ sediment has a Ca concentration of 1 Thomas/m^3, just for convenience; curiously, 1 Thomas = 1 Wicks = 1 Hamecher = 1 Balta = 1 Hudson = 1 O'Leary = 1 Akins).
• Take the area of the oceans to be 3.6 x 10^8 km^2 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$_3$. Calculate the flux of water through the sedimentation process, F_d in m^3/yr. What is the residence time τ_d of an element like Ca or Mg in this ocean?

b. Let us say river water has a constant $[Ca]_r = 10^{-4}$ Wicks/m^3. Recall that $[Ca]_d$ is in steady state, and calculate the river water flux F_r. What is the residence time of H$_2$O in this ocean?

c. Write a differential 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$_2$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$_2$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

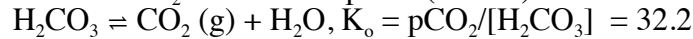ionic solution is proportional to a sum over all ions of *molar* concentration times *charge* squared:

$$conductivity \propto \sum_i z_i^2 c_i$$

a. Estimate the conductivity in ipsu of a solution of 35 mg of $CaCl_2$ per kg H_2O.

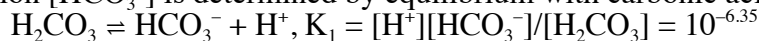b. Estimate salinity (mg per kg of H_2O) for a $MgSO_4$ solution with conductivity 35 ipsu.

4. Seawater chemistry and uptake of atmospheric CO_2

In lecture we saw a plot of the speciation (H_2CO_3, HCO_3^-, 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 CO_2 and it dissolves in the ocean. This is a key issue in the study of global warming...how much 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°C and assume ideal solution, so the numbers do not quite match the figure from lecture.
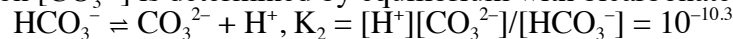
The concentration $[H_2CO_3]$ (in mol/kg) in surface water is determined by equilibrium with the partial pressure of CO_2 in the atmosphere (in bars):
$$H_2CO_3 \rightleftharpoons CO_2 (g) + H_2O, \; K_o = pCO_2/[H_2CO_3] = 32.2$$
The concentration $[HCO_3^-]$ is determined by equilibrium with carbonic acid:
$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+, \; K_1 = [H^+][HCO_3^-]/[H_2CO_3] = 10^{-6.35}$$
The concentration $[CO_3^{2-}]$ is determined by equilibrium with bicarbonate ion:
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+, \; K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] = 10^{-10.3}$$
The hydrogen and hydroxide ion concentrations must satisfy the dissociation of water:
$$[H^+][OH^-] = 10^{-14}$$
And, finally, we toss in enough 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):
$$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

a. For a pre-industrial atmospheric $pCO_2 = 3 \times 10^{-4}$ and an oceanic pH $= -\log([H^+]) = 8$, calculate the concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-, and Ca^{2+}. Which is the major inorganic carbon species at this pH? Also calculate total dissolved $\Sigma CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$.

b. The solubility product $K_{sp} = [Ca^{2+}][CO_3^{2-}]$ 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 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 pCO_2 to 4×10^{-4}, (which it will reach in a couple years), keeping the pH constant at 8 (implicitly, then, adjusting $[Ca^{2+}]$ to maintain charge balance). By what factor does ΣCO_2 increase? Define the C storage capability of the ocean as $d(\Sigma CO_2)/d(pCO_2)$ and calculate it for this exercise.

d. However, what really happens as atmospheric pCO_2 changes is that we hold $[Ca^{2+}]$ constant at the value computed in part (a) 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 ΣCO_2. Does the acidification of seawater increase or decrease the C storage capability of the shallow ocean?