OCN400 - Problem Set #4 **Jim Murray**
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Carbonate Chemistry

1) Assuming you know the following, solve for the concentration of CO_3^{2-} in surface seawater by an online approach. Go the website at **http://cdiac.esd.ornl.gov/ftp/co2sys** and download the program **co2sys.exe**. To do this just follow the instructions given. This will give you a state of the art program by Lewis and Wallace with Dept. of Energy (DOE) funding for performing CO_2 system calculations. Do the calculations for questions 1a and 1b using this program and compare the answers with what you got in Problem Set #3.

When running the program it will ask you questions about your problem. To be consistent, everyone in OCN421 should use when asked : single-input mode, Peng et al constants, PCO2, the Dickson value for KSO4, and the NBS pH scale. Use S=35 , 25°C and 0m.

> **a)** Assume Total $CO_2 = 2.0 \times 10^{-3}$ mol kg^{-1}. Determine the concentration of CO_3^{2-} at pH 8.0.
>
> . **b)** Assume total $CO_2 = 2.0 \times 10^{-3}$ mol kg^{-1} in equilibrium with the atmosphere ($P_{CO2} = 10^{-3.5}$) what is the CO_3^{2-} concentration?

2) How will fossil fuel CO_2 change the pH of the ocean?
Scientists project that P_{CO2} will eventually triple from its pre-industrial value of 280 ppm to at least 850 ppm. Assume alkalinity stays constant at 2.300×10^{-3} eq l^{-1}.
Assume $K_1' = 10^{-6.0}$ and $K_2' = 10^{-9.1}$

a. What will be the initial (at 280ppm) and final (at 850ppm) pH for this model?
d. What are the pros and cons regarding the asumption that the alkalinity stays constant?
c. How would you set up the problem to solve for the pH assuming that $CaCO_3$(s) was at equilibrium with seawater while P_{CO2} was increasing? Don't do any calculations here but see if you write what equation(s) you would use.

Box Models: Particulate carbon flux

3) Using the box model you have worked on in the previous problem sets assume the following values for total CO_2 (e.g. C) and alkalinity (e.g. A) in the surface and deep ocean. Assume V_{mix} = 300 cm y^{-1}.

C_s = 1932 μmol kg^{-1} A_s = 2277 μmol kg^{-1}

C_d = 2256 μmol kg^{-1} A_d = 2374 μmol kg^{-1}

a) Calculate the magnitude of the total carbon flux from the surface ocean (e.g. B) and the fraction of B preserved in sediments (f) for two cases:

Case 1: neglect river input

Case 2: include river input with C_r = 960 μmol kg^{-1}

and $V_r = 4.6 \times 10^{19}$ cm^3 y^{-1}.

Explain if the answers make sense.

b) Use an alkalinity balance for the surface box to calculate the relative contributions of $CaCO_3$ and organic C to the total carbon flux (B). Assume $A_r = C_r$. How does your answer compare with the ratio of $CaCO_3$ to organic C in deep ocean sediment trap samples (see lecture notes)?

c) If V_{mix} was 50% faster during the last glacial maximum, as has been proposed, what would be the new values of B and f?