Marine Chemistry 12.742 Problem Set #8

Question 1

Use the accompanying data table, pore water $[NO_3^-]$ (in μ mol/l) vs depth (in cm), and the additional information below to answer the following questions. Use the additional data:

- Sediment porosity (φ) (cm³ of pore water / cm³ bulk sediment) vs depth below the sediment-water interface (x) in cm:
 φ = 0.70 + 0.14e^{-0.63x}
- The diffusion coefficient for NO_3^- in seawater at 2°C: 330 cm²/y
- D_{sed} for NO₃ varies with sediment porosity as follows: $D_{sed} = D_{sw}\phi^2$

a) Identify the depth of the boundary between the layer in which O_2 is used as the electron acceptor for organic matter decomposition and that in which NO_3^- is used.

- b) Calculate the diffusive flux of NO₃⁻
 - -across the sediment-water interface. Is it directed into or out of the sediments?
 -across the boundary between the oxic and denitrification layers. Is it directed toward or away from the sediment-water interface?
- c) Use your knowledge of organic matter decomposition stoichiometry to calculate: -the rate of N_2 production

-the rate of organic matter oxidation by O₂

-the rate of organic matter oxidation by NO3⁻

depth (cm)	NO3 (micromol/l)
0	23.3
0.1078	25.0276
0.1944	26.2846
0.4005	28.858
0.8133	32.5975
1.0119	33.881
1.2382	35.0346
1.4285	35.7949
1.6384	36.4507
1.8298	36.9085
2.0374	37.2781
2.2629	37.5522
2.6111	37.7597
2.943	37.7559
3.3092	37.5617
3.7131	37.1495
4.0814	36.6141
4.3173	36.1982
4.7371	35.3268
5.1927	34.2039
5.6871	32.791
6.0038	31.7862
6.3364	30.6603
6.6858	29.5065
7.3076	27.5885
8.124	25.3112
8.8684	23.4489
9.3452	22.3526
10.0184	20.9206
10.5531	19.8721
11.1146	18.8479
12.114	17.2007
13.1986	15.6355
14.6229	13.8/54
16.1942	12.2527
18.2333	10.5408
20.1/71	9.23077
22.3214	8.06413
25.9597	6.5711
30.6832	5.24167

Question 2:

Use the sedimentary pore water depth profiles in the figures below. Remember these are real data, and they have some deviations from smooth profiles due to sampling and analytical uncertainty; keep that in mind as you discuss them. NOTE: 10x fold different depth scales for O2 versus trace metals.

Temperature: March = 4 °C, August = 15°C Sedimentation rate: 0.3 mm_{bulk sed}/y Porosity: 0.8 cm³_{water} / cm³_{bulk sed}. (Note: (1-porosity) ~ cm³_{solid}/cm³_{bulk sed}) Density of sedimentary solids: 2.6 g_{solid}/cm³_{solid}. Diffusion coefficients. These values apply to diffusion in sediment pore waters: D_{sed} (O₂) (a) at 4°C: 270 cm²_{sed}/y (b) at 15°C: 355 cm²_{sed}/y D_{sed} (U) (a) at 15 °C: 150 cm²_{sed}/y

(1) How do you account for the difference between bottom water O_2 concentrations in March and August?

(2) Use the shapes of the pore water O_2 , Mn^{2+} , and Fe^{2+} profiles to define zones of net consumption of O_2 and net production of dissolved Mn^{2+} and Fe^{2+} in March and August. How do you explain your observations?

(3) It has been observed that, in many coastal sediments, the rate of sedimentary organic carbon oxidation can be calculated from the sedimentary O_2 consumption rate as if O_2 were the only electron acceptor. With this in mind,

- (a) Use the included graphs to calculate the sedimentary O₂ consumption rates in March and in August.
- (b) Estimate the rate of sedimentary organic carbon oxidation at each time.

(4) The U that is added to the solid phase is called "authigenic" U. Answer the following questions using the dissolved U profiles.

- (a) Over what depth interval in the sediments is there net removal of U from pore waters to the solid phase?
- (b) Calculate the rate of removal of U from the pore waters in August.
- (c) Using your result from question (4), calculate the concentration of authigenic U that you would expect to see in a measurement of the solid phase. State your assumptions.
- (d) Paleoceanographers use changes in the accumulation rate of uranium in sediments to infer changes in the oxygen penetration depth in sediments. Their reasoning is that uranium is soluble in oxic seawater and insoluble in anoxic sediments. U is supplied to the sediments by diffusion across the sediment-water interface. Would you say that these profiles support that use of U accumulation rates in sediments?







Question 3:

The dissolution of CaCO3 in the ocean water column and in surface sediments depends upon bottom water and pore water carbonate ion concentrations, pressure and temperature. Below are two figures from Sarmiento and Gruber showing the surface sediment CaCO3 (% weight) and a vertical section (depth/distance; North Atlantic to North Pacific) of the carbonate ion anomaly ΔCO_3^{-2} relative to the solubility product for calcite and aragonite

- a) Briefly describe the processes effecting carbonate ion anomalies; why do the N. Pacific and N. Atlantic differ?
- b) Consider perpendicular cross-sections to the mid-ocean ridges in the N. Atlantic (30 deg. N), S. Pacific (30 deg. S), and and N. Pacific (30 deg. N). Draw idealized diagrams showing the aragonite and calcite saturation horizons, lysocline, calcite compensation depth, and the vertical profile of CaCO3 rain rate and burial?
- c) How would the ocean carbonate cycle differ if all of the organisms formed aragonite rather than calcite. Consider both the transient response and steady-state response.



Houre 9.3.3: Gridded map of the weight percentage of CaCO3 in the surface sediments. See also color plate 5. Data are from Archer [1996b].



FIGURE 9.3.2: Vertical sections of the difference between the CO_3^2 - concentration and the CO_3^2 - saturation (a) with respect to aragonite, ΔCO_3^2 - (ragonite), and (b) with respect to calcite, ΔCO_3^2 - (calcite), along the track shown in figure 2.3.3a. See also color plate 8. The saturation concentration of CO_3^2 - was calculated using the solubility product for calcite and aragonite from *Mucci* [1983], with the pressure dependence after *Millero* [1983]. The calcium concentration was assumed to be a function of salinity [*Millero*, 1982].