12.007 Problem Set Due March 20

The carbon cycle and microbial energetics

1. What is the major source of chlorine in seawater? How about sodium? How about sulfate?

2. Discuss some processes through which global warming can influence the biological pump, including the concentration of oxygen in the water column, the production of CaCO3 by phytoplankton (calcification), redox stratification and the production of SiO2 by phytoplankton.

3. Selenate (SeO<sub>4</sub><sup>2-</sup>) is a highly toxic inorganic pollutant that occurs at micromolar concentrations in some agricultural wastewaters.

Can a microbe remove selenate from the water by reducing it to elemental selenium (Se) by coupling this reduction to the oxidation of acetate?

Address by:

- A) writing the balanced half-reaction for the selenate/Se couple
- B) writing the balanced half-reaction for the oxidation of acetate at pH = 8
- C) writing the balanced redox reaction coupling the reduction of selenate to the oxidation of acetate and calculating its energy yield
- D) discussing the effect of pH and the concentration of organics and selenate on the energetics of the reactions in C) per mole of acetate and per mole of selenate
- E) discussing whether a microbe could also reduce selenate to selenite [i.e., not all the way to Se(s)] coupled with the oxidation of acetate
- F) Would the microbe gain more or less energy by oxidizing lactate instead of acetate (coupled to the reduction of selenite/Se)?
- G) Would you expect the reduction of selenate to selenite to Se to be carried out by one microbe or multiple microbes? Why? How would you test your hypothesis?

$\frac{1}{2}$ SeO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup> + e <sup>-</sup> = $\frac{1}{2}$ H <sub>2</sub> SeO <sub>3</sub> + $\frac{1}{2}$ H <sub>2</sub> O	pe <sup>0</sup> = + 19.4
$\frac{1}{4}$ H <sub>2</sub> SeO <sub>3</sub> + H <sup>+</sup> + e <sup>-</sup> = $\frac{1}{4}$ Se(s) + $\frac{3}{4}$ H <sub>2</sub> O	pe <sup>0</sup> = + 12.5
acetate: $\frac{1}{4}$ CO <sub>2</sub> (g) + 7/8 H <sup>+</sup> + e <sup>-</sup> = 1/8 CH <sub>3</sub> COO <sup>-</sup> + $\frac{1}{4}$ H <sub>2</sub> O	pe <sup>0</sup> = + 1.27
$CO_2 + H_2O = H_2CO_3^*$	logK = -1.5
$H_2CO_3^* = H^+ + HCO_3^-$	logK = -6.3
$HCO_{3}^{-} = H^{+} + CO_{3}^{-2}$	logK= -10.3

 $\Delta G = n 2.3RT(pe_2-pe_1)$ 

 $\Delta G = \Delta G^{0} + RTIn\{[Red1][Ox2]\}/\{[Ox1][Red2]\}$ 

4. A sulfate-reducing organism oxidizes formate to CO<sub>2</sub> while reducing sulfate to

## sulfide.

a. Write out the two half-reactions and the balanced complete reaction assuming the appropriate species at pH=9.4.

b. Using reduction potentials (Table 7.1 from the Morel and Hering reading), calculate DGo for this metabolism.

c. Discuss how DG would change over the pH range 1-14. State your assumptions about the concentrations of other relevant species.

d. Would these organisms be heterotrophic or autotrophic?

## 5. Read Lavik et al. and answer the following questions:

a. What is annamox? Write the reaction for this metabolism.

b. Where in the water column would you expect annamox to occur?

c. Calculate DG for the reaction describing the oxidation of sulfide with nitrate.

d. Write the similar reaction describing the oxidation of sulfide with oxygen and calculate DG.

e. How do organisms performing metabolisms described in c. and d. acquire their carbon?

f. Which genes are used as tracers of sulfur oxidation? What do these genes do?

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12.007 Geobiology Spring 2013

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