

## GG325 -- PRINCIPLES OF GEOCHEMISTRY

### Homework Set #4 -- Due Fri 2 Nov.

**1 (a)** The annual input of  $\text{SO}_4^{2-}$  into the oceans by rivers is estimated to be  $3 \times 10^{12}$  mole/yr. If  $\text{SO}_4^{2-}$  were at a steady-state concentration in sea water and its only significant input flux to the oceans were the river flux, what would the residence time of  $\text{SO}_4^{2-}$  in the oceans be? The mass of the oceans is  $1.4 \times 10^{24}$  g and the  $\text{SO}_4^{2-}$  concentration in the oceans is 0.028 mol/kg

**(b)** If there were no  $\text{SO}_4^{2-}$  flux out of the oceans to balance the above input flux, so that its concentration was constantly building up due to the river flux, how long would it take to increase the  $\text{SO}_4^{2-}$  concentration by 20%

**2.** The equilibrium temperature dependent law for O isotope fractionation between water ( $\text{H}_2\text{O}$ , described by  $\delta_w$ ) and calcite ( $\text{CaCO}_3$ , described by  $\delta_c$ ) and is:

$$T (\text{°C}) = 16.0 - 4.14 (\delta_{c(\text{PDB})} - \delta_{w(\text{PDB})}) + 0.13 (\delta_{c(\text{PDB})} - \delta_{w(\text{PDB})})^2$$

However, the observed fractionation of oxygen isotopes between seawater and their calcareous shells for many planktonic foraminifera (described by  $\delta_f$ ) follows a different but similar temperature dependent law:

$$T (\text{°C}) = 16.5 - 4.3 (\delta_{f(\text{PDB})} - \delta_{w(\text{PDB})}) + 0.14 (\delta_{f(\text{PDB})} - \delta_{w(\text{PDB})})^2$$

in both of the above equations, all  $\delta$ 's are on the PDB scale and refer to  $^{18}\text{O}/^{16}\text{O}$  ratios [from Berger and Gardner, Journal of Foraminiferal Research, vol. 5, p 102-113 (1975)]. To solve problems using either equation, you will need to use the quadratic formula. The general form for  $ax^2 + bx + c = 0$  is

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

*(Remember, there are 2 roots when you use this equation; in our case, only 1 will "make sense" -i.e., will have a reasonable  $\delta^{18}\text{O}$  value, and thus be the correct answer)*

**(a)** Explain why these organisms do not follow the chemical equilibrium rate law

**(b)** Equatorial seawater today has  $\delta_{w(\text{SMOW})} = +0.1\text{‰}$  and mean surface temperature =  $28^\circ\text{C}$ . Seawater at  $35^\circ\text{N}$  has  $\delta_{w(\text{SMOW})} = -0.3\text{‰}$  and mean surface temperature =  $20^\circ$ . What would  $\delta_{f(\text{PDB})}$  be in foram shells formed in these two locations?

**(c)** Let's say that in the worst case scenario for anthropogenically induced greenhouse warming the sea level elevation temperature at the poles,  $35^\circ\text{N}$  and the equator increases by  $6^\circ\text{C}$ ,  $3^\circ\text{C}$  and  $1^\circ\text{C}$  respectively. What would be  $\delta_{f(\text{PDB})}$  in the same foram shells at  $35^\circ\text{N}$  considering only effects due to the changes in surface seawater temperature indicated?

**(d)** Now let's say that during this temperature shift, 10% of the volume of polar icecaps melt and this water, with  $\delta_{w(\text{SMOW})} = -55\text{‰}$ , is distributed evenly in the top 100m of the oceans. What would  $\delta_{f(\text{PDB})}$  be at  $35^\circ\text{N}$  due to only to the addition of the isotopically-light melt water (i.e., ignore the temperature change calculated in d)?

*Hint:* The volume of the oceans and polar icecaps are  $1370 \times 10^6 \text{ km}^3$  and  $29 \times 10^6 \text{ km}^3$ , respectively. Assume that the oceans are rectangular in shape with a uniform depth of 4000m. [*hint:* calculate the proportion of oceanic volume in the top 100 m relative to the entire oceans, add the melt water to this to make a "new" expanded top layer of (100+x)m depth, x being that added from melt water; then calculate a new  $\delta_{w(\text{SMOW})}$  of the water before attempting to calculate  $\delta_{f(\text{PDB})}$ . This new  $\delta_{w(\text{SMOW})}$  can be assumed to isotopically shifted equally at all latitudes.