

**GG325 -- PRINCIPLES OF GEOCHEMISTRY**  
**Homework set #3 – answers – 20 points each**

**1. The oceans**

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 the only significant sulfate input 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

$$T_{\text{res}} = [A]/(dA/dt) \quad A = 0.028 \text{ mol/Kg} \times \text{kg}/1000\text{g} \times 1.4 \times 10^{24} \text{ g} = 3.92 \times 10^{19} \text{ mol } \text{SO}_4^{2-}$$

$$T_{\text{res}} = 3.92 \times 10^{19} \text{ mol } \text{SO}_4^{2-} / 3 \times 10^{12} \text{ mol/yr} = \mathbf{1.3 \times 10^7 \text{ year}}$$

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 15%

$$15\% \text{ of } 0.028 \text{ mol/Kg} = 0.0056 \text{ mol/Kg} = 5.88 \times 10^{18} \text{ mol } \text{SO}_4^{2-}$$

$$\text{Time} = 5.88 \times 10^{18} \text{ mol } \text{SO}_4^{2-} / 3 \times 10^{12} \text{ mol/yr} = \mathbf{1.96 \times 10^6 \text{ years}}$$

**2. Hydrosphere composition**

a. What is the Alkalinity of seawater with the following composition:

$\text{Na}^+$	0.481 M	$\text{Cl}^-$	0.560 M
$\text{Mg}^{2+}$	0.0544 M	$\text{SO}_4^{2-}$	0.0283 M
$\text{Ca}^{2+}$	0.011 M	$\text{HCO}_3^-$	0.00238 M
$\text{K}^+$	0.011 M		

**see the lecture-17 notes for this problem**

$\text{Alk} = \text{eq}_{\text{conservative cations}} - \text{eq}_{\text{conservative anions}}$  (see lecture notes and the reading). In the list above, Only  $\text{HCO}_3^-$  is non-conservative, so that

$$\text{Alk} = (0.481 + 2 \times 0.0544 + 2 \times 0.011 + 0.011) - 0.560 + 2 \times 0.0283$$

$$\text{Alk} = 0.6228 - 0.6166$$

$$\mathbf{\text{Alk} = 0.0062 \text{ eq/L} = 6.2 \text{ meq/L}}$$

*Does this low value make sense? Yes, because alkalinity is a combo of carbonate (CA) and non-carbonate contributions (and is dominantly CA in most natural waters). The carbonate alkalinity comes from  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and @ pH~8,  $[\text{HCO}_3^-]/[\text{CO}_3^{2-}] \sim 100$ , CA~  $0.00238 + 2 \times 0.01 \times 0.00238 = 0.00476 = 4.8 \text{ meq/L}$ , leaving about 3.8 meq of non-CA alkalinity unaccounted for. The answer to what this missing material might be forms the answer to part b of this problem.*

b. write the charge balance equation for this solution and substitute in the numbers above. Is this solution balanced? If not, what other ion(s) that are not listed might be present in seawater to help balance the charge?

$$\text{eq}_{\text{cations}} - \text{eq}_{\text{anions}} = 0$$

convert molarity data given in the table to meq by multiplying by the ion charge.

$$(0.481 + 2 \times 0.0544 + 2 \times 0.011 + 0.011 + \text{other cations}) = 0.560 + 2 \times 0.0283 + 0.00238 + \text{other anions}$$

$$0.6228 + \text{other cations} = 0.6190 + \text{other anions}$$

$$\mathbf{0.0038 \text{ eq/L} = 3.8 \text{ meq/L} = \text{other anions} - \text{other cations.}}$$

*There is a net unbalanced positive charge, which indicates our table is incomplete (other not-listed chemicals are present). 0.0038 eq of anions are missing if only anions are missing*

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from the table (i.e., missing cations = 0. Seawater is a complex mixture of ions so many things are actually “missing” from this simple table, but there are a few major non-conservative ions that form the majority of the difference (they are listed in the reading lecture notes as  $\text{CO}_3^{2-}$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{HS}^-$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{PO}_4$  conj. bases, organic acid anions). **The most important two, which also account for most of the “missing” alkalinity from part a, are  $\text{B}(\text{OH})_4^-$  and ionized DOC.** I say this because the other “missing” ions in my list include the reduced form of S ( $\text{HS}^-$ ), which is extremely low in high pe environments such as seawater, and nutrient elements (various forms of N and P), which are generally very low (especially in surface waters).

### 3 Weathering

A sediment has a CEC of 70 meq/100 g. The following exchangeable cations make up the CEC:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{H}^+$ . The first 4 were measured at concentrations of 19, 5.9, 4.1 and 1.2 meq/100g, respectively. What is the ECS of  $\text{H}^+$  on this sediment?

$$\text{ECS}_{\text{H}^+} = 70 - [19 + 5.9 + 4.1 + 1.2] = \mathbf{39.8 \text{ meq/100g}}$$

### 4. Soils

a. Name 2 chemicals (or minerals) that precipitate from soil water as the pH changes

*Raising pH causes a sufficient shift in the proportion of carbonate to bicarbonate anions for calcite,  $\text{CaCO}_3$ , to precipitate in a layer we call caliche. It also allows precipitation of hydroxides of Al and Fe (e.g., the minerals Gibbsite and Goethite). Some of you answered  $\text{CaSO}_4$ . This is sometimes found shallow in soils from evaporation, but it does not form from a change in pH.*

b. what is the name of the soil zone where the precipitation occurs?

*The B-zone, or the zone of accumulation*

### 5. Paleoclimate

5a. Explain why these organisms do not follow the chemical equilibrium rate law

*When organisms excrete  $\text{CaCO}_3$  shells, each species creates shells with slightly different temperature relationships, due to “vital” effects, which include fractionation due to differences in metabolism and resulting isotopic composition of internal bodily fluids. Biological fractionation tends to favor  $^{18}\text{O}$  to variable amounts.*

5b. Assume that equatorial seawater today has  $\delta_{\text{w}(\text{SMOW})} = 0\text{‰}$  and mean surface temperature =  $28^\circ\text{C}$ . What would  $\delta_{\text{f}(\text{PDB})}$  be in foram shells formed in this locations?

**See answer table below**

5c. Let's say that in the worst case scenario for anthropogenically induced greenhouse warming the sea level temperature at the equator increases by  $1^\circ\text{C}$ . What would  $\delta_{\text{f}(\text{PDB})}$  be in foram shells growing there assuming that  $\delta_{\text{w}(\text{SMOW})} = 0\text{‰}$  (i.e., the same as in 5b)?

**See answer table below**

5d. Now let's say that during this temperature shift, 10% of the volume of polar icecaps melt and this water, with  $\delta_{\text{w}(\text{SMOW})} = -55\text{‰}$ , is distributed evenly in the top 100m of the oceans. What would  $\delta_{\text{f}(\text{PDB})}$  be in foram shells growing there assuming that the only effect is the addition of the isotopically-light melt water (i.e., ignore the temperature change calculated in c)?

### ANSWERS

*– Ocean volume in top 100 m is  $(100/4000) * 1370 * 10^6 \text{ km}^3 = 34250000 \text{ km}^3 = V_1$*

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- 10% of ice volume to add to this is  $0.10 \times 29 \times 10^6 \text{ km}^3 = 2900000 \text{ km}^3 = V_2$
- $\delta_{w(SMOW)}$  of the mixture of the two is a weighted mean  $[(-55\text{‰} \times V_1) + (-0.3\text{‰} \times V_2)] / (V_1 + V_2) = -4.29\text{‰}$

**answer table**

	$\delta_{w(PDB)}$	$\delta_f(PDB)$	$\delta_f(PDB)$	<i>If you notice, the predicted temperature shift alone from global warming would have little effect on <math>\delta^{18}\text{O}</math> in the forams, whereas the glacial melt water addition would have a large effect. How did I pick the "good" root? The PDB standard is a <math>\text{CaCO}_3</math> shell material, so foram shells should have a similar <math>\delta^{18}\text{O}</math>. Seawater on the PDB scale is very negative (about -30‰). Because the SMOW standard is a seawater, other seawaters would have similar <math>\delta^{18}\text{O}</math> on the SMOW scale and <math>\text{CaCO}_3</math> shells would be isotopically heavy compared to this (about +30‰)</i>
		<b>root 1</b>	root 2	
		<b>"good"</b>	"bad"	
<i>problem 5b</i>	-29.94	<b>3.25</b>	-32.42	
<i>problem 5c</i>	-29.94	<b>3.45</b>	-32.61	
<i>problem 5d</i>	-34.10	<b>-0.71</b>	-36.78	