

GG325 -- PRINCIPLES OF GEOCHEMISTRY
Homework set #3 - answers

1. The Hydrosphere:

Tables 10.8 and 1.1 in "the hydrosphere" lecture notes give two different estimates for the volume of water in the polar ice caps and other glaciers. If the glaciers are at steady-state (for volume) and the flux of water added to them each year (which equals the flux removed as well) is $90 \text{ km}^3/\text{yr}$, what is the implied residence time (T_{res}) of water in the glaciers with for each of the volume estimates?

Table 10.8 $T_{\text{res}} = 29 \times 10^6 \text{ km}^3 / 90 \text{ km}^3/\text{yr} = 322,000 \text{ years}$
 Table 1.1 $T_{\text{res}} = 43.4 \times 10^6 \text{ km}^3 / 90 \text{ km}^3/\text{yr} = 482,000 \text{ years}$

2. Hydrosphere composition

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

Na ⁺	0.481 M	Cl ⁻	0.560 M
Mg ²⁺	0.0544 M	SO ₄ ²⁻	0.0283 M
Ca ²⁺	0.011 M	HCO ₃ ⁻	0.00238 M
K ⁺	0.011 M		

see the lecture-17 notes for this problem

$Alk = \sum eq_{\text{conservative cations}} - \sum eq_{\text{conservative anions}}$ (see lecture notes and the reading). In the list above, Only HCO₃⁻ is non-conservative, so that

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

$$Alk = 0.6228 - 0.6166$$

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

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 HCO₃⁻ and CO₃²⁻ and @ pH~8, [HCO₃⁻]/[CO₃²⁻] ~ 100, CA ~ 0.00238 + 2x0.01x 0.00238 = 0.00243 = 2.4 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?

$$\sum eq_{\text{cations}} - \sum eq_{\text{anions}} = 0$$

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

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

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

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

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 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

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major non-conservative ions that form the majority of the difference (they are listed in the reading lecture notes as CO_3^{2-} , $\text{B}(\text{OH})_4^-$, HS^- , NH_4^+ , H_3PO_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 (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. How does ECS differ from CEC?

CEC is the total amount of exchange cations adhered to a solid material in meq/100 g, ECS is the total amount of a particular exchange cation species adhered to a solid material in meq/100 g.

3b. A sediment has a CEC of 70 meq/100 g. The following exchangeable cations make up the CEC: Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ . The first 4 were measured at concentrations of 20, 5.7, 4.1 and 1.5 meq/100g, respectively. What is the ECS of H^+ on this sediment?

$$\text{ECS}_{\text{H}^+} = 70 - [20 + 5.7 + 4.1 + 1.5] = \mathbf{38.7 \text{ meq/100g}}$$

4a. What does “Zero Point of Charge” mean for particles surfaces?

This is the pH at which the net charge on a surface is zero

b. Are particle surfaces without charge at the ZPC?

No, there will be both positively and negatively charged functional groups on the surface. The quantity of each are equal, so that the net charge is zero.

5. Soils

a. How does pH change with depth in a typical soil zone, and why?

pH almost always increases (the soil becomes less acidic) with depth, primarily due to a decrease in the organic acid content of the solids and soil water.

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

The pH change described above causes a sufficient shift in the proportion of carbonate to bicarbonate anions for calcite, 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 CaSO_4 . This is sometimes found shallow in soils from evaporation, but it does not form from a change in pH.

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

The B zone, or the “zone of accumulation”. The pH shift begins below the A zone, and gives the B-zone some of its defining characteristics, such as accumulation of pH sensitive precipitation minerals.