

Environmental Geochemistry Problem Set 5

Rivers, Lakes and Fluxes to the Oceans

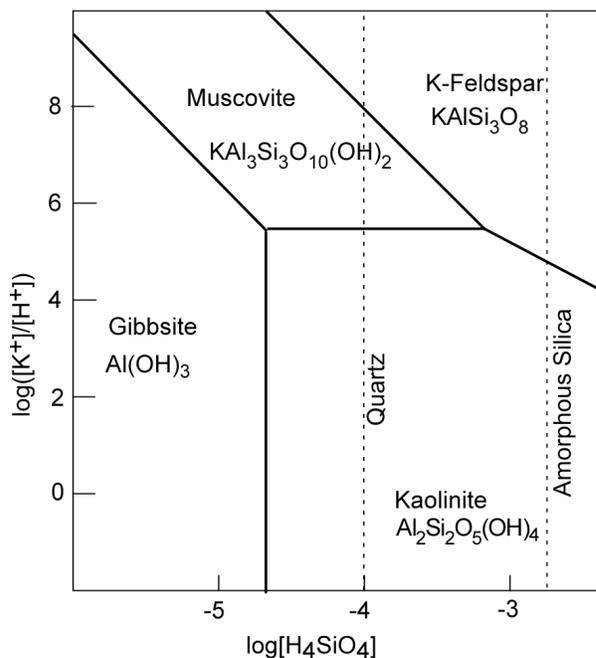
1. The Congo river has the following composition (mg/kgw):

	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ⁻²	HCO ₃ ⁻	SiO ₂
	6.87	2.37	1.38	1.99	1.40	1.40	1.17	13.43	10.36

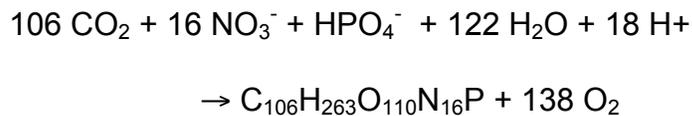
What kind of River is this based on the Stollard-Edmunds classification scheme (where $\Sigma m z^+$ is the total milliequivalents/kgw from the *cation* charge). Note the following atomic masses (in g/mol): Ca 40.1, Mg 24.3, Na 23.0, K 39.1, Cl 35.5, S 32.1, O 16.0, C 12.0, H 1.0, Si 28.0)

$\Sigma m z^+$	Category
<0.2	transport limited
0.2-0.45	weathering limited
0.45-3	carbonates/shales/evaporites
>3	evaporites

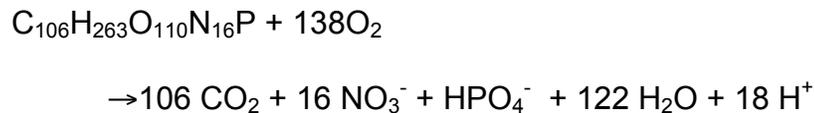
Now, plot the composition on the K-Si-H diagram below. What minerals would you expect in the Congo basin soil?



2. A lake of 10^6 m^3 has an average depth of 30 m and a thermocline at 5 m depth. The lake has a P concentration of 800 ppb (atomic mass of P = 31 g/mole; 1ppb = 1microgram/kg). Calculate the amount of organic carbon that will be fixed during the summer in the epilimnion given the Redfield reaction



Now calculate how much oxygen will be consumed in the hypolimnion when all this organic matter sinks to the bottom given the respiration reaction



3. a) Using the data in the table below estimate the residence times of U in the ocean with respect to sinks and sources. The other information you require is that the mass of the oceans is $1.35 \times 10^{21} \text{ kg}$, the concentration of U in seawater is 13.2 nM/kg and the atomic mass of U is 238. Is [U] in steady state?

Sources (10^{10} g U/yr)	
Rivers	1.14
Sinks (10^{10} g U/yr)	
Oxic, deep sea sediments	0.08
Metalliferous sediments	0.14
Anoxic/Suboxic sediments	0.40
Corals and molluscs	0.08
Oceanic Crust Alteration (low T)	0.23
Hydrothermal alteration	0.04

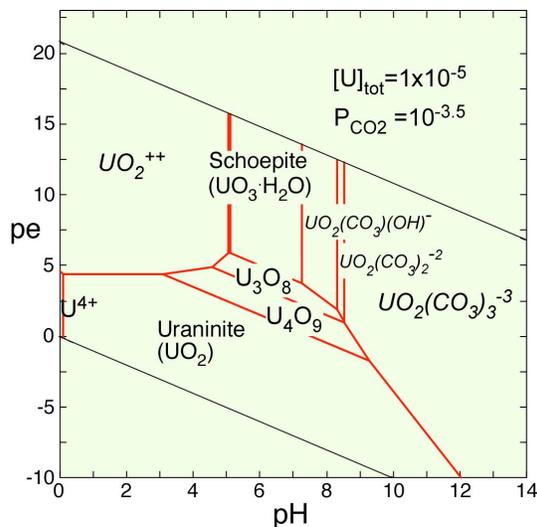
b) In reducing (anoxic) marine sediments, the concentration profile of U with depth was found to be (Klinkhammer and Palmer, 1991):

U (nmole/l)	sample depth (cm)
17.0	0.2
14.2	0.4
13.8	1.2
11.2	1.6
9.3	2.5
5.8	3.5
3.9	5
3.0	6.5
3.0	7.5
2.9	8.5
2.8	9.5

The diffusive flux of U from the seawater into the sediments is given by Ficks first law:

$$J = -D \left(\frac{\partial[U]}{\partial z} \right)_{z=0}$$

with $D = 3 \times 10^{-6} \text{ cm}^2/\text{sec}$. Calculate the flux of U from seawater into the reducing sediments given the measured concentration profile. Hint, plot the data to work graphically work out the flux. Given the that total area of reducing sediments in the ocean is $2.9 \times 10^7 \text{ km}^2$, calculate the global flux of U from seawater into anoxic sediments. How does this compare with fluxes worked out in part a) ? The drop in [U] suggests that something is removing [U] from the sediment porewater. In light of the pe-pH diagram for U, what must be happening (Hint, Uraninite is very insoluble) ?



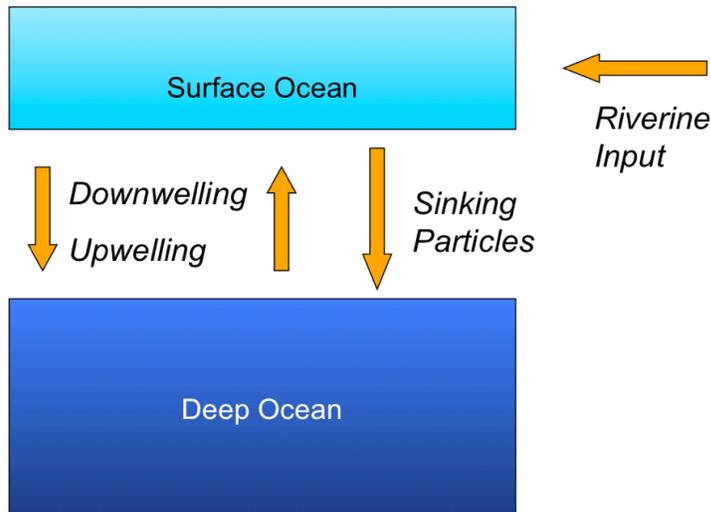
4. Use the following data to work out the net flux of a) Sr into the oceans from hydrothermal sources and b) the flux of seawater that circulates through the hydrothermal system and c) the time it takes for all of the oceans to circulate through the hydrothermal system :

Source	[Sr] mol/kg	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr Flux (mol/yr)
Rivers	8.90×10^{-7}	0.7119	
Hydrothermal	1.26×10^{-4}	0.7035	
Sea Water	9.00×10^{-5}	0.70916	

The mass of seawater is 1.35×10^{21} kg and the flux of river water into the oceans is 3.7×10^{16} kg/yr. Hint: from mass-balance, we have

$$(^{87}\text{Sr}/^{86}\text{Sr}_{\text{sw}})(F_{\text{rw}} + F_{\text{ht}}) = F_{\text{rw}}(^{87}\text{Sr}/^{86}\text{Sr})_{\text{rw}} + F_{\text{ht}}(^{87}\text{Sr}/^{86}\text{Sr})_{\text{ht}}$$

5. Broecker (1971) developed a “two-box model” for the oceans:



The volume discharge of rivers is 3.7×10^{13} m³/yr; the water transfer between the surface and deep oceans by upwelling or downwelling is 30 times the river discharge. Given the following concentrations (moles/m³):

	C_{rivers}	C_{surface}	C_{deep}
P	1.3×10^{-3}	2×10^{-5}	2.3×10^{-3}
NO ₃	3×10^{-2}	3×10^{-5}	3×10^{-2}
DIC*	1.2	1.95	2.30
Ca	0.36	10.2	10.3

*DIC = $\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$

a) Calculate the flux of Ca lost from the surface ocean by biological uptake (as CaCO_3) assuming that the surface oceans are in steady state with respect to Ca. We can then assume that solid CaCO_3 particles will sink to the deep ocean. This provides a sink for inorganic carbon (as CaCO_3) into the deep ocean. How does this compare with the annual production of CO_2 from fossil fuels (5.4×10^{15} g C/yr; the atomic mass of carbon is 12 g/mole.).

b) Now calculate the total net flux of C that is taken up by photosynthesis in the surface ocean. To do this, calculate the net flux of dissolved inorganic carbon (DIC) to the deep ocean (this works as a tracer because organic carbon will be eventually respired to $\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$). Given the result from a), what fraction of particulate carbon is organic?

c) If we assume that the total dissolved carbon in the oceans is at steady state, what must the flux of carbon be to the sediments? Assuming only carbon as CaCO_3 can be deposited, what fraction of CaCO_3 particles, therefore, must accumulate as sediments on the seafloor?

d) Now calculate the C:N:P ratio of the particulate matter sinking to the deep ocean. How does this compare with that found in the Redfield molecule $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$ used to proxy for average biomass?

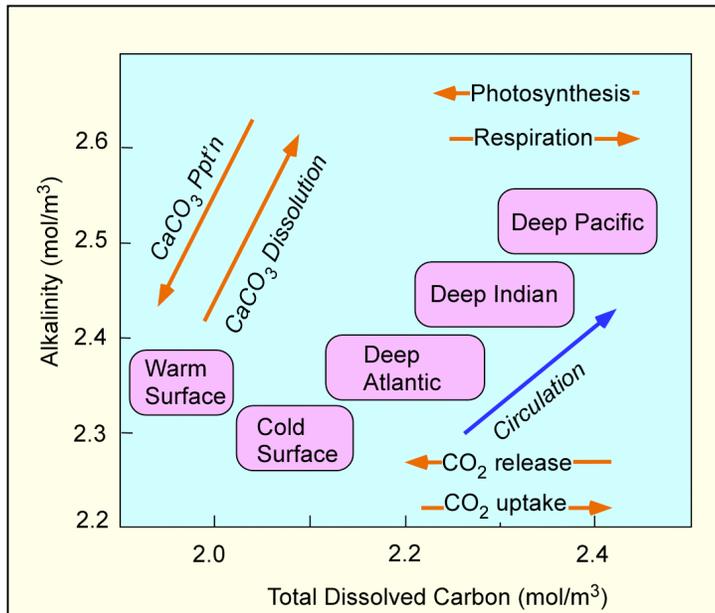
6. The molar volume change ΔV for the dissolution of CaCO_3



is $-37 \text{ cm}^3/\text{mole}$ (recall that $1 \text{ cm}^3/\text{mole} = 0.1 \text{ J/bar}$). Because ΔV is negative, the pressures of the deep ocean will favour dissolution of CaCO_3 so that CaCO_3 sediments may not form. At 1 bar, the pK for the above reaction is 6.37. Prove that

$$pK(P) = pK_{1\text{bar}} + (P - 1)\Delta V / (2.303RT)$$

If the pressure of the deep oceans increases by 1 bar for every 10m of depth calculate the solubility of CaCO_3 with depth in the ocean. Here is a plot of alkalinity vs. total dissolved carbon in the oceans:



Assuming that $[\text{Ca}^{+2}] = 0.01\text{M}$ and that, to a good approximation,

$$[\text{CO}_3^{-2}] = \text{Alkalinity} - (\text{Total dissolved Carbon})$$

Calculate the calcite compensation depth in the different oceans. Some hints: don't confuse kJ with J and assume $T=298\text{K}$.

7. Given the following thermodynamic data:

	ΔG_f
Illite $KAl_2[AlSi_3O_{10}](OH)_2$	-5600.
Kaolinite $Al_2Si_2O_5(OH)_4$	-3799.
H_2O	-237.14
K^+	-292.49
H^+	0.0
H_4SiO_4	-1308.

Work out the equilibrium constant for the hypothetical reverse weathering reaction:



If the pH of seawater is 8.0, what is the concentration of K that would be buffered by the above reaction? The observed concentration of K in seawater is 0.01 mol/kg. (Advanced topic: The activity coefficient for K^+ in 35 ‰ salinity is 0.6. Does this make a significant difference?).

8. As we learned in Lecture 2, some anaerobic bacteria can utilize various electron acceptors (e.g., MnO_2 , $FeOOH$) to oxidize organic matter. Other bacteria can use some inorganic species (e.g., Fe^{+2} , Mn^{+2} , NH_4^+) as a source of electrons. We can assess these processes in a sediment profile using Fick's first and second laws: The general form of Fick's second law (not given in Lecture) is:

$$\left(\frac{\partial C}{\partial t}\right)_z = -\left(\frac{\partial F}{\partial z}\right)_t + R$$

where C is concentration, x is depth, F the flux (moles/cm²-sec) and R is the rate at which the component is produced or consumed by (bio)chemical reactions. The flux has two parts: first, there is the *diffusive flux* which is given by Fick's first law:

$$F_{Diff} = -D\left(\frac{\partial C}{\partial z}\right)_t$$

next is the *advective flux* which results from the burial of sediments. For now, we will neglect the advective flux so that

$$\left(\frac{\partial C}{\partial t}\right)_z = D\left(\frac{\partial^2 C}{\partial z^2}\right) + R$$

If the system were at steady state, then the concentration at any depth is not changing with time so

$$D\left(\frac{\partial^2 C}{\partial z^2}\right) + R = 0$$

On the attached figure, is a typical sediment profile . Based on discussion in problem 2, we find that, if we neglect advection (burial), a chemical species is being produced when

$$\frac{d^2 C}{dz^2} < 0$$

and consumed when

$$\frac{d^2 C}{dz^2} > 0$$

(where z is depth and C is the concentration of the chemical species). An easy way to work this out is to draw a secant line between two points on the profile. It follows that if $d^2C/dz^2 < 0$, then the function is concave upward (falls above the line); if $d^2C/dz^2 > 0$ then the function is concave downward (falls below the line).

Diagram each zone where each chemical species (O_2 , NO_3^- and Mn^{2+}) is being produced or consumed. Describe the biogeochemical processes that are occurring in each zone (e.g., oxidation, nitrification etc.).

Pore Water Concentration

