Lecture 10 – Carbonate chemistry and acid base

(1) Many of the Lakes in New England have become acidified due to industrial emissions.
The pH of one such lake is 5.2. In descending order of concentration (highest to lowest), the inorganic carbon speciation in this lake would be:

a. H_2CO_3, HCO^{3-}, CO_3^{2-}
b. HCO^{3-}, CO_3^{2-}, H_2CO_3
c. CO_3^{2-}, HCO^{3-}, H2CO3
d. HCO_3^-, H_2CO_3, CO_3^{2-}

The ocean pH is regulated by:

(a) the conversion of sulfate to sulfide
(b) the exchange of nitrogen with the atmosphere
(c) the solution and precipitation of silicate minerals in seawater
(d) the carbonate system
(e) non of these

Suppose you bubble a seawater sample with N_2 gas until a white precipitate forms.
Which of the following statements is most likely **true**?

1. Alkalinity is unchanged
2. The precipitate is sodium bicarbonate ($NaHCO_3$)
3. Total CO_2 (ΣCO_2) is unchanged
4. The precipitate is calcium carbonate ($CaCO_3$)
5. pH goes down

As a result of $CaCO_3$ precipitation:

a. Σ_{CO2} goes down $Ca^{2+} + CO_3^{2-} = CaCO_3$
b. pH goes up
c. P_{CO2} goes down
d. Alkalinity stays constant
e. respiration goes up

When (Alk-ΣCO_2) is high

(a) pH is low
(b) pH is high more CO_3^{2-} relative to HCO_3^- $(HCO_3^- + 2CO_3^{2-}) - (HCO_3^- + CO_3^{2-})$
(c) pH is not related to this value
(d) more $CaCO_3$ will dissolve
(e) photosynthesis in low

(2) What is the alkalinity of each of the following solutions?

a) One mole of $MgSO_4$ dissolved in 400 liters of CO_2-free distilled water.
b) One mole of Na_2CO_3 dissolved in 1000 liters of CO_2-free distilled water.
c) One mole of KCl dissolved in 5000 liters of CO_2-free distilled water.
d) One mole of NaCl and 2 moles of $Ca(HCO_3)_2$ in 1000 liters of CO_2-free distilled water.
e) Average deep ocean water, where $[CO_3^{2-}] = 90$ µM, $[HCO_3^-] = 2350$ µM, $H_2CO_3 + CO_2 = 45$ µM. You may calculate the carbonate alkalinity and neglect other species.

a) and c) ALK = 0; no change in carbonate bicarbonate or borate
b) There is one mol of CO_3^{2-} in 1000 L, which is 2 equivalents in 1000 liters or 2 meq/l
d) 2x2 = 4 equivalents HCO_3^- in 1000 liters = 4 meq/l
e) Alkalinity = $HCO_3^- + 2CO_3^{2-} + OH^- - H^+$
We can usually approximate alkalinity by neglecting OH^- and H^+ since they are relatively small, and almost equal to each other in seawater. So 2350 + 2 x 90 = 2440 meq/l
Note that CO_2 and H_2CO_3 do not affect alkalinity and never will.

(3) The deep water of the Black Sea does not get replenished very often thus dissolved oxygen is absent and hydrogen sulfide is very high.

a. What is the sulfide (S^{2-}) concentration in the deep water of the Black Sea. Use the graphical or algebraic approach (your choice).

Total sulfide (ST) equals 400µM; pH is 7.7
There are two apparent acidity constants for H_2S in seawater:
$K_1' = 10^{-7}$ and $K_2' = 10^{-14}$

The equations to consider:
$H_2S = H^+ + HS^-$ $K_1' = 10^{-7}$ $K_1 = [H^+][HS^-] / [H_2S]$ $[HS^-] = K_1 [H_2S]/a_{H+}$
$HS^- = H^+ + S^{2-}$ $K_2' = 10^{-14}$ $K_2 = [H^+][S^{2-}] / [HS^-]$ $[S^-] = K_2 [HS^-]/a_{H+}$
Total S = $H_2S + HS^- + S^{2-} = 400 \times 10^{-6}$ M $= 10^{-3.39}$

For this we need to first calculate the S^{2-} concentration at these conditions
$S_T = [S^{2-}] \{a_{H+}^2/K_1K_2 + a_{H+}/K_2 + 1\}$
$[S^{2-}] = S_T / \{a_{H+}^2/K_1K_2 + a_{H+}/K_2 + 1\} = 1.67 \times 10^{-10}$

b. Is iron sulfide (FeS) supersaturated?
Remember that the solubility reaction is:
$FeS = Fe^{2+} + S^{2-}$
The apparent solubility constant in seawater is: $K'sp = 10^{-19}$
The concentration of Fe^{2+} is 200 nM

$200 \times 10^{-9} \times 1.67 \times 10^{-10} = 3.34 \times 10^{-17} > 10^{-19}$ so the water is supersaturated with respect to FeS

(4) I made a 1liter solution with 1 mole $NaHCO_3$ and 0.5 moles Na_2CO_3.

(a) What is the alkalinity of this solution?
(b) If no CO_2 escaped what is the DIC?
(c) What are the two major carbonate species in solution?

(a) Alk = $[HCO_3^-] + 2[CO_3^{2-}]$ 1 mole HCO_3^{-3} and ½ mole CO_3^{2-} so it is 1 + 2 x ½ = 2 equivalents
(b) C_T = DIC = $[HCO_3^-] + [CO3^{2-}]$ = 1 + 0.5 = 1.5 moles/liter
(c) $[HCO_3^-]$ and $[CO_3^{2-}]$

(5) The Alk of a sample of surface water is 2.35 meq/l and its ΣCO_2 is 2.15 mmol/l. The Alk of a sample from 4 km depth at the same location are 2.45meq/l and the ΣCO_2 is 2.40 mmol/l. What are the pH and $[CO_3^{2-}]$ for each sample? What is the saturation index for these samples with respect to calcite? Ksp =4.5 x 10^{-7}, (Ca) = 1.03 x 10^{-2} M

Alk = $[HCO_3^-] + 2[CO_3^{2-}]$; DIC = $[HCO_3^-] + [CO_3^{2-}]$;
$[HCO_3^-]$ = 2[DIC] - Alk $[CO_3^{2-}]$ = Alk-DIC
$[HCO_3^-] = [H^+] + [CO_3^{2-}]$ $K_2 = 10^{-9}$ $K_2 = [H^+] \times [CO_3^{2-}] / [HCO_3^-]$ $H^+ = K_2 [HCO_3^-]/[CO_3^{2-}]$

So: For surface water: $[CO_3^{2-}]$ = 200 μM; $[HCO_3^-]$ = 1.95 mM; and pH = 8.0
For deep water: $[CO_3^{2-}]$ = 50 μM; $[HCO_3^-]$ = 2.35 mM; and pH = 7.3

$(Ca^{2+})(CO_3^{2-})$ = surface: $1.03 \times 10^{-2} \times 200 \times 10^{-6} = 2.06 \times 10^{-6} > 4.5 \times 10^{-7}$ super saturated
$(Ca^{2+})(CO_3^{2-})$ = deep: $1.03 \times 10^{-2} \times 50 \times 10^{-6} = 5.15 \times 10^{-7} > 4.5 \times 10^{-7}$ super saturated but not by much

(6) The popular press and a few scientists claim that the health of coral reefs is crucial to humanity because reef $CaCO_3$ represents a sink for anthropogenic CO_2.

a. Explain the qualitative effect of $CaCO_3$ formation in reefs (skeletogenesis) on alkalinity and ΣCO_2
$Ca^{2+} + CO_3^{2-} == CaCO_3$ $Ca^{2+} + 2HCO_3^- == CaCO_3 + CO_2 + H_2O$
$CaCO_3$ ppt. Alk goes down, DIC goes down, Alk change = 2xDIC change;
But the on a short term this could actually be a source of atmospheric CO_2 since HCO_3^- is used and not atmospheric CO_2!!
b. The expression for P_{CO2} in terms of alkalinity and ΣCO_2 is: $P_{CO2} = \frac{(2\Sigma CO_2 - Alk)^2}{K'(Alk - \Sigma CO_2)}$
Use this expression to support or refute this idea (e.g. that reefs are a sink for CO_2)
You may find it useful to plug demonstration numbers into this equation for comparison purposes. A typical surface value for ΣCO_2 is 2.0 mM and for Alk is 2.2 meq/l. What value of P_{CO2} is this water in equilibrium with and how would it change if about 0.1mM of ΣCO_2 was removed to form reef material. K' = 4.5 x 10^4 mmol l^{-1} atm^{-1}.
Using the above equation and keeping in mind that 0.1 mM change in DIC will correspond to 0.2 meq/l change in Alk. You will find that 0.1 mM reduction in DIC thus 0.2 meq/l reduction on Alk will result in higher P_{CO2} thus this does not support the reef as a sink for CO_2 (on short time scales).

(7) A sample of seawater has a carbonate alkalinity of 2400 μeq/l and TCO_2 = 2325μmol/l.

For this water the $[CO_3^-]$ = 75μM and $[HCO_3^{2-}]$ = 2250 μM

Calculate the new carbonate alkalinity, TCO_2, $[HCO_3^-]$ and $[CO_3^=]$ if the following occur:

a) 10 mg of foraminiferal shells are dissolved in 1 liter of the sample. ($CaCO_3$ molecular weight is 100 g/mole.

If 10 mg of $CaCO_3$ is dissolved 0.1mM or100 μmol $CO3^{2-}$ is added;
So the new Alkalinity would be 2400 + 100x2 = 2600
The new $CO3^{2-}$ would be 75 + 100 = 175 μM
The new $[HCO_3^-]$ would be Alk – $2[CO_3^{2-}]$ thus 2250
New T_{CO2} will be 2325 + 100 =2425 μmol/l

b) 10 μmol of POM is completely respired in 1 liter of the seawater. You can use the simplifying assumption that one mole of dissolved carbon dioxide will react with one mole of carbonate ion to produce 2 moles of bicarbonate.

e.g. $CO_2 + CO_3^= + H_2O$ <---> $2HCO_3^-$

Respiration of 10 μM of POM would release 10μmol CO_2 produced thus adding 10μmoles to the T_{CO2}. There is no charge change so no change in alkalinity.
T_{CO2} = 2325 + 10 = 2335
As can be seen from the above equation each mole of CO_2 produced will consume a mole of CO_3^{2-} so 75-10 = 65μM
HCO_3^- on the other hand will increase be 2 moles for every mole of CO_2 produced thus 2250 + 20 = 2270 μM

(8) How will fossil fuel CO_2 change the pH of the ocean? Write the equations

Scientists project that P_{CO2} will eventually double from its pre-industrial value of 280ppm to at least 600ppm it is now 370ppm.
Assume alkalinity stays constant at 2.300 x 10^{-3} eq l^{-1}. DIC is now 1.95(mmol/kg)
Assume $K_H = 10^{-1.53}$ $K_1' = 10^{-6.0}$ and $K_2' = 10^{-9.1}$

a. What will be the final pH for this model
b. How valid is the assumption about const Alk?
c. After 1000 years when the water mixed down deep how will this change CCD lysocline?

$CO_2 + H_2O = HCO_3^- + H^+$ nothing else happening pH will decrease.

Using 370ppm today the P_{CO2} = 10.91μM. We can calculate from K_H and 600ppm that the P_{CO2} will be 17.7μM and the change in T_{CO2} (1950 + 6.79 =1956.8); from that get HCO_3^- (1613.6) and CO_3^{2-} (343.2); pH = 8.327 so it is lower by 0.012 pH units

The assumption is valid if no dissolution of $CaCO_3$ occurs

pH is a little lower and CO_3^{2-} is lower so there will be more dissolution and the CCD will become shallower.

(9) Going from the deep North Atlantic to the deep North Pacific, alkalinity increases in seawater from 2350 to 2475 μEq kg^{-1} while total CO_2 increases from 2200 to 2375 μM kg^{-1}. On average what is the relative contributions of $CaCO_3$ dissolution and organic matter respiration for producing these changes.

Δ alk = 125, this is only due to $CaCO_3$ dissolution so 125/2 = 62.5μM $CaCO_3$ dissolved;
ΔDIC = 175, this is a combination of $CaCO_3$ dissolution and OrgC oxidation.
We can subtract the dissolution to evaluate the respiration: 175-62.5 = 112.5μM C form respiration; This gives a ratio of 1.8 orgC oxidized for 1 $CaCO_3$ dissolved.

(10) Using the elemental composition of marine particulate material as collected in sediment traps listed below (Broecker and Peng, 1982) (Relative to P = 1 mole) what changes in deep-ocean DIC and Alk do we predict if typical sediment trap particles respire and dissolve.

	P	N	C	Ca	Si
Soft Parts	1	15	105	0	0
Hard Parts	0	0	26	26	50
Composite	1	15	131	26	50

The Org.C : $CaCO_3$ in particulate matter is 105 : 26 (4 : 1)
$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$ or $CO_2 + H_2O + CaCO_3 = Ca^{2+} + 2HCO_3^-$
$O_2 + CH_2O = CO_2 + H_2O = H^+ + HCO_3^-$

	1 mol $CaCO_3$	4 mol Org. C.	Composite
ΔDIC	1	4	5
ΔCa	1	0	1
ΔAlk	2	0	2

DIC of the composite matter changes by 5 while Alk changes only be 2
so ΔDIC =2/5 ΔAlk, more change in DIC.
$Alk_C - DIC = ([HCO_3^-] + 2[CO_3^{2-}]) - ([HCO_3^-] + [CO_3^{2-}] + [CO_2]) = [CO_3^{2-}] - [CO_2] \cong [CO_3^{2-}]$
Degradation of Org.C. and dissolution of $CaCO_3$ in the ratios in particulate matter cause a decrease in the carbonate ion concentration because $\Delta Alk - \Delta DIC = \Delta[CO_3^{2-}]$ and alkalinity changes less than DIC.
$a_{H+} = \{ [HCO_3^-] / [CO_3^{2-}] \} K_2'$ $pH = -\log a_{H+}$ $[CO_3^{2-}]$ down => a_{H+} up => pH down