Lecture 11 Diagenesis, Redox Chemistry Organic C Preservation

(1) Is seawater normally an oxidizing or reducing medium? Oxidizing

Write the oxidation numbers for all of the atoms in the following compounds:
N_2; NO_2^-; NO_3^-; Fe_2O_3; $FeOOH$; MnO; MnO_2; $S_2O_3^{2-}$

0;   3+, 2-;   5+, 2-;   3+, 2-;   3+, 2-, 1+;   2+, 2-;   4+, 2-;   2+, 2-;

Answer the following questions for: $2Mn^{2+} + O_2 + 2H_2O == 2MnO_2 + 4H^+$
The oxidation # of Mn changes from 2+ to 4+.   The oxidation # for O changes from 0 to 2-. The oxidizing agent is Mn and the element that gets reduced is O. The half-cell oxidation reaction is $Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e$ and the half-cell reduction reaction is $1/4 O_2 + H^+ + e = ½ H_2O$.
If equilibrium is achieved in seawater (pH 8) the E^0_{cell} for this reaction would be +0.81 V.
Compute the equilibrium constant for the reaction.

$E^0_{cell} = 0.0592/n \, logK_{cell}$ $logK = n/0.0592 \times 0.81 = 27.36; K = 2.3 \times 10^{27}$

(2) What controls organic C content in sediments?

o   overlying productivity
o   mineral surface area
o   water depth
o   season
o   sedimentation rate

What does not support the theory that mineral surfaces control on organic matter
        preservation:
   1. Correlation between clay content in the sediment and % organic matter
   2. The empirical relation between the organic matter content and the "one molecule
      deep full coverage on the surface area".
   3. the observation that when this organic matter is released from minerals it is
      utilized by organisms
   4. the difficulty to mechanically separate the organic matter from the associated
      sediments.
   5. The correlation between bottom water oxygen content and organic matter
      preservation in sediments

Why do the deep waters of Saanich Inlet become anoxic?
   1. because O_2 released by photosynthesis in surface waters escapes to the atmosphere
   2. because nitrate is utilized as an electron acceptor
   3. because reducing power is introduced by sinking organic particles
   4. because the increased acidity of the deep waters causes a marked decrease in Eh
   5. none of these
   6. due to seasonal stratification

The Oxygen Exposure time depends on:
1. distance form shore
2. sedimentation rate
3. bottom water oxygen content
4. bioturbation of the sediment
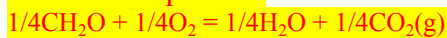5. type of organic matter in the sediment

(3) Uranium is more soluble in its oxidized U^{+6} form than in its reduced U^{+4} form. Is the concentration of dissolved U likely to be greater or less in the black sea relative to seawater?

Lower as the water in the black sea is reducing thus U^{+4} will be the abundant phase and it is less soluble.

(4) When diagenesis proceeds in marine sediments, there is a natural sequence of compounds used to oxidize organic matter. Describe the sequence of redox pairs and draw a hypothetical vertical profile of sediment column with the appropriate species found in pore waters. In what major way would you expect this sequence to change in fresh water sediments compared to marine sediments? How would you expect the particulate Mn and Fe profiles in this sediment to be?

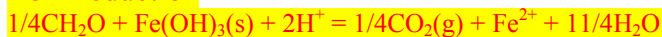The sequence of redox pairs is:

Aerobic Respiration
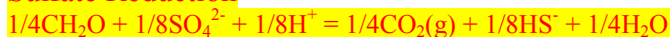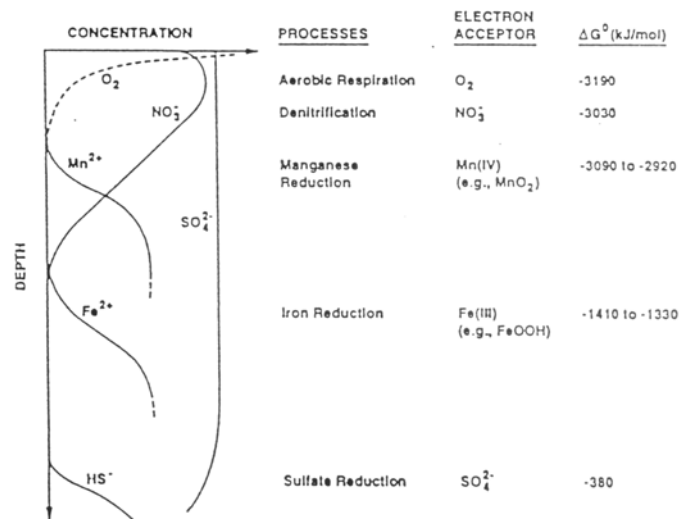$1/4CH_2O + 1/4O_2 = 1/4H_2O + 1/4CO_2(g)$

Denitrification
$1/4CH_2O + 1/5NO_3^- + 1/5H^+ = 1/4CO_2(g) + 1/10N_2(g) + 7/20H_2O$

Manganese Reduction
$1/4CH_2O + 1/2MnO_2(s) + H^+ = 1/4CO_2(g) + 1/2Mn^{2+} + 3/4H2O$
Iron Reduction
$1/4CH_2O + Fe(OH)_3(s) + 2H^+ = 1/4CO_2(g) + Fe^{2+} + 11/4H_2O$

Sulfate Reduction
$1/4CH_2O + 1/8SO_4^{2-} + 1/8H^+ = 1/4CO_2(g) + 1/8HS^- + 1/4H_2O$

Methane Fermentation
$1/4CH_2O = 1/8CO_2(g) + 1/8CH_4$

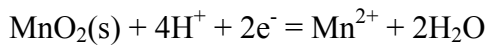| CONCENTRATION	PROCESSES	ELECTRON ACCEPTOR	ΔG^0 (kJ/mol)
O_2	Aerobic Respiration	O_2	-3190
NO_3^-	Denitrification	NO_3^-	-3030
Mn^{2+}	Manganese Reduction	Mn(IV) (e.g., MnO_2)	-3090 to -2920
SO_4^{2-}			
Fe^{2+}	Iron Reduction	Fe(III) (e.g., FeOOH)	-1410 to -1330
HS^-	Sulfate Reduction	SO_4^{2-}	-380

In fresh water sediments sulfate reduction might not be prominent as these waters are low in sulfate. Particulate Fe and Mn will precipitate at the oxic anoxic boundary where Mn and Fe diffusing up "see" oxygen.

(5) What would be the Mn^{2+} in equilibrium with MnO_2 in natural seawater at pH=8 in equilibrium with P_{O2} = 0.20 thus, pE = 12.58. How would you answer change for the Black Sea with pH= 8 and pE = -4? So under anoxic conditions would you expect manganese to be in the form of Mn^{2+} or MnO_2?

Assume:
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$ logK = 2pE°= 41.6

$K = [Mn^{2+}]/ (H^+)^4 (e)^2$
log K = log $[Mn^{2+}]$ – 4log (H^+) – 2log (e)
log (Mn^{2+}) = log K - 4pH - 2pE
for seawater log (Mn^{2+}) = -15.56 or (Mn^{2+}) = $10^{-15.56}$ or 2.7 x 10^{-16} not abundant
for the black sea (Mn^{2+}) = 3.98 x 10^{17} so Mn^{2+} is a lot more abundant in anoxic conditions

b) In oxygenated surface seawater dissolved Mn^{2+} = 10^{-9}. This thermodynamic calculation does not appear to correctly describe the distribution of Mn species in seawater since the concentration of dissolved Mn ranges from 0.1 - 10 nM in seawater. Why not?

(a) Equilibrium does not exist in this case. (b) Ligands and complexation of Mn^{2+} in solution increases it total concentration over that expected from equilibrium considerations in ideal solutions.
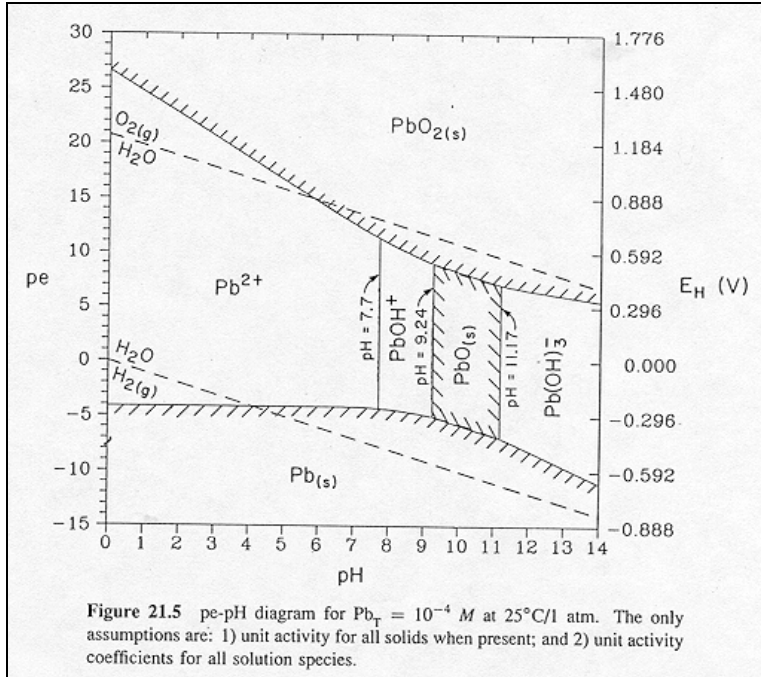
(6) In anoxic basins dominated by sulfate reduction what will the dominant Iodine species be? $IO_3^- +6H^+ + 6e- == I^- + 3H_2O$ logK = 110.1;   pE = -4.5 ?
Compare this with oxygenated seawater (pE =13), assume pH is 8 at both cases

logK = log $\{[I^-]/[IO_3^-]\}$ + 6pH +6pE = 110.1
log $\{[I^-]/[IO_3^-]\}$ = 89.1 for anoxic and –15.9 for seawater;   so $[I^-]/[IO_3^-]$ = 1.26 x 10^{89}
e.g. I^- dominant in anoxic conditions and 1.26 x 10^{-16} thus the dominant form will be iodate IO_3^- in seawater

(7) Please answer the following questions with the use of the pE/pH plot below for various species of lead. In this figure, solid phases are indicated by dashes entending along phase boundaries toward the center of the stability field. As with all such stability field applications, assume that the system is at equilibrium:

(a) What is the expected major species of lead under surface seawater conditions? $PbOH^+$, $PbO_2(s)$
(b) Under what pH range is $PbO_2(s)$ stable under oxic conditions? From pH 7-14
(c) Over what pE range can two soluble lead species coexist? –6 to 12
(d) What chemical product may form if you drop metalic lead, $Pb_{(s)}$, into acidic (pH = 2) water? Pb^{2+}
(e) What two chemical species can PbO(s) directly convert to without any net transfer of electrons? $Pb(OH)_3^-$, $PbOH^+$

Figure 21.5 pe-pH diagram for $Pb_T = 10^{-4}$ M at 25°C/1 atm. The only assumptions are: 1) unit activity for all solids when present; and 2) unit activity coefficients for all solution species.
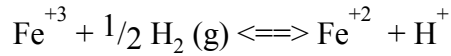
(8) Has the sediment composition in the profiles presented here changes much with depth? Explain. Where is the oxic anoxic boundary in these profiles? Why do both dissolved Fe and Mn increase downward from the transition? How would you expect the dissolved U in this profile to behave? What will the sulfate pore water profile look like?
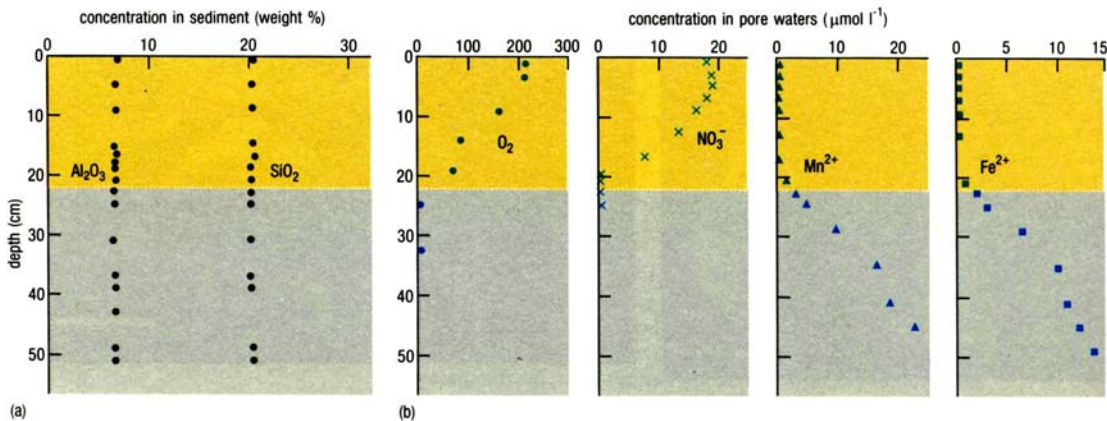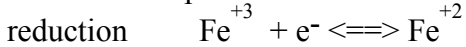

In the upper 20 centimeters the major change in composition would be organic matter oxidation as indicated by the loss of oxygen and nitrate. Below that oxides in the sediment are also lost releasing Mn^{2+} and Fe^{2+} into solution. The major aluminum-silicates have not changed.
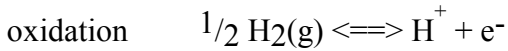
(9) OXIDATION - REDUCTION OF IRON "RUST"

Which oxidation state of Fe (+2 or +3) is expected to be more abundant in seawater (pE = 13.75 and which in the deep waters of the black sea (pE = -3.5)? Consider this reaction:

$$Fe^{+3} + 1/2\ H_2\ (g) \Longleftrightarrow Fe^{+2} + H^+$$

Which is composed of two half reactions:

reduction	$Fe^{+3} + e^- \Longleftrightarrow Fe^{+2}$	$\log K_2 = 13.0$
oxidation	$1/2\ H_2(g) \Longleftrightarrow H^+ + e^-$	$\log K_3 = 10$

By convention, $K_3 = 1$ ($\Delta G° = 0$)

$$K_1 = K_2\ x\ K_3 \Longrightarrow K_1 = K_2 = \frac{(Fe^{+2})}{(Fe^{+3})(e^-)}$$

$$\log K_1 = -\log(e^-) + \log\frac{(Fe^{+2})}{(Fe^{+3})}$$

For seawater: log (Fe^{2+}/Fe^{3+}) = 13 - 13.75= -0.75; (Fe^{2+}/Fe^{3+}) =0.177 Fe^{3+} abundant
For the black sea: log (Fe^{2+}/Fe^{3+}) = 13 - -3.5 = 16.5; (Fe^{2+}/Fe^{3+}) =3.16 X10^{16} Fe^{2+} abundant

Note analogy to pH, and acid-base reactions.   Recall that pH= pK + log $(A^-)/(HA)$
By convention, the reduced species is in the numerator, oxidized in the denominator.

(10) In ocean waters with very low oxygen concentrations such as the oxygen minimum zone off Peru ($O_2 < 5$ µmol/l), denitrification reactions are of importance:

$$NO_3^- + orgC == CO_2 + \tfrac{1}{2}N_2$$
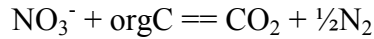
(a) If both NO_3^- and N_2 are present what would you expect the pE to be if this redox couple NO_3^- / N_2) would buffer the pE level?

(b) What will the partial pressure of oxygen be at this pE?

(c) What Iodine species would be dominant in these conditions (IO_3^-, I^- or I_2).

The following information might be useful: (assume 25ºC, pH 8, 1atm, $pN_2 = 0.8$ atm, $NO_3^- = 40$µM)

$NO_3^- + 6H^+ + 5e = \tfrac{1}{2} N_2 + 3H_2O$	log K = 105.3
$O_2 + 4H^+ + 4e = 2 H_2O$	log K = 83.1
$IO_3^- + 6H^+ + 5e = I^- + 3H_2O$	log K = 110.1
$\tfrac{1}{2}I_2 + e = I^-$	log K = 10.5

(a) $K = \dfrac{[pN_2]^{\frac{1}{2}}}{[NO_3^-] [H^+]^6 (e)^5}$;

log K = ½ log [N_2] – log [NO_3^-] – 6 log [H^+] – 5 log (e)
105.3 = ½ log [0.8] – log [40 x 10^{-6}] + 6 pH + 5 pE
5 pE = 105.3 - ½ log [0.8] + log [40 x 10^{-6}] - 6 pH
5 pE = 105.3 – (-0.0484) + (-4.398) – 48 =52.95
pE = 10.59

(b) $K = \dfrac{[H_2O]^2}{[pO_2] [H^+]^4 (e)^4}$;

log K = -log [pO_2] – 4 log [H+] – 4 log (e)
log [pO_2] = - log K + 4pH + 4pE
log [pO_2] = -83.1 + 32 + 42.36 = -8.74
pO_2 =1.8 x 10^{-9} Very little oxygen !!!

(c) $IO_3^- + 6H^+ + 5e = I^- + 3H_2O$ solve this for pH = 8 and pE = 10.59

log K = log {[I^-]/[IO_3^-]} + 6pH + 6pE = 110.1
log {[I^-]/[IO_3^-]} = -1.44   So: [I^-]/[IO_3^-] = 0.036
The dominant form will be IO_3^- (Iodate) but both are present and if the pE was 10 I^- would have been dominant.

Similarly solve for $\tfrac{1}{2}I_2 + e = I^-$ you would find that [I^-]/[I_2]$^{\frac{1}{2}}$ = 0.8 e.g I_2 more abundant.

(11) The Black Sea is the world's largest permanently anoxic water body. It is a semi-enclosed marginal sea with a physical and chemical structure that is determined by its hydrological balance. Seawater flows in through the Bosporus to the deep layer of the basin. Freshwater inflow from European rivers keeps the salinity low in the surface layer. As a result the water column is strongly stratified with respect to density. A consequence is that the surface layer (about 0 to 50m) is well oxygenated while the deep layer (100m to 2000m) has no oxygen and high sulfide concentration. At the boundary between the oxic surface and anoxic deep layers there is a suboxic zone (from approximately 50m to 100m depth) where O_2 and HS^- are essentially both absent. The distributions of nutrients (e.g. NO_3^-, $NH4^+$, PO_4) and metals (e.g. Mn, Fe) and the absence of O_2 and HS^- suggest the occurrence of unique or unusual metabolic processes within the suboxic zone (e.g., anaerobic Mn(II), Fe(II), NH_4^+, HS^-, and S(0) oxidation and the possibility for unusual photosynthetic reactions).

Amy C. has proposed that nitrate reacts with ammonia to produce N_2 (g).
Using the half-reactions in Table 7.3 of the lecture notes do the following:

a) Write a balanced reaction for $NO_3 + NH_4^+$ to produce N_2 (g)

0.8 NH_4^+ + 0.075 NO_3^- == 0.05 H^+ + 0.1 N_2 + 0.225 H_2O

b) The equilibrium constant for this reaction?

E^0 = 0.75-0.36 = 0.39
E^0 = 0.0592/n logK   logK = (n/0.0592) x E^0 = 6.58;   K =3.8 x 10^6