10 Evolution of the Oceans

I. Chemical evolution of the oceans
   A. concerned with where water and salts come from

II. Origin of water in the oceans **show timeline**
   A. original source of this water and other gasses (CO_2 etc.) may not have been the material that formed the original Earth
   B. recent work suggests that volatile-rich comets from the outer (colder) parts of the solar system may have provided these materials early in the Earth's history
      1. process known as impact degassing
      2. shock-induced degassing of volatiles from these comets
      3. occurred during the period of heavy bombardment
   C. early volcanic activity also likely played a small role in contributing these volatiles
      1. similar processes still occur today - hot springs, hydrothermal vents
   D. in addition to water this degassing also added other volatiles elements to the early earth's surface (atmosphere)
      1. Cl (as HCl), N (as N_2), S (as H_2S), and CO_2
         a. "excess volatiles" - Rubey (1940's)
      2. their abundance on the earth's surface was greater than that which could be accounted for by weathering of igneous rocks.
      3. most were initially found as gasses although most now reside in crust or oceans
         a. only N is still predominantly found in the atmosphere

III. Initial history of the ocean (Hadean – 4.6 to 3.8 bybp)
   A. after period of heavy bombarment the Earth's surface became more quiescent
      1. condensation of water vapor from atm leads to the formation of the oceans
   B. Hadean thought to end as moderate conditions began to occur on the Earth's sfc.
      1. 3.8 by boundary based on Isua metasediments
      2. generally taken to be evidence for water-laid sediments and early continental land masses
   C. zircon results suggests this may have occurred earlier **zircon data**
      1. liquid water may have existed much earlier
      2. trace elements in these zircons also provides early evidence for the formation of cont. crust **color timeline**
      3. early Earth may have become quiescent earlier than once thought

IV. Early oceans (regardless of time of formation)
   A. oceans are initially fairly acidic as acidic excess volatiles in the atm. began to dissolve in the oceans
   B. these began to react with basic igneous rocks
   C. cause a pH rise as a result of these weathering rxns.
      1. titrate the acids in the excess volatiles
   D. rxn of interest:
      1. cation-rich Al-silicates + H^+ $\rightarrow$ cation poor-clays + SiO_2 + diss. cations
   E. protons came from these acidic excess volatiles

1. left behind the anions (Cl^-, S^{-2} and HCO_3^-)

F. these anions and the cations weathered from rocks led to an increase in the salt content of the early oceans.
   1. assuming present-day weathering rates this could have occurred fairly rapidly
      a. 100's of millions of years

G. as the pH rose above approx. 7.5, carbonate minerals ($CaCO_3$) began to ppt.
   1. began to buffer the pH of the oceans
      a. biol. or chem ppt.?
      b. Stromatolites **strom. picture**
   2. regardless of mechanism this led to a large drop in atmos. CO_2
   3. initial atmosphere likely had a much higher total pressure and partial pressure of CO_2
   4. most of this CO_2 now sequestered in carbonate rocks.

V. With the onset of these reactions (weathering, carbonate buffering) it appears that the cation concentration of the oceans reached a "steady state"

A. "steady-state" - not a chemical equilibrium
   1. inputs equal outputs
   2. concentrations remains constant

B. over the last 700 my the concentrations of the major ions in seawater have probably not changed by more than a factor of 2 (2x or 0.5x their present amounts).
   1. seawater composition constrained by the distribution of evaporite minerals in the geologic record.
   2. major changes in seawater composition would lead to a different evaporite mineral sequence

VI. Major differences between ancient ocean and present ocean

A. surface waters were much warmer - ~50˚C

B. ancient ocean had no dissolved oxygen (no free O_2 in the atm.)

C. sulfate content much lower
   1. sulfur occurred primarily as H_2S (ancient) rather than as SO_4 (as it does today)

D. CO_2 much higher than it is today - as a result pH was lower

E. Fe existed as dissolved Fe(II)
   1. once oxygen concentrations began to rise on the Earth occurred the iron was oxidized to Fe(III) which forms an extremely insoluble oxide.

VII. Controls on chemical composition of seawater

A. assume that rivers are the predominant source of materials to the oceans
   1. can we use river data to estimate fluxes of major ions to oceans

B. what controls the chemistry of the oceans ?
   1. early models of the ocean formation assumed that the oceans formed by one way rxns.
      a. igneous rock + "excess" volatiles → seawater + sediments + air
   2. get good agreement (with regard to concentrations of non-volatiles)
      a. however the process occurs much too rapidly given the age of the ocean
      b. see the calculation on p. 92 of text

c. calculation actually gets you the average residence time of salt in the oceans (~100 my)

3. implies that crustal materials are being recycled
   a. tectonic/rock cycle
   b. materials are being brought to the ocean primarily by weathering reactions
   c. eventually removed and recycled back into the crust
   d. consistent with what we talked about earlier regarding an early period of unidirectional change on the Earth and a later period where recycling processes were more important.

C. further evidence for this type of recycling comes from comparing the composition of river water and seawater.
   1. comparison indicates that seawater is not simply concentrated river water
      a. look at rel. proportions of major ions in **Table**
   2. such a process would lead to the formation of a highly alkaline (pH 10) soda lake similar to the Dead Sea or the Great Salt Lake.

D. in addition to the differences in pH the proportion of cations in such a body would be vastly different than that which is observed in the oceans.

E. these recycling processes also affect different elements differently
   1. lead to different relative concentrations of river water vs. seawater
   2. also lead to different residence times for the major ions in seawater

VIII. Source of major ions to seawater

A. the major source of most cations and anions to the oceans is rivers.
   1. the source of these ions are weathering reactions which occur on continents.
   2. similar to the original processes that initially led to an increase in the salinity of the oceans

B. mechanical and chemical weathering
   1. mechanical weathering breaks materials into smaller pieces.
      a. some gets transported to oceans as part. material
   2. chemical weathering
      a. weathering of ionic materials (dissolution)- calcite, halite, etc.
      b. weathering of rocks
         (i) a type of acid-base titration
         (ii) carbonic acid (from the atmosphere) plus basic igneous rocks
            - re-write weathering equation
   3. end-products are cations, diss. silica, and clays, bicarbonate
   4. look at avg. comp. of river water- bicarbonate is a major anion

C. products of weathering are clay minerals
   1. disordered Al-silicates
   2. these are carried to the oceans
      a. detrital material or "red clays"
      b. simply pass through the system from continents to marine sediments

D. a variety of processes are responsible for the removal of these elements from the oceans to maintain steady state conditions

IX. Why are river water and seawater so different ? **Table**

A. different both in absolute as well as relative concentrations
   1. rw is dominated by Ca^{2+} and bicarbonate
   2. sw dominated by Na^{+} and $Cl^{-\backslash}$

B. also has been observed that the major ion composition of seawater has remained fairly constant over long periods.

C. we therefore assume that the ocean is in steady-state with respect to these major ions.
   1. $\sum$ inputs = $\sum$ outputs
      a. concentration doesn't change with time (dC/dt = 0).
      b. not quite the same as thermodynamic equilibrium.
   2. using a one box model can define residence time (τ)
      a. $\tau = A_T/(dA/dt)$
      b. total amount in the ocean divided by either the total input or ouput rate
         (i) if more than one input/removal term you need to sum all inputs/removals
         (ii) τ is the average time an element spends in the ocean before it is removed.
      c. τ is also a measure of the reactivity of an element
         (i) short τ = reactive; long τ = less reactive

D. Different elements in seawater have different residence times **show first Table**
   1. examples: $\tau(Na^{+}) = 5.5 \times 10^{7}$ yr, $\tau(Ca^{2+}) = 8.3 \times 10^{5}$ yr, $\tau(Si) = 1.8 \times 10^{4}$ yr
      a. need to know
         (i) vol. of ocean - 1.4×10^{21} liter
         (ii) annual river flow - 4.6×10^{16} l/yr
         (iii) average rw and sw calculations

$$\tau_{Na} = \frac{(468)(1.4x10^{21})}{(0.26)(4.6x10^{16})} = 5.5x10^{7}\,yr$$

$$\tau_{Ca} = \frac{(10.3)(1.4x10^{21})}{(0.38)(4.6x10^{16})} = 8.3x10^{5}\,yr$$

      b. order of reactivity is Si > Ca > Na
      c. consistent with what we know about the oceans
      d. Si and Ca used by organisms to make shells while Na is unreactive
      e. τ (Ca) > τ (Si) because of differences in their input and reactivity in the ocean
      f. compare with original calculation of the age of the oceans
   2. because most of the major ions in seawater are relatively unreactive they have long residence time.
      a. this allows them to "accumulate" in the ocean
         (i) large A_T in spite of small input (i.e. conc. in river water)
      b. also helps explain constancy of composition of seawater
         (i) Marcet's principle
         (ii) [Ion]/Sal or [Ion]/[Cl] is a constant in the oceans
      c. τ of most major elements is substantially larger than avg. mixing time of the ocean (500-1000 yr)
      d. all inputs are well mixed
      e. don't see significant vertical or horizontal variation of most major ions
   3. salinity variations controlled largely by evaporation or precipitation **salinity map**