EPSS C113/213 Biological and Environmental Chemistry

The Oceans.
Reading: Chapter 9-10 of Schlesinger

Ch. 9: The oceans.

Lecture 14:

1. Circulation
    a. Unlike troposphere, ocean strongly stratified, limited vertical mixing.
        i. Heating primarily from above (absorption of sunlight).
        ii. 95% of ocean water dark, last at surface near poles (cold → dense). (Fig. 9.2)
        iii. Mixing time ~1000 years.
        iv. Differences with ancient oceans?
    b. Surface circulation driven primarily by wind stress, rapid overturning/mixing of top ~100m.
        i. Coriolis, creation of gyres/boundary currents.
        ii. Fast equilibration with atmosphere (CO_2, O_2)
2. Stratification of NPP, nutrients
    a. CO_2, sunlight available only at surface (consumed)
    b. phosphate, nitrogen, iron consumed to support photosynthesis
    c. some productivity "falls" out of surface mixed layer – carbon and nutrients are decomposed, trapped in deep waters.
    d. Surface waters become O-rich, N, P, Fe-poor; deep waters N, P, CO_2-rich
    e. Productivity maximized in areas where N, P, Fe supplied to surface
        i. Upwelling deep water
        ii. Coastal runoff/dust
        iii. California!!
3. Oceanic sources/sinks of carbon
    a. CO_2 more soluble in cold water, consumed by photosynthesis, created by respiration. Most dissolved CO_2 in form of HCO_3^-
        i. CO_2 exsolves when deep, cold water with respired CO_2 exposed and warming at surface (at low latitudes)
        ii. CO_2 dissolved when water cools at surface.
        iii. CO_2 dissolution also driven by photosynthesis
        iv. How to detect dissolution/exsolution of CO_2?
4. Other dissolved species
    a. Dominated by easily-leached (basic) cations (Na^+, Mg^{2+}, Ca^{2+}, K^+).
    b. Major anions related to dissociated/neutralized natural acids (SO_4^{2-}, HCO_3^-). Cl^- most abundant ion, dominated by oceanic reservoir (very long mean residence time).
        i. Most added by weathering/soil forming reactions.
        ii. Cl^-, SO_4^{2-} also directly sourced from volcanism/hydrothermal activity

iii. Inputs balanced by loss to hydrothermal alteration, subduction, formation of evaporites, cycling via aerosols.
iv. Ca^{2+}, CO_2 cycles closely coupled via $CaCO_3$ deposition.

c. +3, +4, +5 ions rare in ocean water
   i. Not easily dissolved (small source)
   ii. Easily removed (sorption to particles, hydrothermal fixation)
   iii. Fe^{3+}, Si^{4+}, $Mn^{2+/3+/4+}$ consumed as nutrients
   iv. Typically short residence times (less than 100,000 years)

5. NPP
   a. Oceanic NPP ≈ Terrestrial NPP – Oceans less productive/m^2, but cover more area.
   b. Issues measuring NPP in seawater? (to be covered in Chap. 7)
   c. Also measured by green-ness proxy.
   d. NPP concentrated at coasts, equator, poles.
   e. Very low NPP in most gyres.
6. Fate of oceanic NPP
   a. Much like terrestrial ecosystems, most NPP lost to bacterial decomposition (~60-70%, i.e., ~35% of GPP), "herbivores" (zooplankton) secondary.
   b. Only ~10-20% of NPP exported to dark water (>100m)
   c. < 5% survives below 3000m
   d. <1% stored in sediments (~10^{14}g/yr)
7. Diagenesis/decomposition of sedimentary organic C
   a. Oxygen-consuming respiration limited to free water, uppermost part of sediment
   b. Sulfate-reducing respiration common in subsurface. Most H_2S produced is re-oxidized at the sediment/water interface.

Lecture 15: Carbonate cycling

8. Biogenic carbonate minerals
   a. Many organisms promote reaction of dissolved HCO_3^- to form $CaCO_3$
      i. $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + H_2O + CO_2$
      ii. Acid-forming or base-forming reaction?
      iii. Effects of variation in CO_2 abundance in seawater?
   b. Deep water is cold and CO_2-rich, increasing solubility of $CaCO_3$, warm surface waters are CO_2-poor, supersaturated in $CaCO_3$
      i. → $CaCO_3$ produced near surface can be redissolved at depth
      ii. carbonate compensation depth (CCD) – depth below which $CaCO_3$ dissolved faster than it accumulates.
      iii. Typical CCD-depth ~4000-5000m, deepest in Atlantic (young deep water – less accumulated CO_2)
   c. Ca2+ formed by weathering-reactions in soils → net sink of CO_2.
      i. Net reaction: $CaSiO_3 + CO_2 \rightarrow SiO_2 + CaCO_3$
      Real reaction in two steps, usually at some distance from each other:
      ii. $CaSiO_3 + 2H_2CO_3 \rightarrow Ca^{2+} + SiO_2 + 2HCO_3^-$ (weathering)

    iii. $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2$ (carbonate deposition)
  d. Dominant carbonate sinks are shallow seafloor.

9. Nutrient cycles
   a. Nutrients like N, P, Fe, Si* used up to support productivity of surface waters. Ultimately transported to deep water, depleted near surface, particularly where surface water is "old".
   b. Deep waters become progressively enriched with nutrients + CO_2.
      i. Atlantic vs. Pacific?
   c. Productivity concentrated at sites of upwelling.
   d. N, P, C, O abundance variations linked by requirements of photosynthesizing organisms
      i. Typical net reaction (Redfield):
      ii. $106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$
      iii. 106C:16N:P → Redfield ratio
      iv. Upwelling water contains ~$800C_{inorg}$:16N:P, thus N and P are limiting, Cinorg (≈HCO_3^-) available in excess of needs
      v. Change of limitation possible near external nutrient sources i.e. coastal/agricultural runoff, dust settling
      vi. Biological N-fixation (dinoflagellates) may create local nutrient source in So. Cal ocean, disrupt Redfield ratio. Other N-poor surface waters get N-fixation by cyanobacteria
   e. O-P feedback
      i. Oxygen production in ocean limited by N+/-P+/-Fe.
      ii. P-release to deep water affected by O_2 abundance
         1. $2Fe_2O_3.H_3PO_4$ (adsorbed) + $2H_2O \rightarrow 4Fe^{2+}$(bio-available) + $2H_2PO_4^-$(bio-available) + O_2+ $6OH^-$
         2. More O_2 in deep water → less available Fe, P, lower productivity after mixing → less O2 produced
         3. Less O_2 → more available Fe, P, higher productivity after mixing → more O_2 produced.
         4. Negative feedback, buffering O_2 production.
   f. Trace nutrients
      i. Generally not limiting, but Fe is limiting in parts of the Pacific
      ii. Zn limitation inhibits $CO_2 \leftrightarrow HCO_3^-$ interconversion, slowing photosynthesis
      iii. Hg toxicity
   g. Biotic influences on weathering, greenhouse(?)
      i. DMS (CH_3SCH_3) released by decay of microbes, some survives to exchange into the atmosphere
      ii. Fate of DMS (net reaction)
      iii. $CH_3SCH_3 + O_2 \rightarrow H_2SO_4.nH_2O$ (acid droplet) + CO_2
      iv. Actually oxidized by •OH
      v. May contribute ~10% of modern sulfate aerosol
      vi. H_2SO_4 strongly attracts water vapor, nucleates clouds
      vii. H_2SO_4 precipitates in rain, snow, speeds weathering of soils