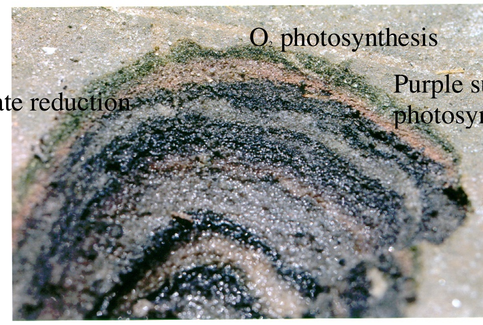
EPSS C113/213 Biological and Environmental Chemistry
Feb 26 – March 2, 2018

Ch. 7: Wetlands biogeochemistry (cont'd)

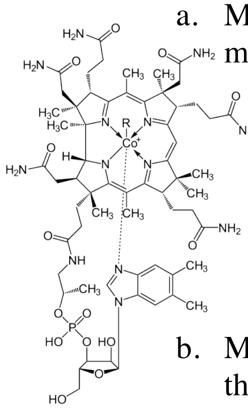
1. pH dependence.
    a. H^+ appears on the left side of $O_2 \rightarrow H_2O$ reaction, indicating that the reaction will be most favorable at low pH.
    b. Eh of O_2 highest at low pH (Fig. 7.2)
    c. Fe^{3+} tends to react to make hydroxides and oxide minerals, except at very low pH
        i. $Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + e^-$
        ii. So Fe^{3+}/Fe^{2+} redox potential also highest at low pH.
        iii. Fe^{2+} most easily oxidized at high pH, because necessary Eh is lower.
    d. Typical Eh values of Earth surface environments are bounded by the stability of water, because it is so abundant.
2. Typical Eh's of terrestrial environments.
    a. Oxygenated environments have Eh ≥ 600 mV
        i. Stable oxidation state of Fe?
    b. In areas with slow O_2-diffusion or advection, decomposition of organic matter may reduce Eh.
        i. Soil/sediment gradients may be ~mm to cm
        ii. Lake gradients may be ~m
3. As O_2 is depleted, successively less powerful oxidants are used by organisms to continue decomposition
        i. Denitrification:
        $5CH_2O + 4H+ + 4NO_3– \rightarrow 2N_2+ 5CO_2 + 7H_2O$ Eh < 747mV
        ii. Manganese reduction:
        $CH_2O + 4H^+ + 2MnO_2 \rightarrow 2Mn^{2+} + CO_2 + 5H_2O$
        Eh < 526mV
        May be visible as partial "bleaching" since MnO2 is usually black
        iii. Iron reduction:
        $CH_2O + 8H^+ + 2Fe_2O_3 \rightarrow 4Fe^{2+} + CO_2 + 5H_2O$
        Eh < –47mV
        Completion of "bleaching" reaction, Fe_2O_3 is usually reddish
        iv. Metal-reducing reactions often involve intermediate reducing agents like H_2.

4. Sulfate reduction:
   $2CH_2O + 2H^+ + SO_4^{2-} \rightarrow H_2S + CO_2 + 2H_2O$
   Eh < –244



   a. Particularly stinky
      Predominant source of gaseous S to the atmosphere → background sulfate acidity of rain/weathering.
   b. Fe^{2+}, if available, will react to make FeS and FeS_2.
   c. May also react to form organic-bound S
5. Production of H_2, CH_4 may accompany low-O_2 ecologies where SO_4^{2-} is scarce or already used up.
   a. Low energy yield: methanogenesis out-competed by sulfate reduction where sulfate is available.
   b. Much H_2, CH_4 re-oxidized at it diffuses upwards into higher-Eh zones.
   c. Methane release efficiency may be increased by ventilation in vascular plants
      i. Rice cultivation → methane increase in atmosphere?
6. Energy available from decomposition greatest at high Eh, lowest at low Eh (by at lot! 80% -90%)

7. Biomethylation



   a. Micro-organisms in highly reducing environments can biomethylate metals (i.e., Hg).
      i. Hg^0 largely inert with moderate vapor pressure, ~mixed in atmosphere.
      ii. Oxidation to Hg^{2+}, then deposition in precipitation.
      iii. $Hg^{2+} + CH_3^- \rightarrow HgCH_3^+$
      iv. Typically catalyzed by B-12 like protein (Cobalamin – image)
      v. Mechanism of Hg^0 oxidation patchy, not well understood. May be similar to O_3 destruction mechanism in polar stratosphere.
   b. Methyl-Hg vastly more toxic than inorganic forms, concentrated up the food chain (fat-soluble, attracted to S-bearing proteins).

   Lecture ??

2. Wetlands productivity
   a. NPP typically high, if nutrients are available.
   b. Net ecosystem productivity also often high, due to oxygen limitation in soil/sediment.
   c. Peat bogs have low NPP (nutrient poor), but high NEP – dominated by slow decomposition.
   d. Global warming may enhance decomposition of peat bogs – major possible source of positive CO_2 feedback.

3. Lake productivity
    a. Much productivity microbial (away from shore) – must be measured indirectly.
        i. O_2 production in suspended lakewater bottles
            1. Long incubation needed
            2. Animal, zooplankton respiration must be corrected
        ii. ^{14}C incorporation from inorganic $NaH^{14}CO_3$
            1. ^{14}C more sensitive (short incubation)
            2. Only insoluble organic compounds detected
            3. Some plankton may be too small to capture in filters.
    b. Limiting nutrient typically P (retained in soils).
    c. Most intense productivity in both environments associated with rooted, emergent vascular plants.
    d. Some N-fixation typical, but may be limited by Fe, Mo availability.
4. Lake ecosystem productivity
    a. Much higher long-term potential than oceans because of strong oxygen limitation in soils
        i. Lawrence Lake: ~7.8% long term sequestration of C
        ii. Even here, ~11/12 organic C respired in the water column, most at lake bottom.
    b. May be similar to soil as C-sink.
5. Human-induced perturbations
    a. Lakes strongly affected by fertilization of agricultural fields, enhances productivity/redox stratification.
    b. "Cultural eutrophication" – high (algal) productivity
    c. May lead to fish-kill, fouling of drinking water supplies.