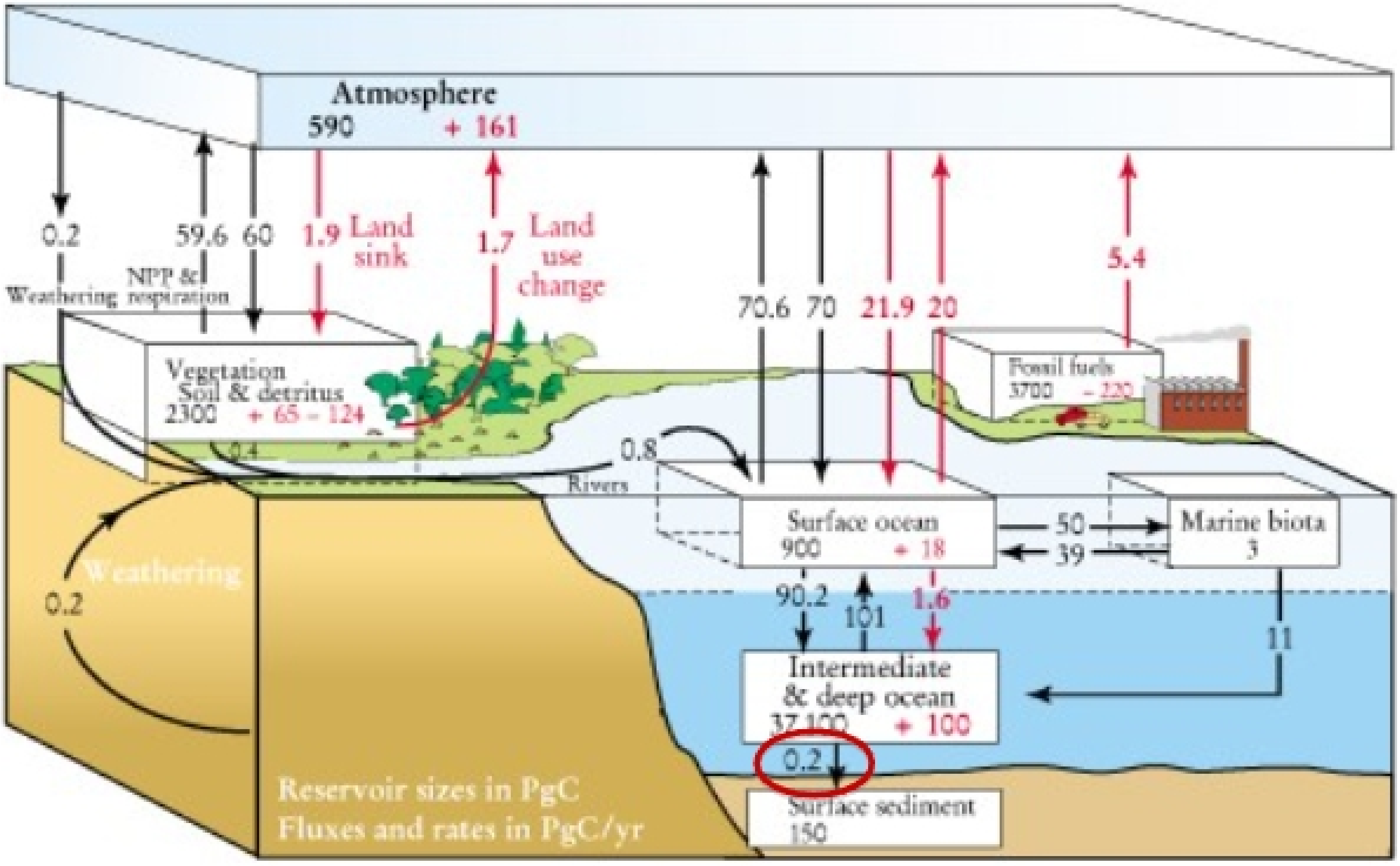
Lecture 18 Redox Environments in the Oceans

Diagenesis in Sediments
Anoxic Basins

Global Carbon Cycle – Fate of organic matter in sediments



Redox Half Reactions

written as reductants
in terms of 1 e^-

Table 8.6a. Equilibrium Constants of Redox Processes Pertinent in Aquatic Conditions (25°C)

Reaction		pe° (= log *K*)	pe° (W)[a]
(1) $\frac{1}{4}O_2(g) + H^+ + e^-$	$= \frac{1}{2}H_2O$	+20.75	+13.75
(2) $\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	$= \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+21.05	+12.65
(3) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3(10^{-3}) + \frac{3}{2}H^+ + e^-$	$= \frac{1}{2}MnCO_3(s) + H_2O$	—	+8.9[b,c]
(4) $\frac{1}{2}NO_3^- + H^+ + e^-$	$= \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	+14.15	+7.15
(5) $\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	$= \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.90	+6.15
(6) $\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+15.14	+5.82
(7) $\frac{1}{2}CH_3OH + H^+ + e^-$	$= \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$	+9.88	+2.88
(8) $\frac{1}{4}CH_2O + H^+ + e^-$	$= \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$	+6.94	−0.06
(9) $FeOOH(s) + HCO_3^-\ (10^{-3}) + 2H^+ + e^-$	$= FeCO_3(s) + 2H_2O$	—	−0.8[b,d]
(10) $\frac{1}{2}CH_2O + H^+ + e^-$	$= \frac{1}{2}CH_3OH$	+3.99	−3.01
(11) $\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^-$	$= \frac{1}{6}S(s) + \frac{2}{3}H_2O$	+6.03	−3.30
(12) $\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^-$	$= \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	+5.25	−3.50
(13) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^-$	$= \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	−3.75
(14) $\frac{1}{2}S(s) + H^+ + e^-$	$= \frac{1}{2}H_2S(g)$	+2.89	−4.11
(15) $\frac{1}{8}CO_2(g) + H^+ + e^-$	$= \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+2.87	−4.13
(16) $\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^-$	$= \frac{1}{3}NH_4^+$	+4.68	−4.68
(17) $H^+ + e^-$	$= \frac{1}{2}H_2(g)$	0.0	−7.00
(18) $\frac{1}{4}CO_2(g) + H^+ + e^-$	$= \frac{1}{24}(glucose) + \frac{1}{4}H_2O$	−0.20	−7.20
(19) $\frac{1}{2}HCOO^- + \frac{3}{2}H^+ + e^-$	$= \frac{1}{2}CH_2O + \frac{1}{2}H_2O$	+2.82	−7.68
(20) $\frac{1}{4}CO_2(g) + H^+ + e^-$	$= \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	−1.20	−8.20
(21) $\frac{1}{2}CO_2(g) + \frac{1}{2}H^+ + e^-$	$= \frac{1}{2}HCOO^-$	−4.83	−8.33

[a] Values for pe° (W) apply to the electron activity for unit activities of oxidant and reductant in neutral water, that is, at pH = 7.0 for 25°C.

[b] These data correspond to $(HCO_3^-) = 10^{-3}$ M rather than unity and so are not exactly pe° (W); they represent typical aquatic conditions more nearly than pe° (W) values do.

[c] Alternatively one may consider the reaction.

$\frac{1}{2}MnO_2(s) + 2H^+ + e^- = \frac{1}{2}Mn^{2+}\ (10^{-6}\ M) + H_2O$; pe° (W) = 9.8

[d] $Fe(OH)_3(am) + 3H^+ + e^- = (Fe^{2+})\ (10^{-6}\ M) + H_2O$; pe° (W) = 1.0