Week 4 -- September 23, 2003

Photosynthesis

$106\ CO_2 + 16\ NO_3^- + H_2PO_4^- + 122\ H_2O \rightleftharpoons C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$

$106\ CO_2 + 16NH_4^+ + H_2PO_4^- + 106\ H_2O \rightleftharpoons C_{106}H_{261}O_{110}N_{16}P + 106\ O_2$

Nitrogen-fixation NF= f(O_2, Fe)

$2\ N_2 + 4\ H^+ + 3\ CH_2O + 3\ H_2O \longrightarrow 4\ NH_4^+ + 3\ CO_2$ (9)

Nitrification NI= f(O_2) i.e. $O_2 \geq 20\ \mu M$

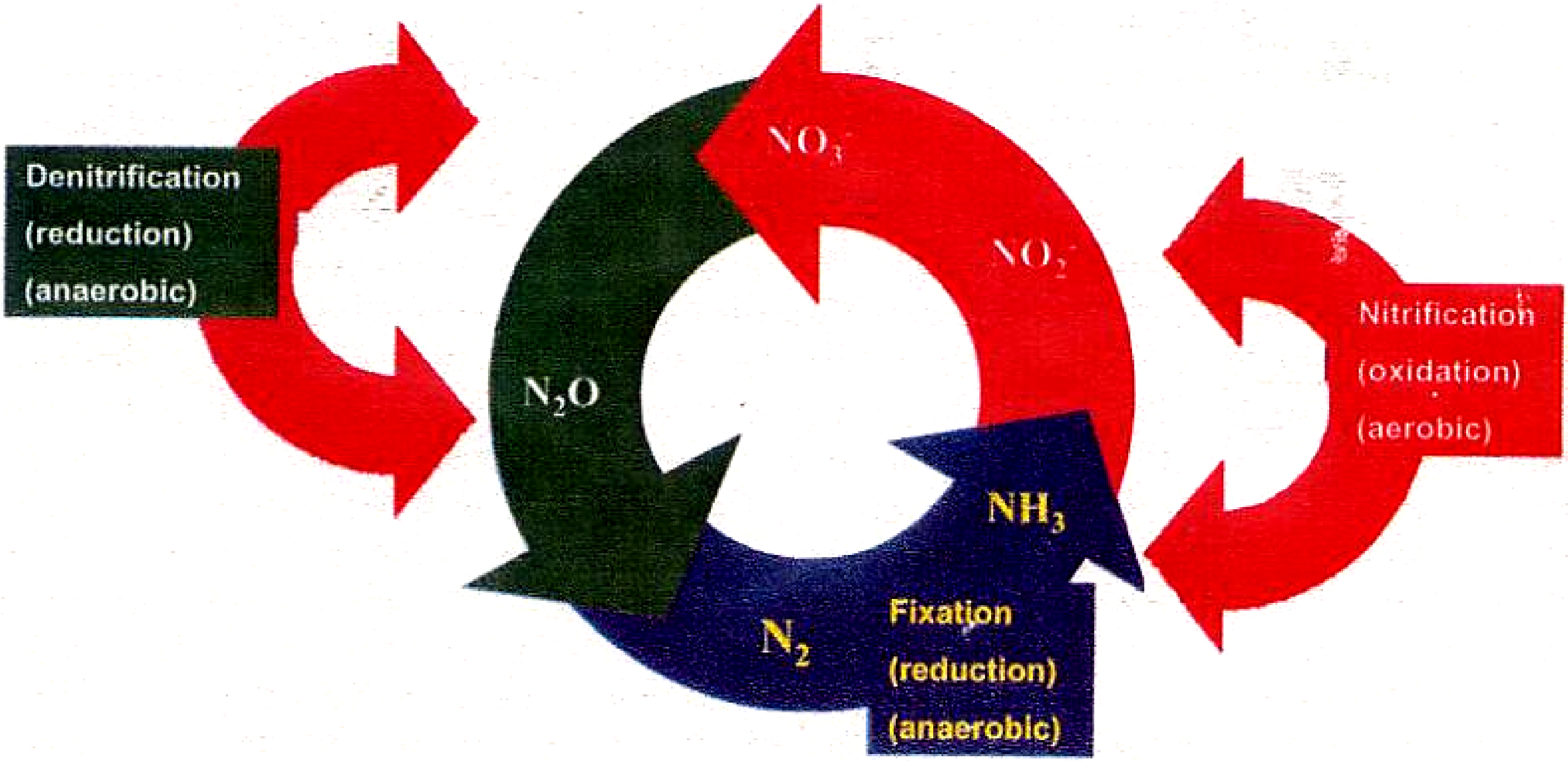
$NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + 2\ H^+ + H_2O$

Denitrification ON=f(O_2, NO_3^-) i.e. $O_2 \leq 5 \mu M$

$C_{106}O_{110}H_{261}N_{16}P + 84.8\ HNO_3 \longrightarrow 106\ CO_2 + 42.4\ N_2 + 16\ NH_3 + H_3PO_4 + 148.4\ H_2O$

$C_{106}O_{110}H_{263}N_{16}P + 94.4\ HNO_3 \longrightarrow 106\ CO_2 + 55.2\ N_2 + H_3PO_4 + 177.2\ H_2O$

The Nitrogen Cycle



Denitrification
(reduction)
(anaerobic)

NO_3^-

NO_2^-

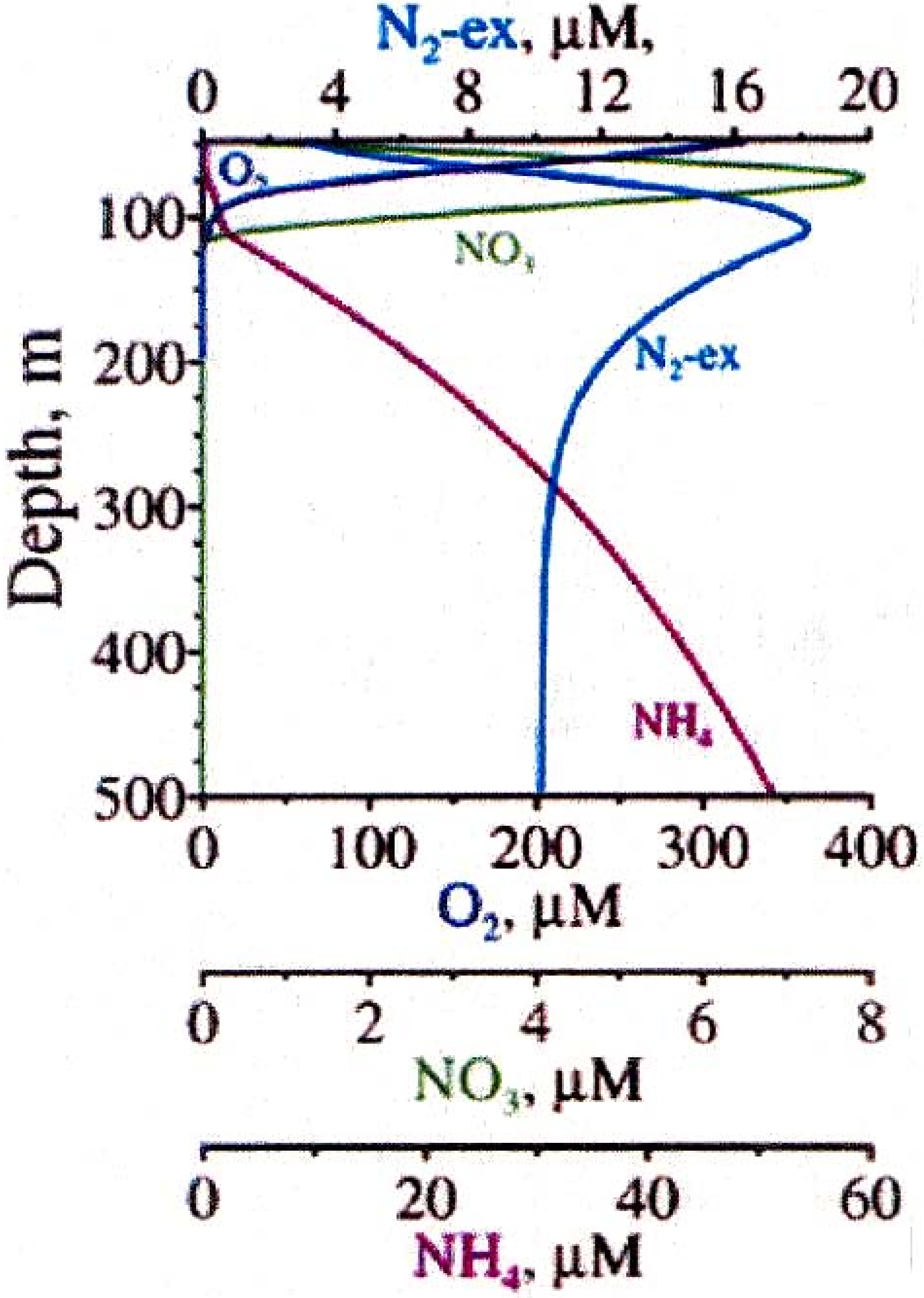
Nitrification
(oxidation)
(aerobic)

N_2O

NH_3

N_2

Fixation
(reduction)
(anaerobic)


N2-ex, µM,
0
4
8
12
16
20
O2
NO3
N2-ex
NH4
Depth, m
100
200
300
400
500
0
100
200
300
400
O2, µM
0
2
4
6
8
NO3, µM
0
20
40
60
NH4, µM

Anabaena sp.

TABLE 42-2

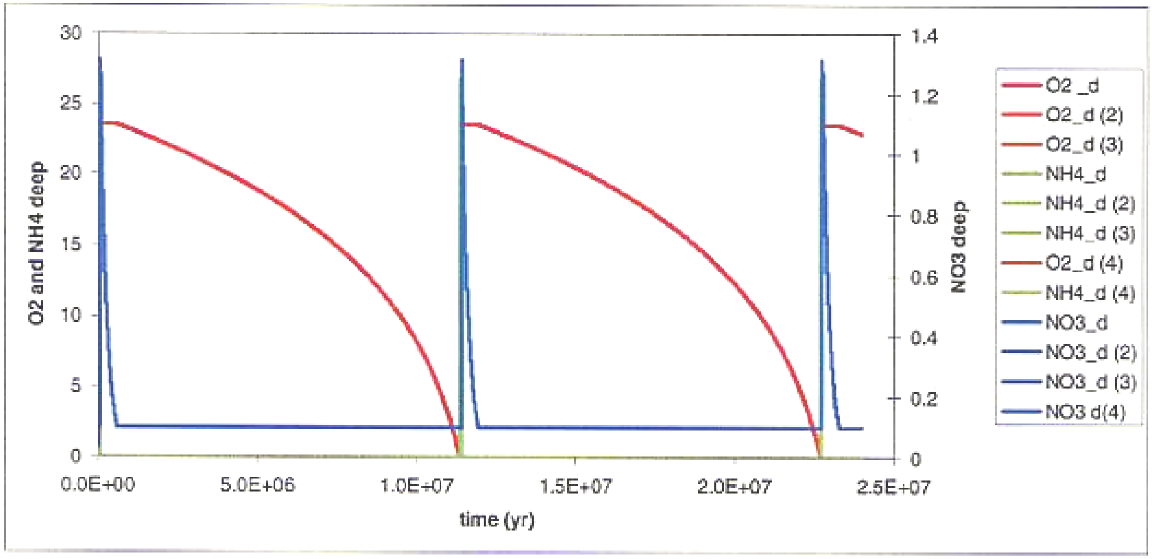
The biochemical processes involved in the nitrogen cycle, their biological occurrence, and their energy yield (from Delwiche 1970).

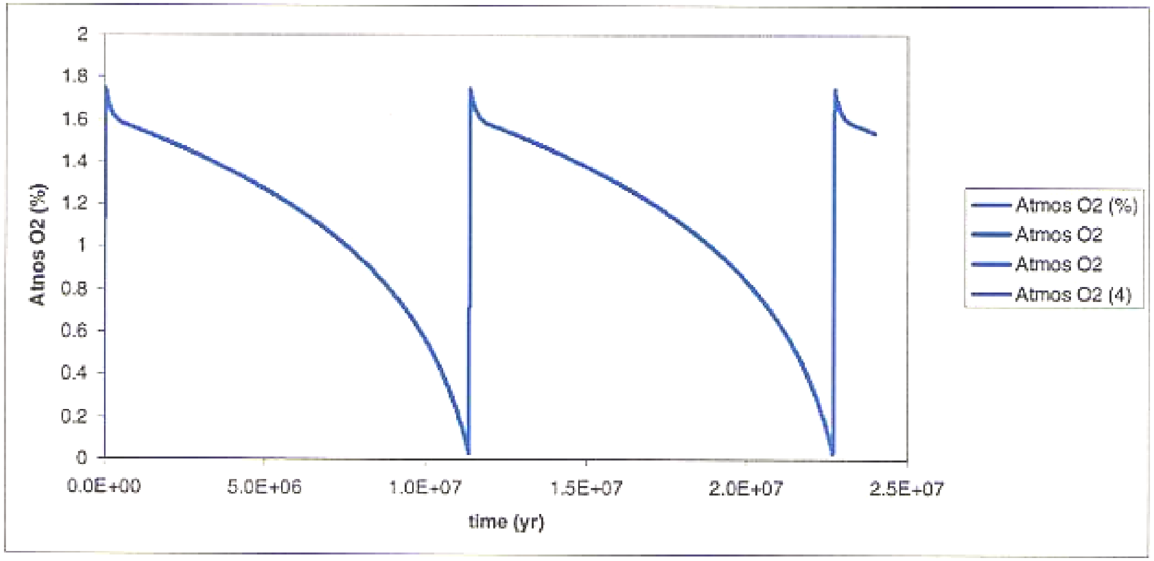
Process*	Organism	Yield (kcals/mole)
Respiration†		
(1) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	Virtually universal	686
Denitrification		
(2) $C_6H_{12}O_6 + 6KNO_3 \rightarrow 6CO_2 + 3H_2O + 6KOH + 3N_2O$	*Pseudomonas denitrificans*	545
(3) $5C_6H_{12}O_6 + 24KNO_3 \rightarrow 30CO_2 + 18H_2O + 24KOH + 12N_2$	*Pseudomonas denitrificans*	570
(4) $5S + 6KNO_3 + 2CaCO_3 \rightarrow 3K_2SO_4 + 2CaSO_4 + 2CO_2 + 3N_2$	Anaerobic sulfur bacteria	132
Ammonification		
(5) $C_2H_5NO_2 + 1\frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O + NH_3$	Many bacteria, most plants and animals	176
Nitrification		
(6) $NH_3 + 1\frac{1}{2}O_2 \rightarrow HNO_2 + H_2O$	*Nitrosomonas* bacteria	66
(7) $KNO_2 + \frac{1}{2}O_2 \rightarrow KNO_3$	*Nitrobacter*	17.5
Nitrogen fixation		
(8) $2N + 3H_2 \rightarrow 2NH_3$	Some blue-green algae, *Azotobacter*	— 147.2

* $C_6H_{12}O_6$ = glucose; CO_2 = carbon dioxide; $C_2H_2NO_2$ = glycine (an amino acid); $CaSO_4$ = calcium sulfate; $CaCO_3$ = calcium carbonate; HNO_2 = nitrous acid; KNO_2 = potassium nitrite; KNO_3 = potassium nitrate; KOH = potassium hydroxide; NH_3 = ammonia; N_2O = nitrous oxide; S = sulfur.

† Included for comparison.

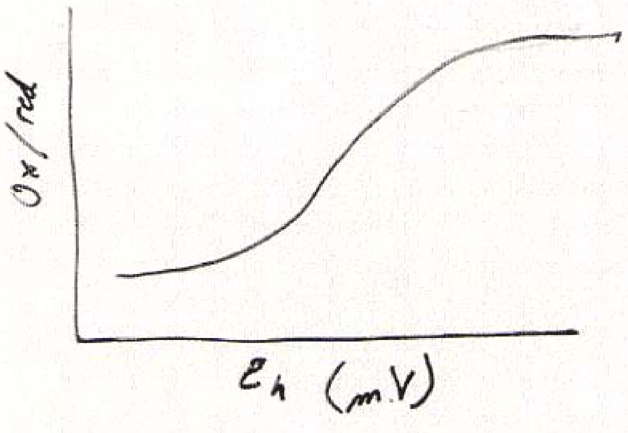
PO4: **2.122e-3** shelf: **3.0e6** knito2: **5.0e-3** mds:**5.0e6** mhd: **100.0e6**





Week 4 – September 25, 2003

The Nernst equation



$$E = (E_0 + 2.3RT)/(nF \log_{10} [A_{ox}]/[A_{red}])$$

where T is Kelvin
R is the Boltzmann gas constant

at 298 K (25°C)

$$\Delta E_h = (\Delta E_0' + 59)/\left(n \log_{10} \frac{[A_{ox}]}{[B_{red}]} \Big/ \frac{[A_{red}]}{[B_{ox}]}\right)$$

where ΔE_h is the difference for two
half cells

$$[A_{ox}] + [ne^-] + m[H^+] \rightleftharpoons [A_{red}]$$

where m is # of protons involved in reduction of Aox

The <u>Redox</u> <u>potential</u> for this reaction

is

$$E = E_{m7} + 59/n \log \left([A_{red}]/[A_{ox}] + [H^+]^m\right)$$

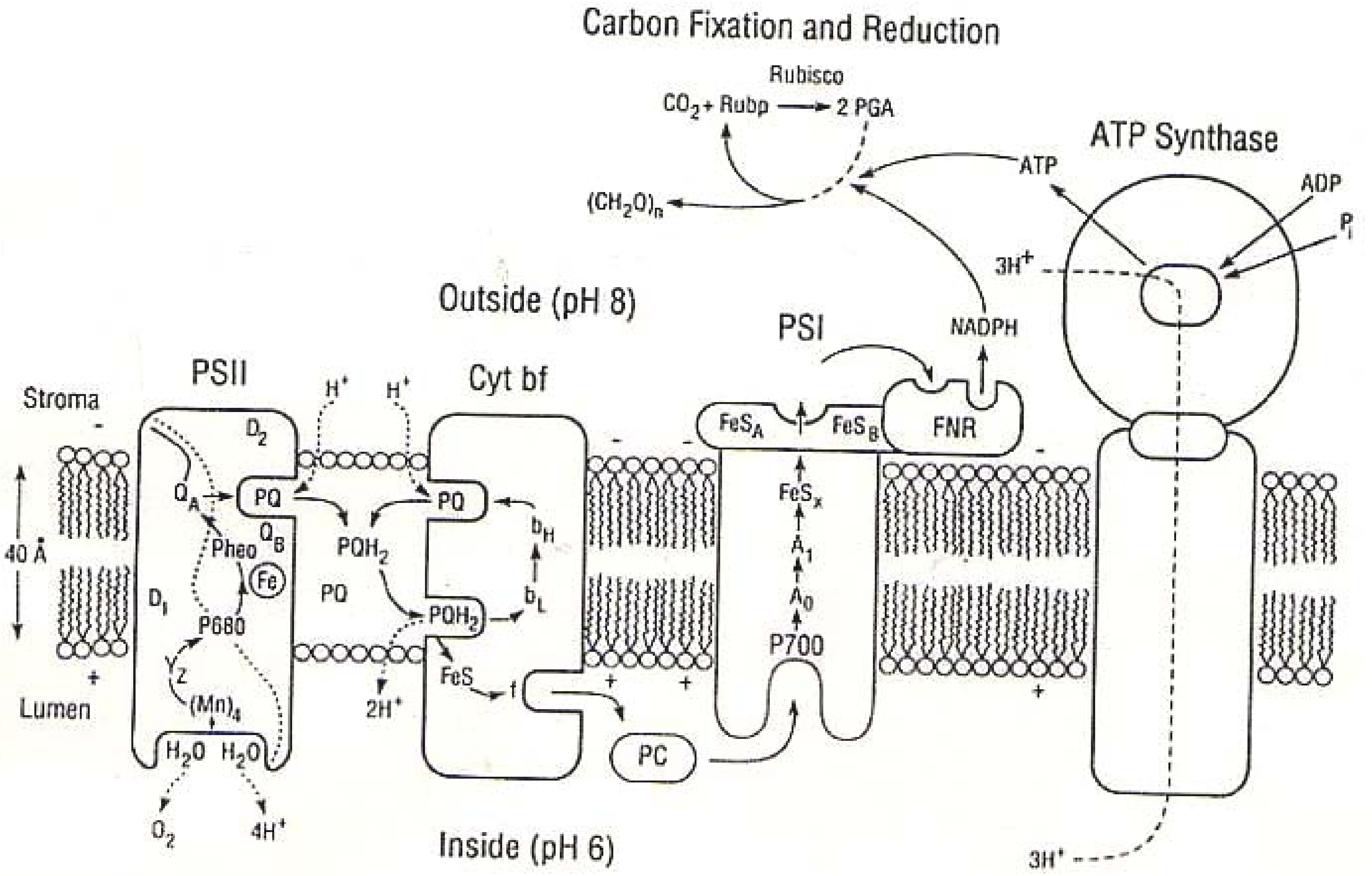
or

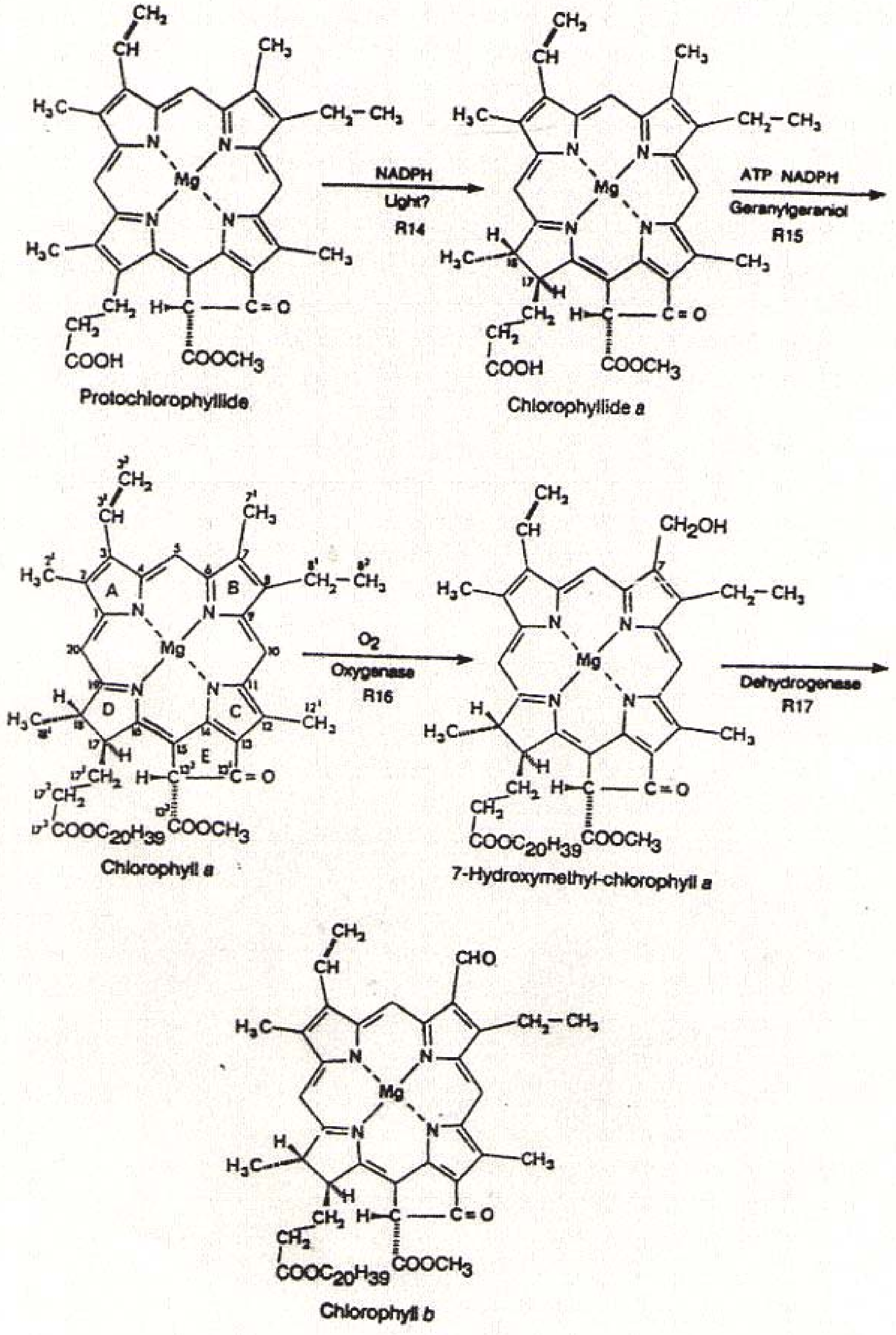
$$E = E_{m7} + 59/n \log\left(\frac{[A_{red}]}{[A_{ox}]}\right) + 59(m/n)\,pH$$

Table 4.1 Mid-point potentials for some common electron carriers in photosynthesis research

	$ox + n(e^-) + m(H^+) \rightleftharpoons red$			Change in E_m(mV) when pH increased by 1 unit
	n	m	E_{m7}(mV)	
Dithionite ox/red	1	0	−610	0
Methyl viologen ox/red	1	0	−450	0
CO_2/CH_2O	2	2	−430	−60
Ferredoxin ox/red	1	0	−430	0
$H^+/\frac{1}{2}H_2(H_2$ 1 atm)	1	1	−420	−60
$NAD^+/NADH$	2	1	−320	−30
$NADP^+/NADPH$	2	1	−320	−30
Menaquinone/menaquinol	2	2	−74	−60
Plastoquinone/plastoquinol	2	2	−0	−60
Fumarate/succinate	2	2	+30	−60
Ubiquinone/ubiquinol	2	2	+40	−60
Ascorbate ox/red	2	1	+60	−30
PMS ox/red	2	1	+80	−30
$DCPIP/DCPIPH_2$	2	2	+220	−60
TMPD ox/red	1	0	+260	0
$DAD/DADH_2$	2	2	+275	−60
Cytochrome *f* (ox/red)	1	0	+350	0
Cytochrome c_{553} (ox/red)	1	0	+370	0
Plastocyanin (ox/red)	1	0	+380	0
Ferricyanide ox/red	1	0	+420	0
P_{700}/P^+_{700}	1	0	+480	0
O_2(1 atm)/$2H_2O$(55 M)	4	4	+840	−60
P_{680}/P^+_{680}	1	0	+1100	0

DAD is 2,3,5,6-tetramethylphenylene diamine; PMS is phenazine methosulphate; TPMD is N,N,N',N'-tetramethyl-p-phenylene diamine; DCPIP is 2,6-dichlorophenolindophenol. (Adapted from Nicholls DG and Ferguson SJ. *Bioenergetics*. London: Academic Press, 1992)


Carbon Fixation and Reduction
Rubisco
CO_2 + Rubp → 2 PGA
$(CH_2O)_n$
ATP Synthase
ATP
ADP
P_i
$3H^+$
NADPH
PSI
Outside (pH 8)
PSII
Cyt bf
Stroma
H^+
H^+
D_2
FNR
FeS_A
FeS_B
Q_A
PQ
PQ
FeS_x
PQH_2
b_H
Q_B
40 Å
Pheo
A_1
Fe
D_1
PQ
A_0
PQH_2
b_L
P680
P700
Y_Z
FeS
f
$2H^+$
Lumen
$(Mn)_4$
H_2O
H_2O
PC
O_2
$4H^+$
Inside (pH 6)
$3H^+$
-
+


Protochlorophyllide
NADPH
Light?
R14
Chlorophyllide a
ATP NADPH
Geranylgeraniol
R15
Chlorophyll a
O_2
Oxygenase
R16
7-Hydroxymethyl-chlorophyll a
Dehydrogenase
R17
Chlorophyll b

Carbon Pools in the Major Reservoirs on Earth

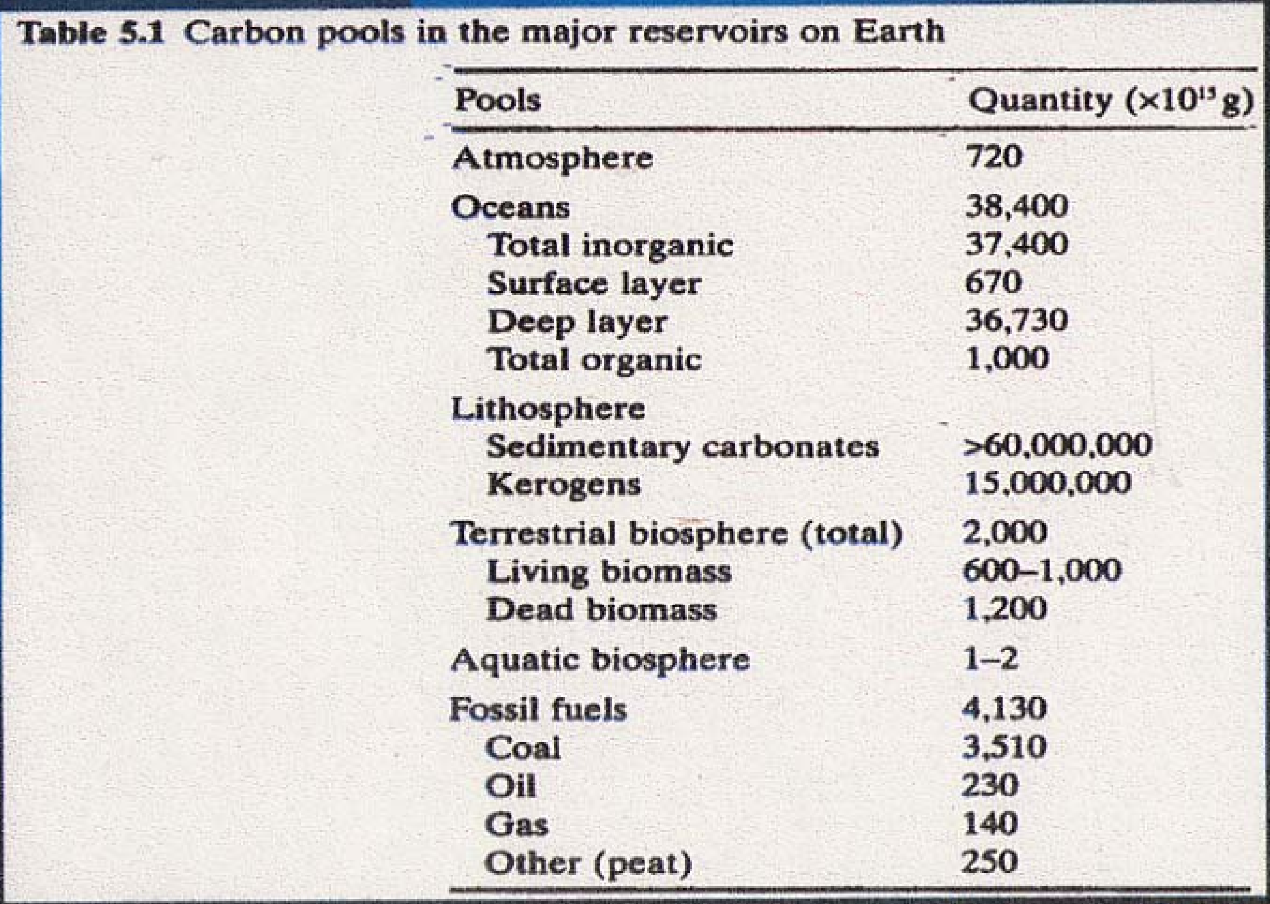
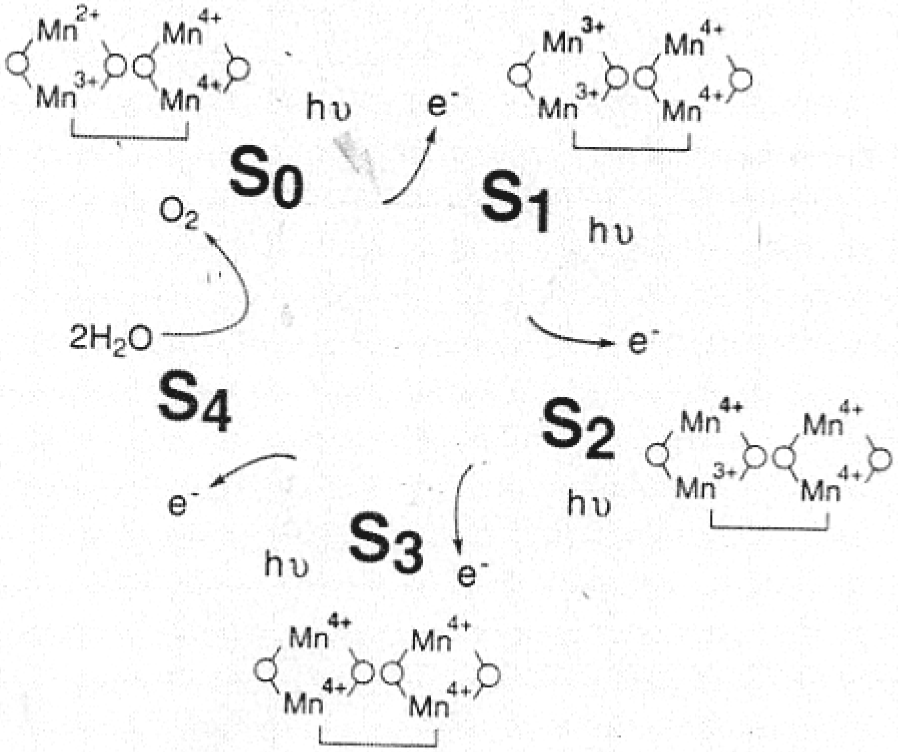


Table 5.1 Carbon pools in the major reservoirs on Earth

Pools	Quantity ($\times 10^{15}$ g)
Atmosphere	720
Oceans	38,400
Total inorganic	37,400
Surface layer	670
Deep layer	36,730
Total organic	1,000
Lithosphere	
Sedimentary carbonates	>60,000,000
Kerogens	15,000,000
Terrestrial biosphere (total)	2,000
Living biomass	600–1,000
Dead biomass	1,200
Aquatic biosphere	1–2
Fossil fuels	4,130
Coal	3,510
Oil	230
Gas	140
Other (peat)	250

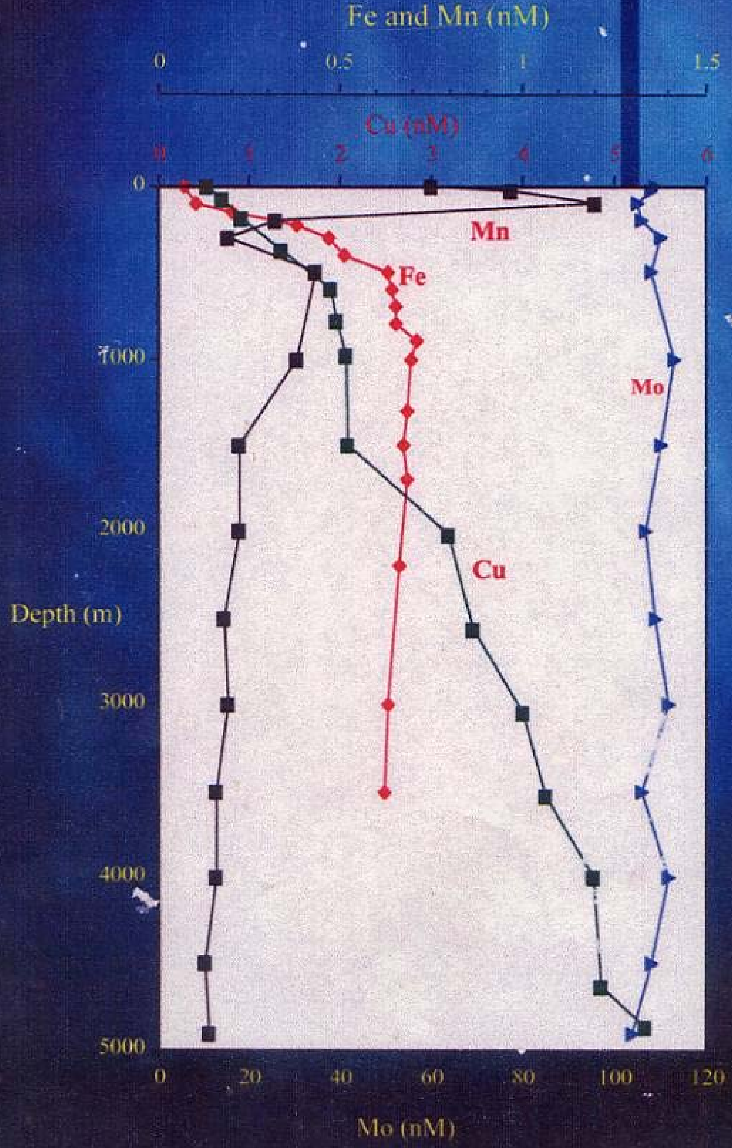
From: Falkowski & Raven. Aquatic Photosynthesis. p. 130 (1997)

The manganese clock



One by one, photons progressively build up a charge within the oxygen-evolving centre of Photosystem II until there is enough energy to strip, in one fell swoop, four electrons from two water molecules to produce an oxygen molecule. The five-step process is known as the 'water-oxidising clock' or 'Kok's clock' after its initial propounder.

TRACE METALS IN THE CENTRAL NORTH PACIFIC



Data compiled by R. Sherrell, Rutgers Univ.

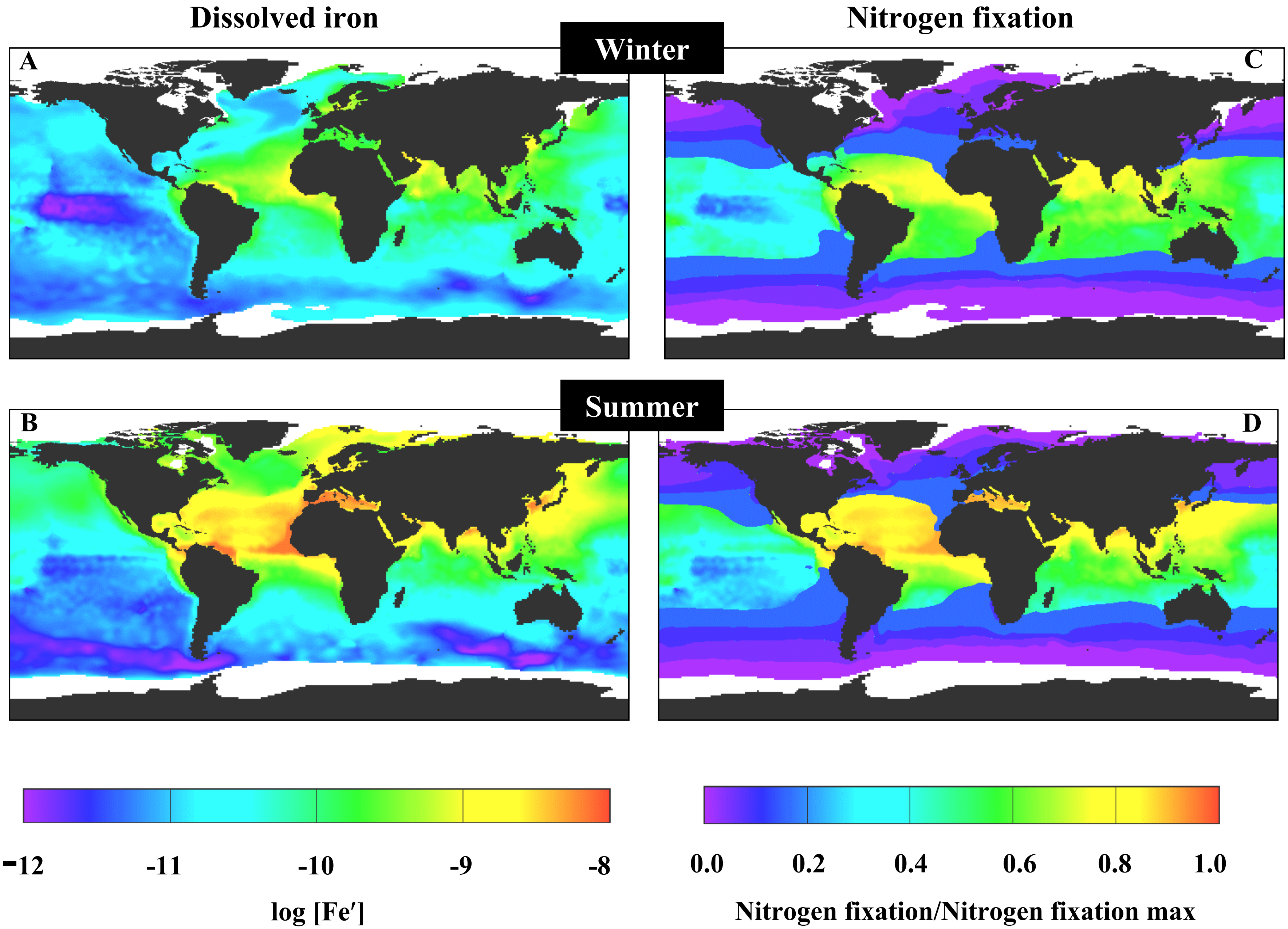


Figure 6. Berman-Frank et al.