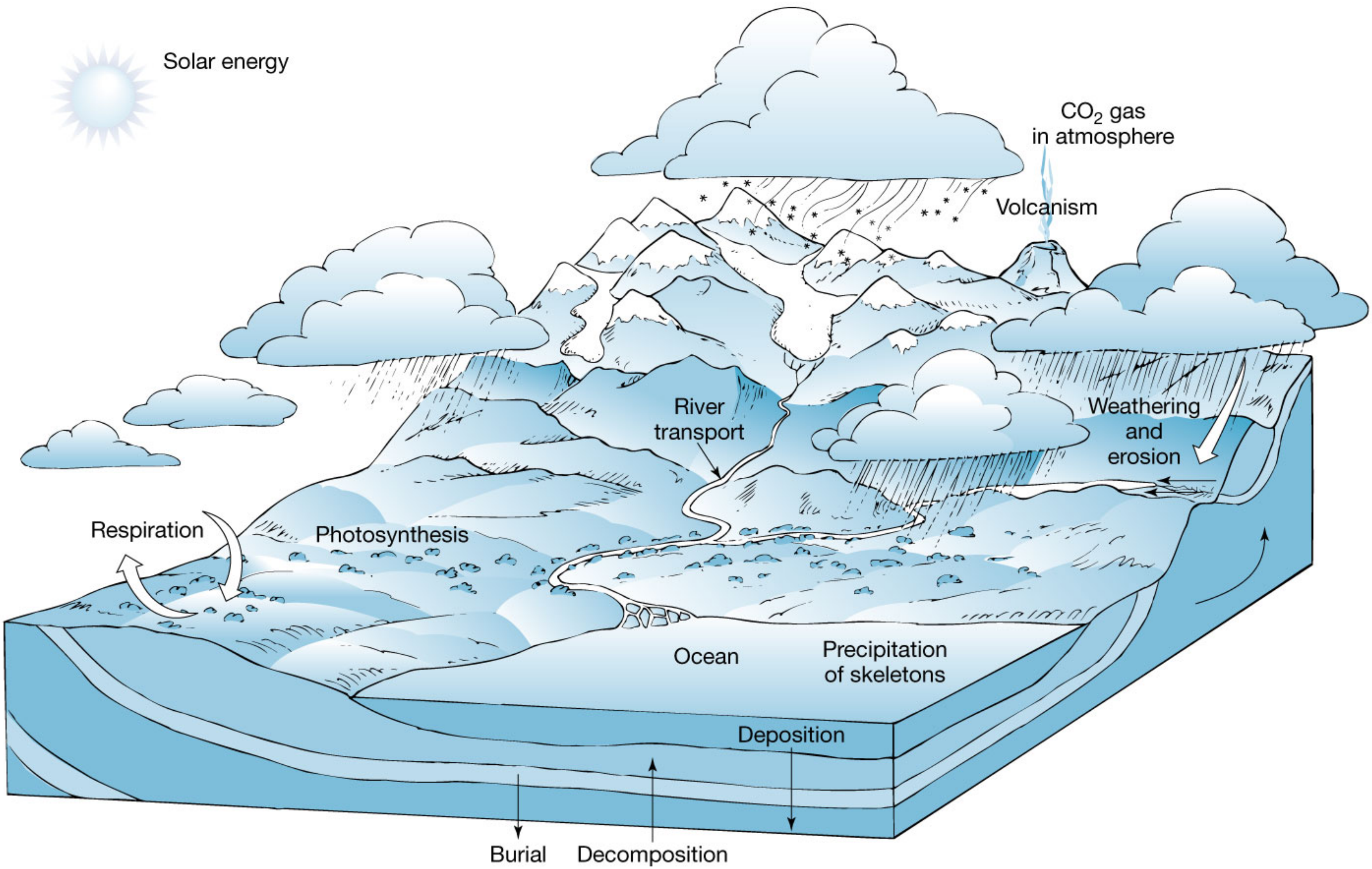
Chapter 8:
The Carbon (and other) Cycles:

- Why is the C cycle important?
- Short-term organic C cycle
- Long-term organic C cycle
- Long-term inorganic C cycle
- Related to P- and N-cycles

Why is the C cycle important?

1. Carbon (C) is the fourth most abundant element in the Universe, after hydrogen (H), helium (He), and oxygen (O)
2. C is *the* building block of life. It is the element that anchors all organic substances, from fossil fuels to DNA.
3. CO_2 is an important greenhouse gas
4. It regulates the acidity of the oceans
5. On Earth, carbon cycles through the land, ocean, atmosphere, and the Earth's interior in a major biogeochemical cycle.

Fig. 8-1 … but with no numbers!



Units Are Important

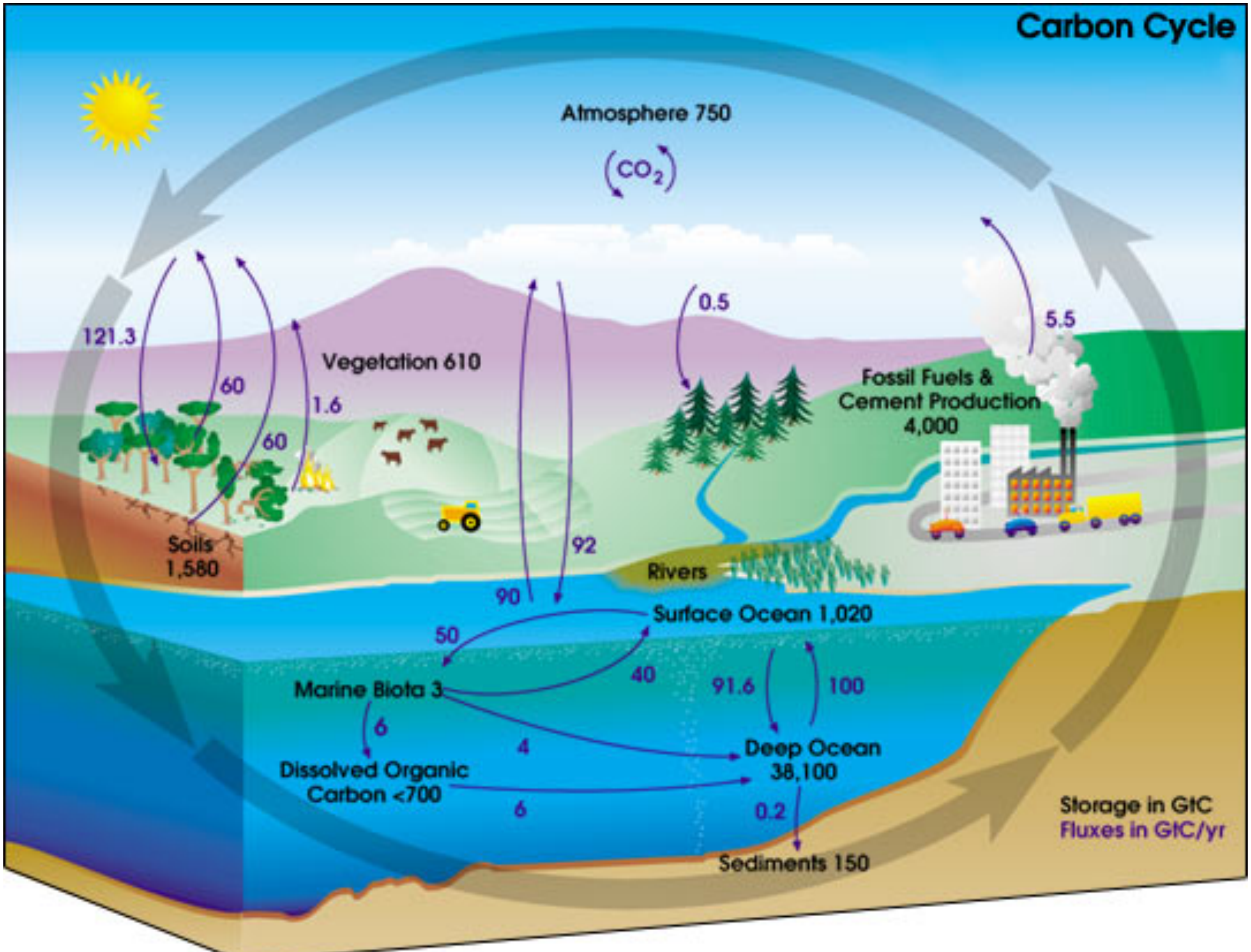
Always write down the units, if any, that should accompany a number. Numbers by themselves aren't much use.

- We will use "Gigatons" (Gton) to quantify the carbon cycle (not to mention others)
- 1 Gton = 10^9 metric tons
- 1 metric ton = 1000 kg
- 1 Gton = 10^{12} kg = 10^{15} g = 1 "petagram"
- "kilo" = thousand, "mega" = million, "giga" = billion, "tera" = trillion, "peta" = 10^{15}…

C cycle: CO_2 in atm, C in vegetation, decomposition…

..path includes inorganic C (no C or H bonds) and organic C portions, terrestrial and marine components, and a variety of timescales

Fig. 8.1



Total amounts of stored carbon in black, annual carbon fluxes in purple.

C reservoirs:
Note boxes not to scale

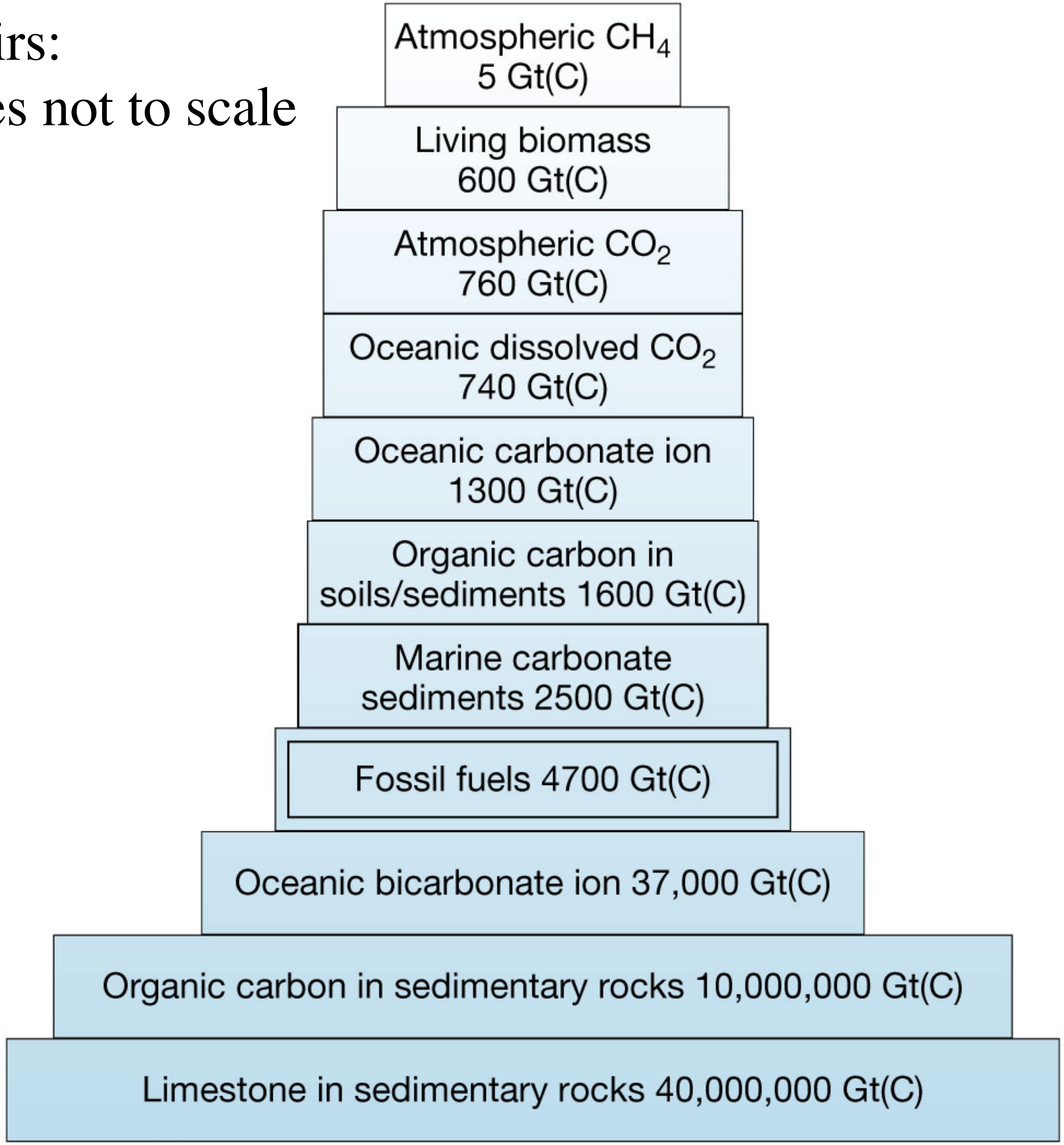
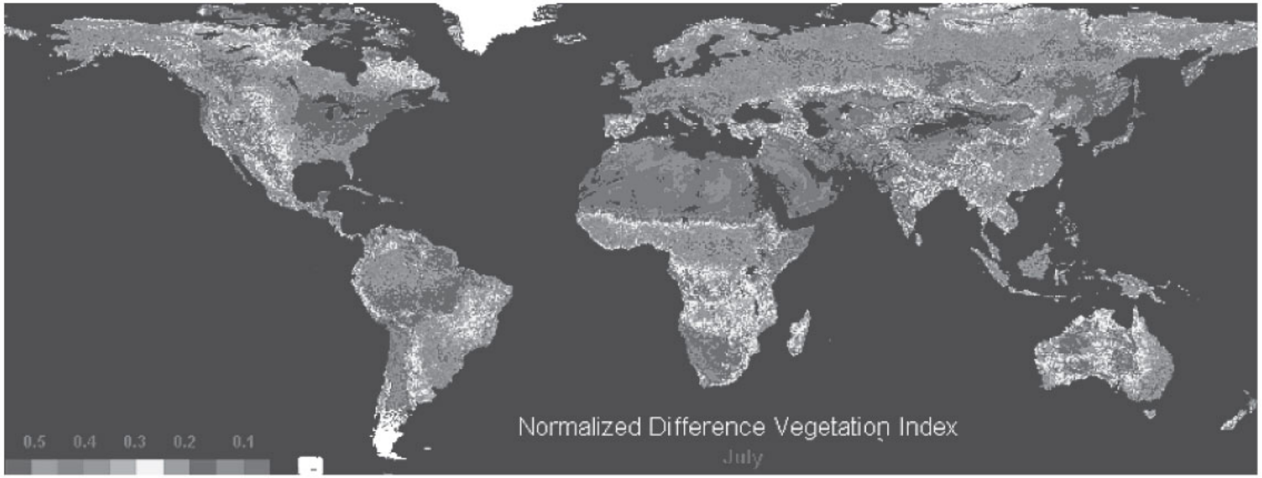
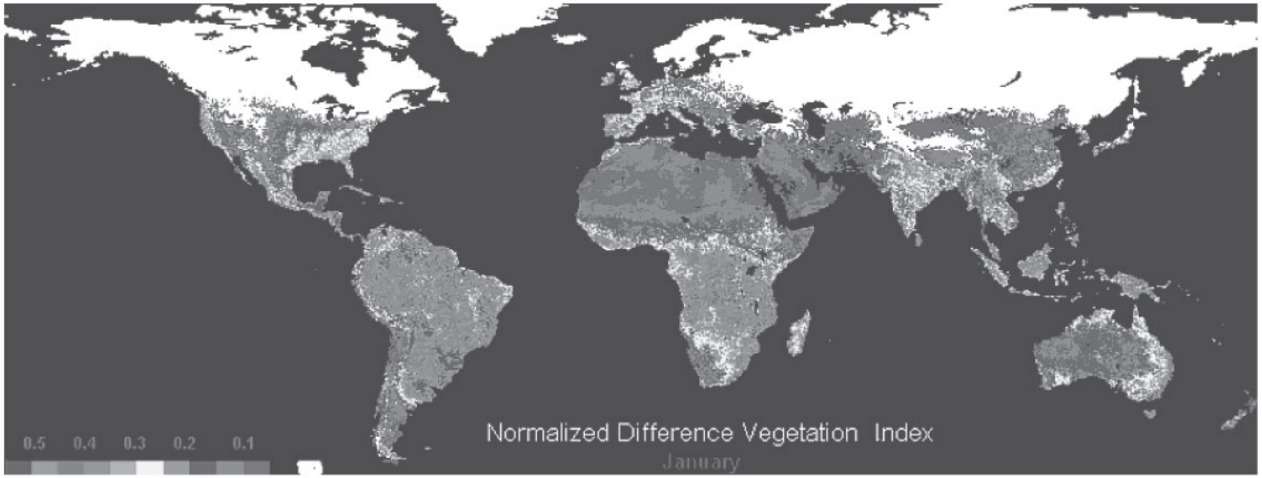


Fig. 8.3


Normalized Difference Vegetation Index
July
0.5 0.4 0.3 0.2 0.1

(a)


Normalized Difference Vegetation Index
January
0.5 0.4 0.3 0.2 0.1

(b)

Fluctuations in atmospheric CO_2:

3 years' data showing

- photosynthesis and respiration,
- increase in anthropogenic CO_2

(Mauna Loa is in N. hemisphere)

(This is old data- this year the peak for Mauna Loa was over 390 ppm)

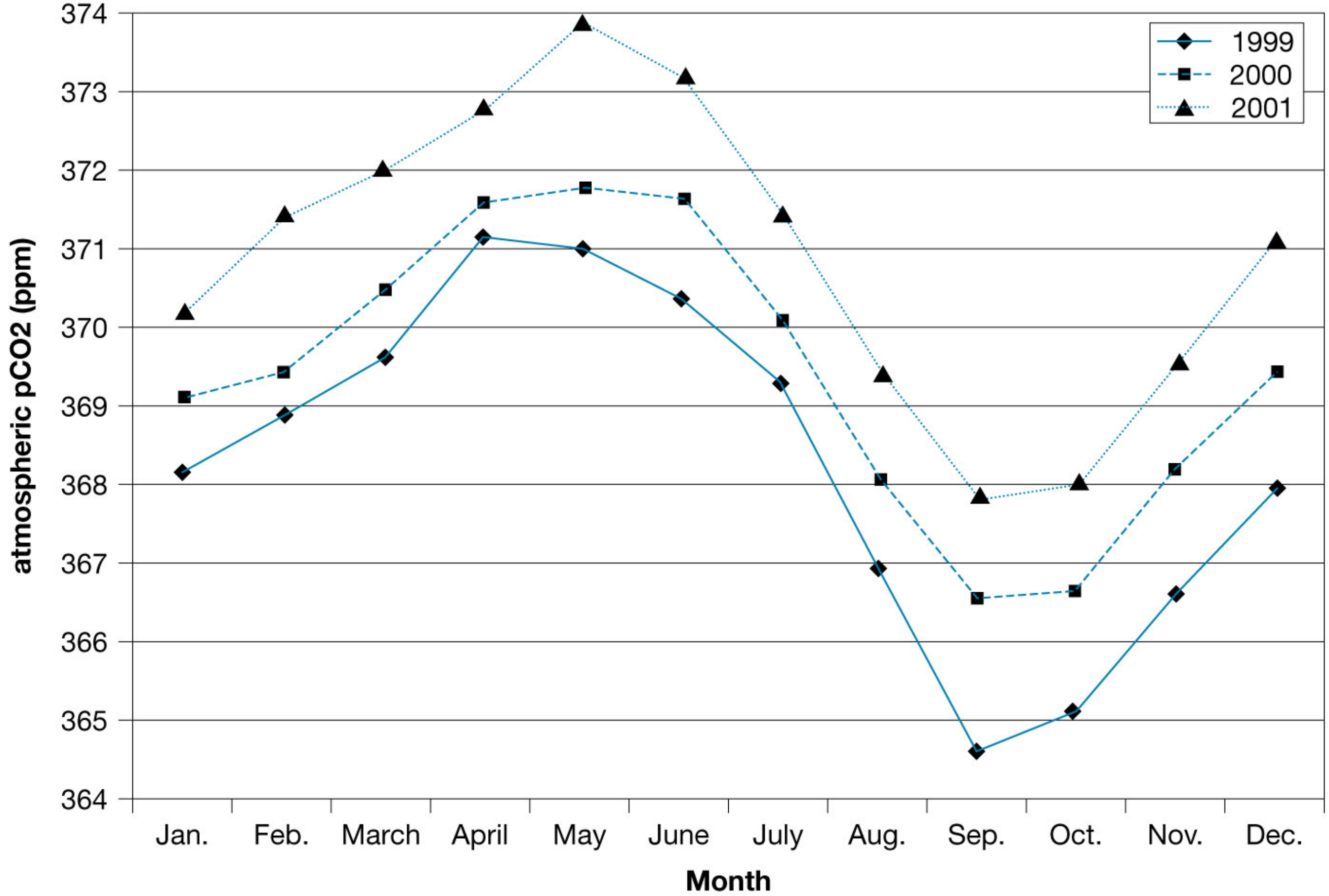
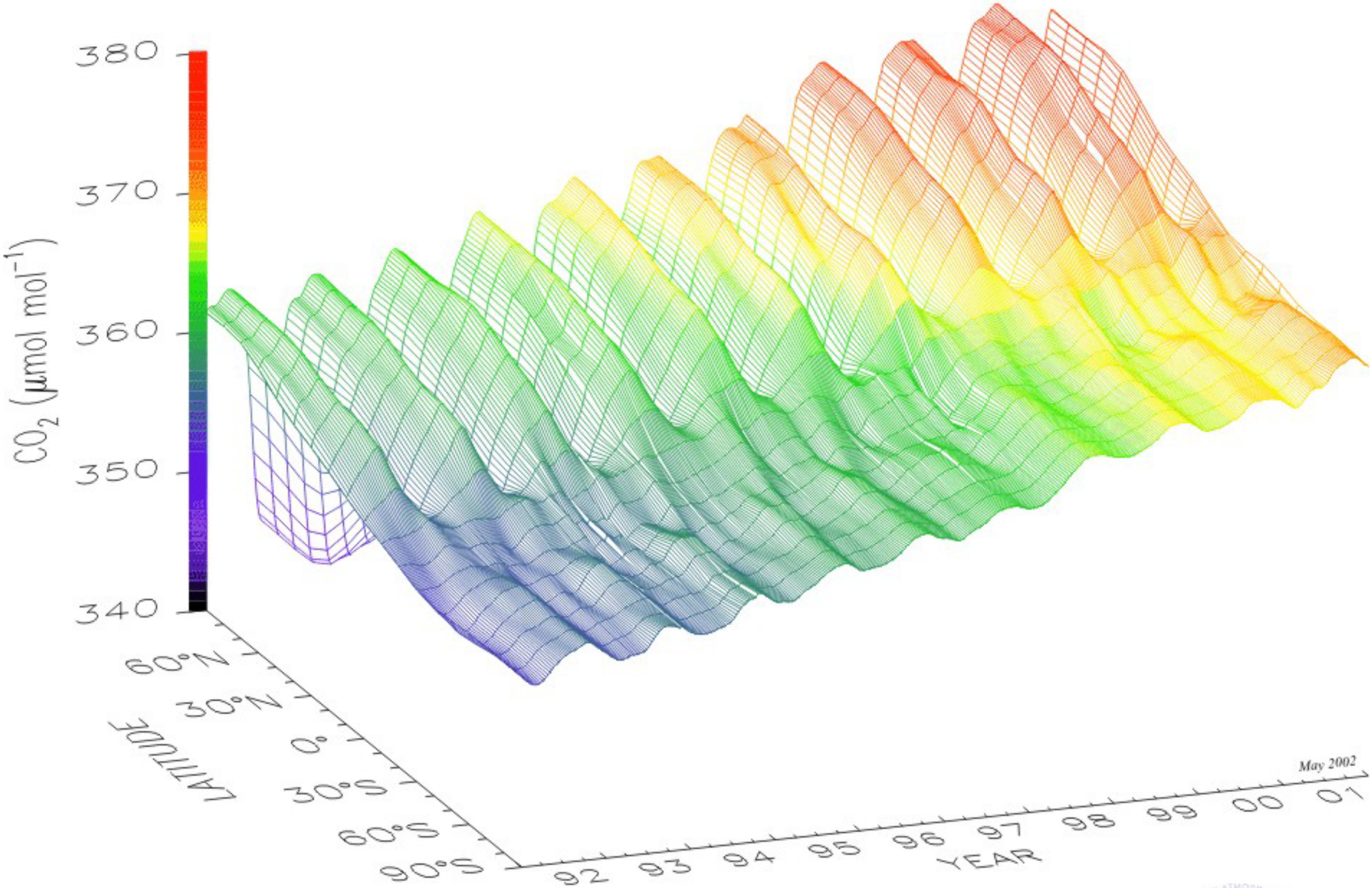


Fig. 8.4

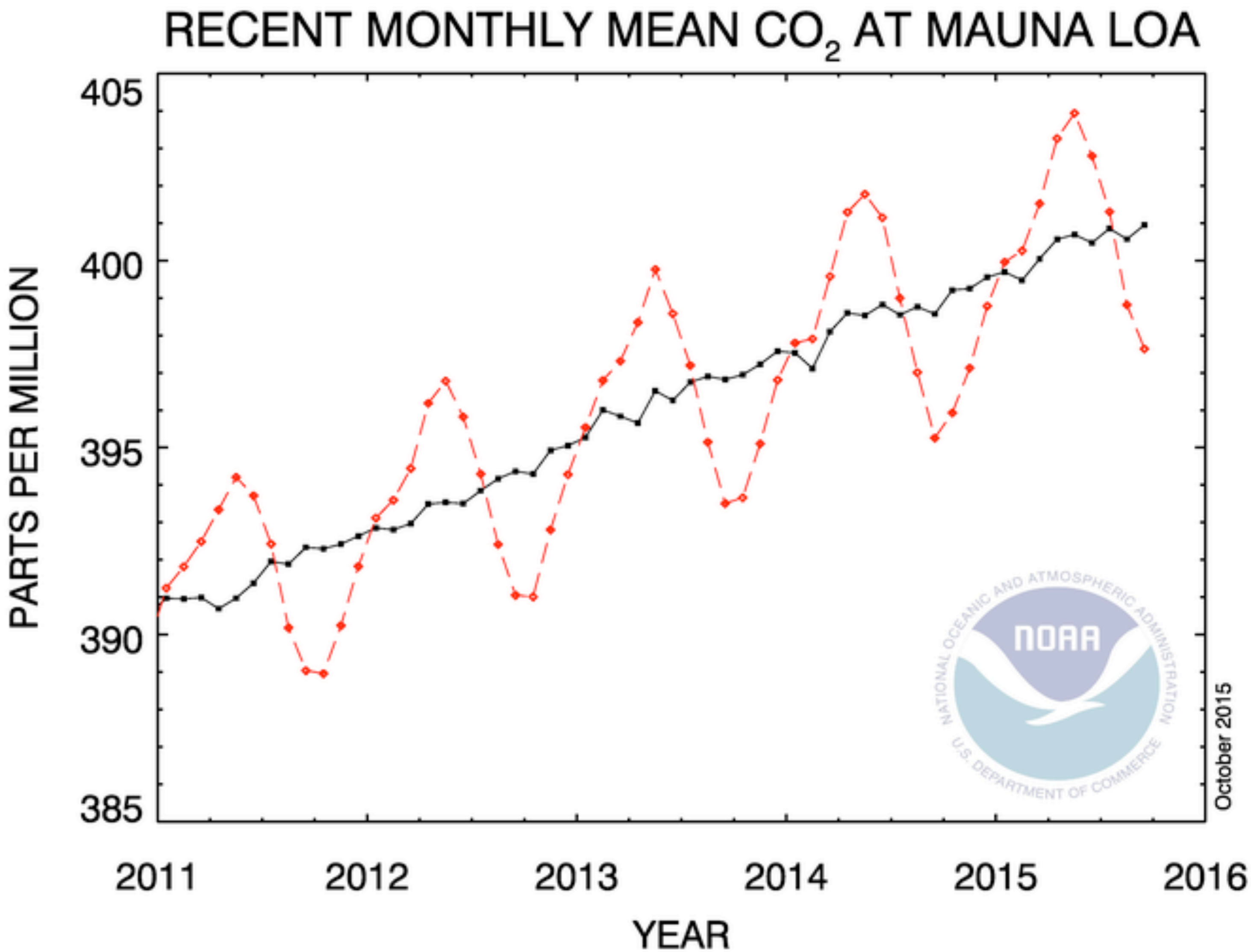
Global Distribution of Atmospheric Carbon Dioxide

NOAA CMDL Carbon Cycle Greenhouse Gases

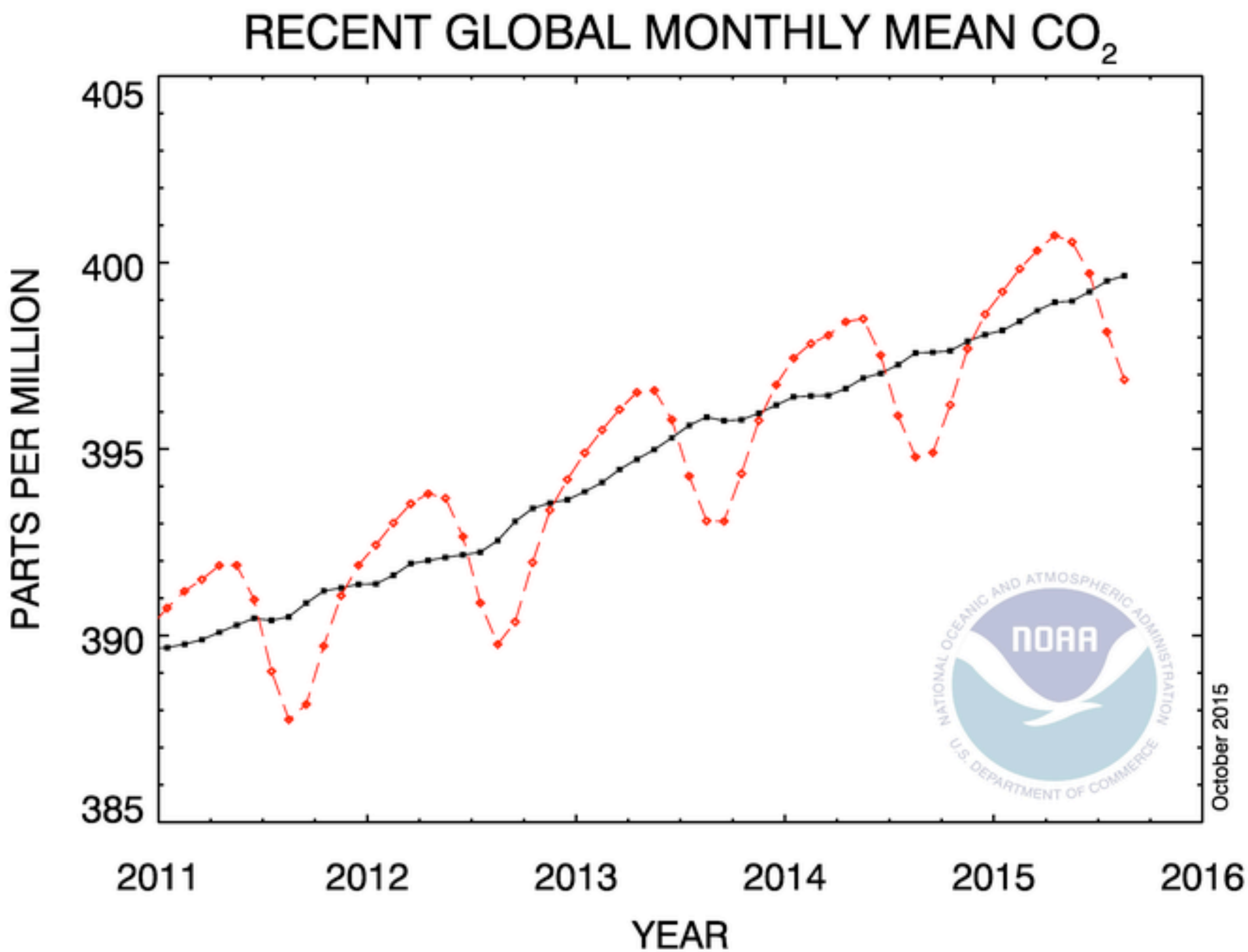


Three dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the NOAA CMDL cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Principal investigators: Pieter Tans and Thomas Conway, NOAA CMDL Carbon Cycle Greenhouse Gases, Boulder, Colorado, (303) 497-6678 (ptans@cmdl.noaa.gov, http://www.cmdl.noaa.gov/ccgg).

http://www.esrl.noaa.gov/gmd/ccgg/trends/



http://www.esrl.noaa.gov/gmd/ccgg/trends/



Atmosphere is a C reservoir with inflow and outflow

Steady state: inflow = outflow, amount of C in reservoir is constant

Is the atmosphere at steady state wrt C cycle

…on an annual basis?

…on a longer-term basis?

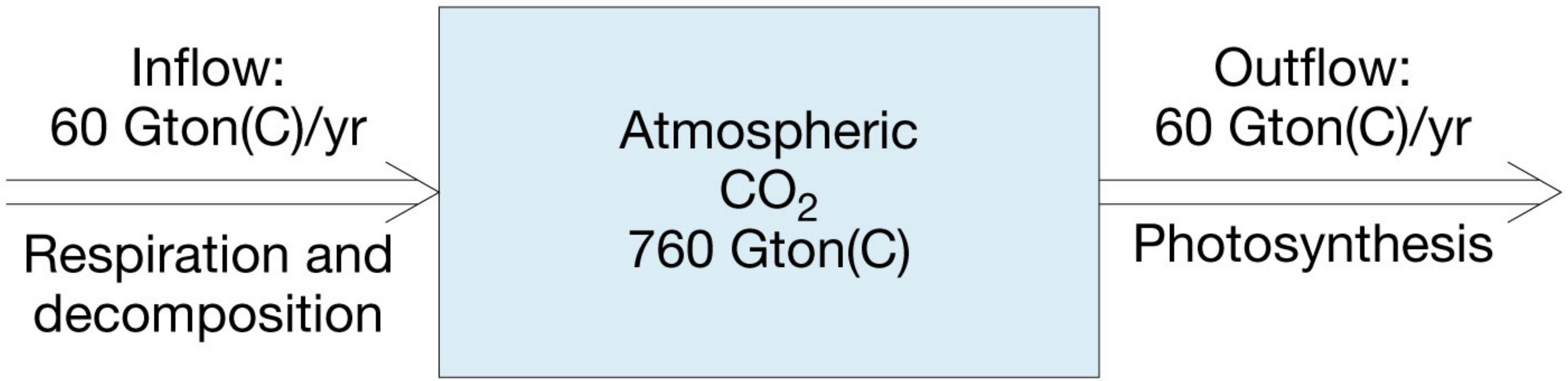
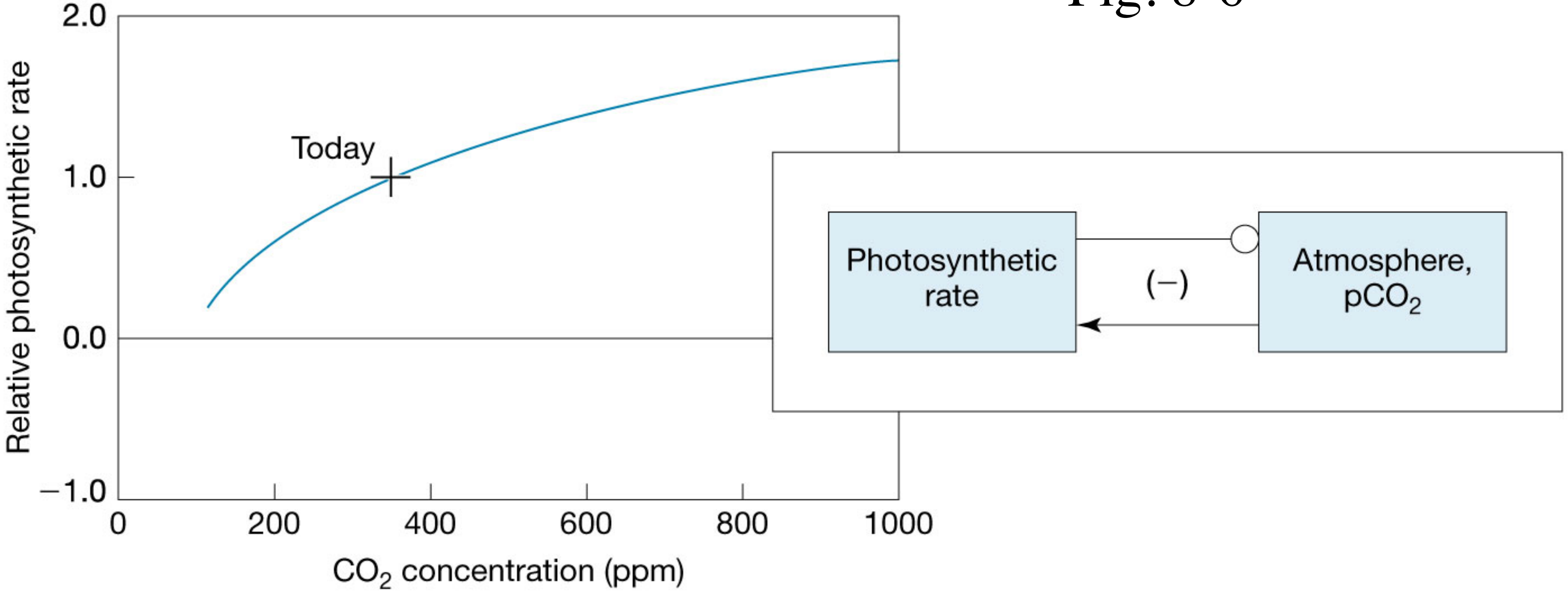


Fig. 8-5

Feedback loop for increased CO_2 inflow to atmosphere:

Fig. 8-6



…but what happens when you burn rainforests…

At steady state:

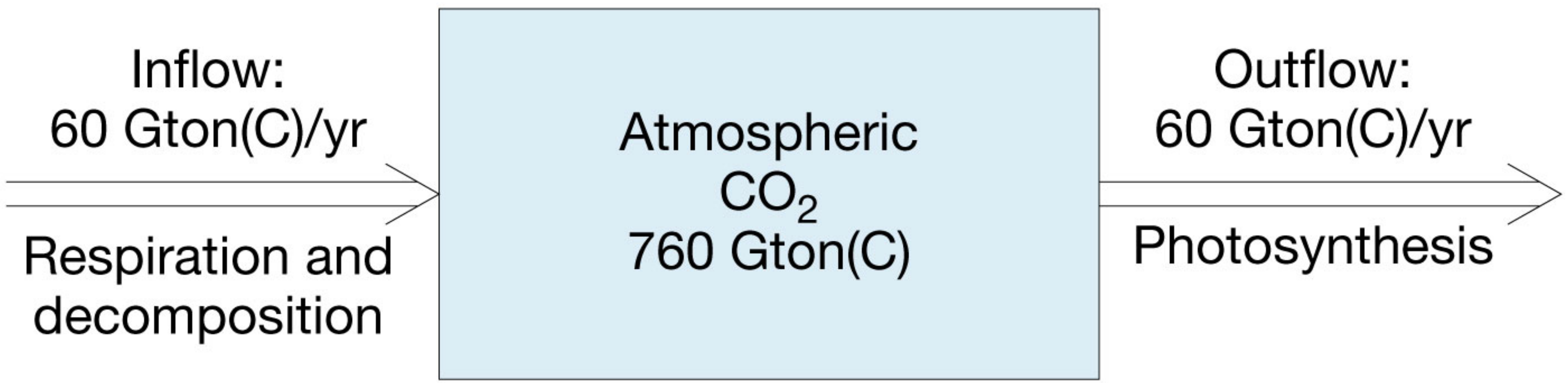
Residence time = reservoir size/inflow rate or outflow rate

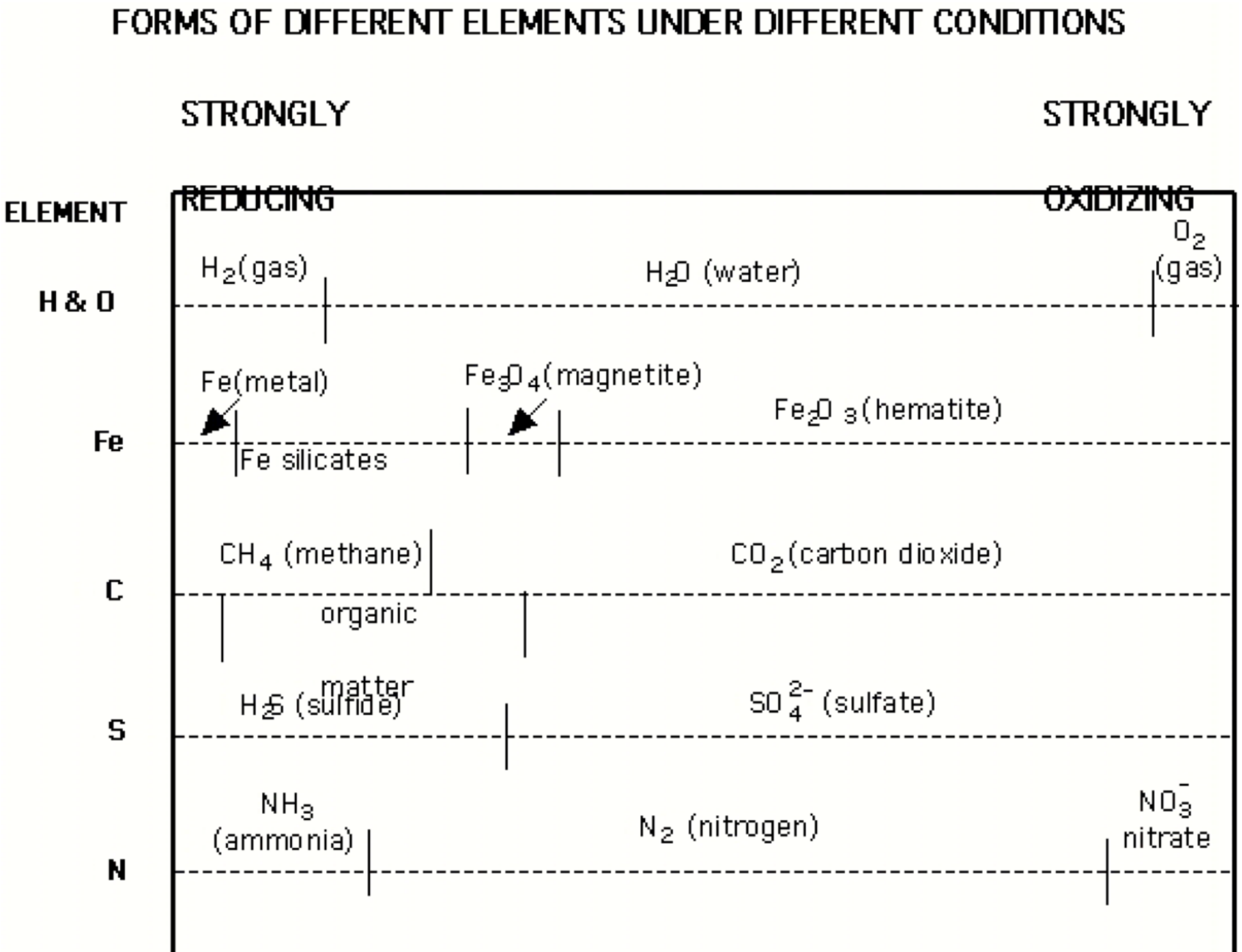
760 Gton C/ 60 Gton C = 12.7 years

12.7 years is the *average* length of time a C atom spends in the atmosphere with respect to plant growth and decay only!

(analogous to half-life)

If no steady state " residence time" is called "characteristic response time"--a useful concept




FORMS OF DIFFERENT ELEMENTS UNDER DIFFERENT CONDITIONS
STRONGLY REDUCING
STRONGLY OXIDIZING
ELEMENT
H & O
H_2(gas)
H_2O (water)
O_2 (gas)
Fe
Fe(metal)
Fe silicates
Fe_3O_4(magnetite)
Fe_2O_3(hematite)
C
CH_4 (methane)
organic matter
CO_2(carbon dioxide)
S
H_2S (sulfide)
SO_4^{2-} (sulfate)
N
NH_3 (ammonia)
N_2 (nitrogen)
NO_3^- nitrate

Oxidation Is Loss (of electrons)

Reduction Is Gain (of electrons) = OIL RIG

$CH_2O + O_2 \rightarrow H_2O + CO_2$ (Oxidation of carbon!)

$0.5O_2 + CH_2O \rightarrow 2H^+ + 2e^- + CO_2$

Where do the electrons go? To oxygen:

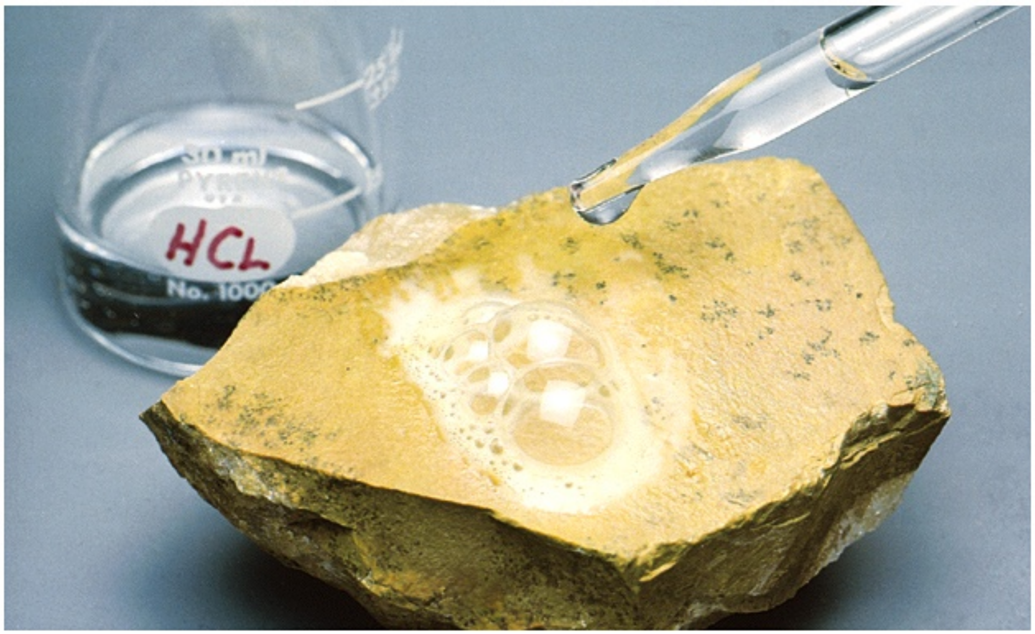
$0.5O_2 + 2e^- + 2H^+ \rightarrow H_2O$

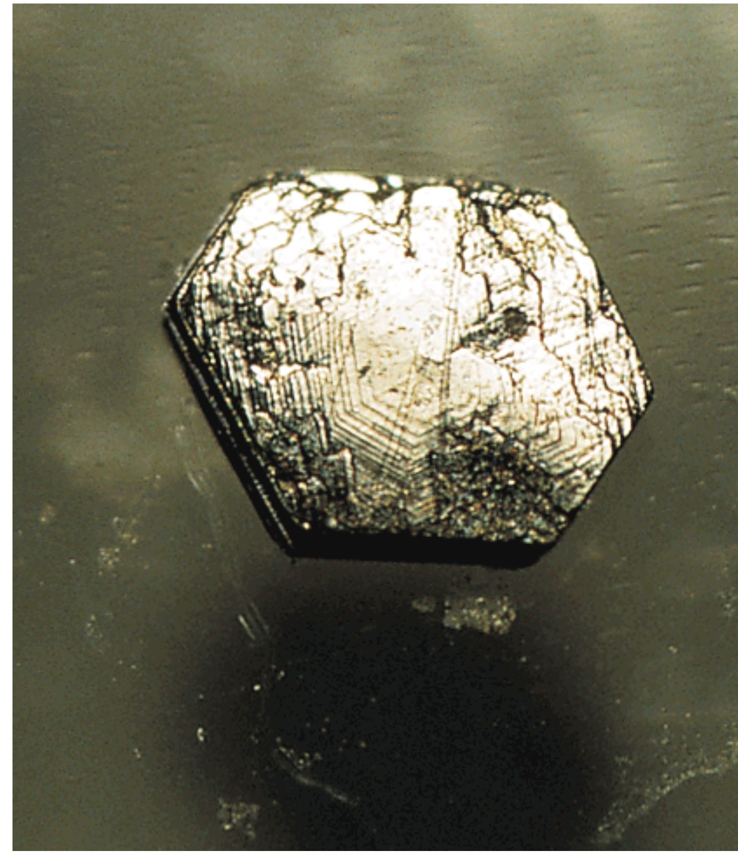
Oxidized (combined with O):

- CO_2
- carbonate (CO_3^{2-})

Reduced (combined with C, H, N, etc.)

Which mineral has:
oxidized C
reduced C?





+light

$$H_2O + CO_2 \rightarrow CH_2O + O_2$$

Organic matter

Short-term **terrestrial**
Organic C cycle

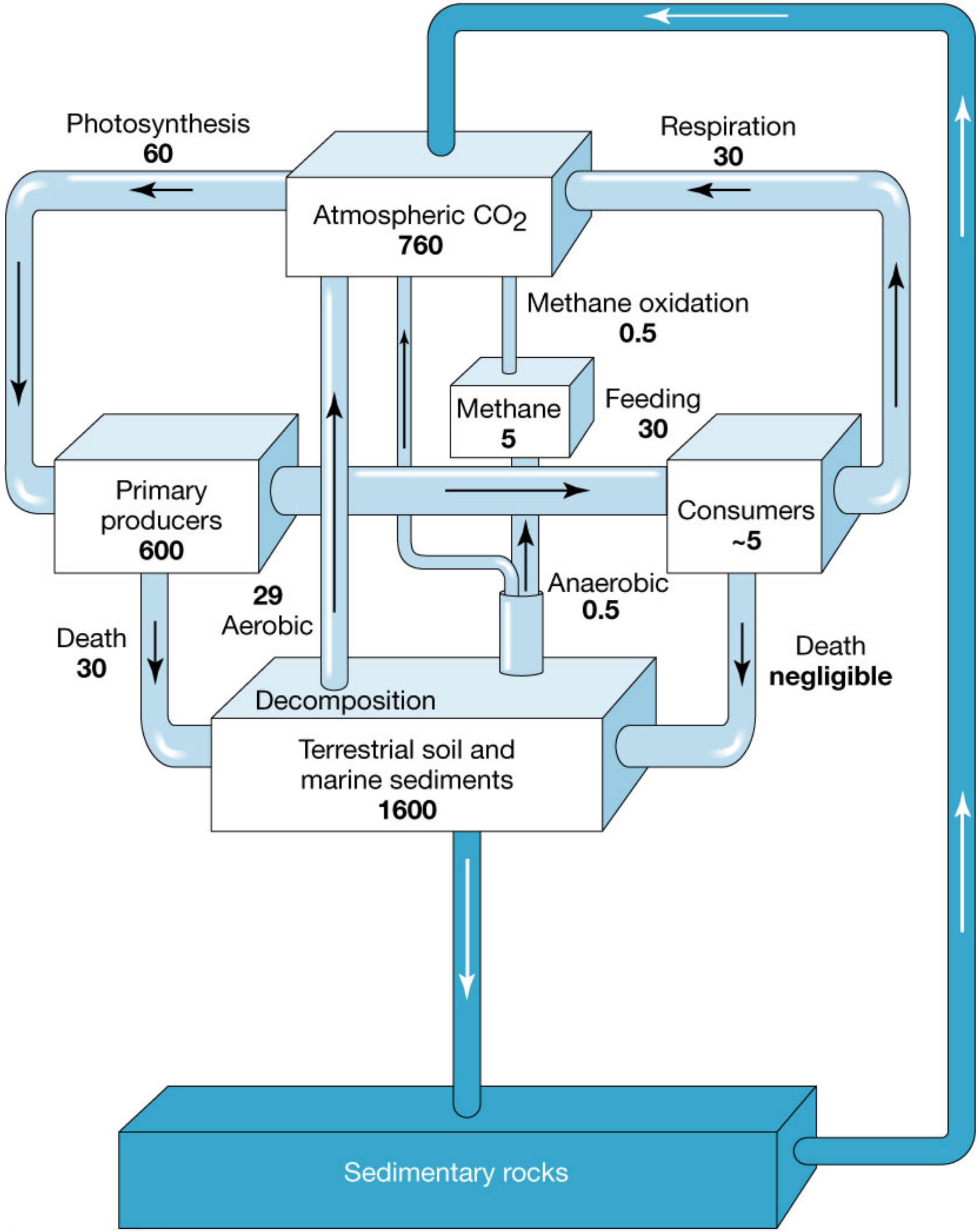


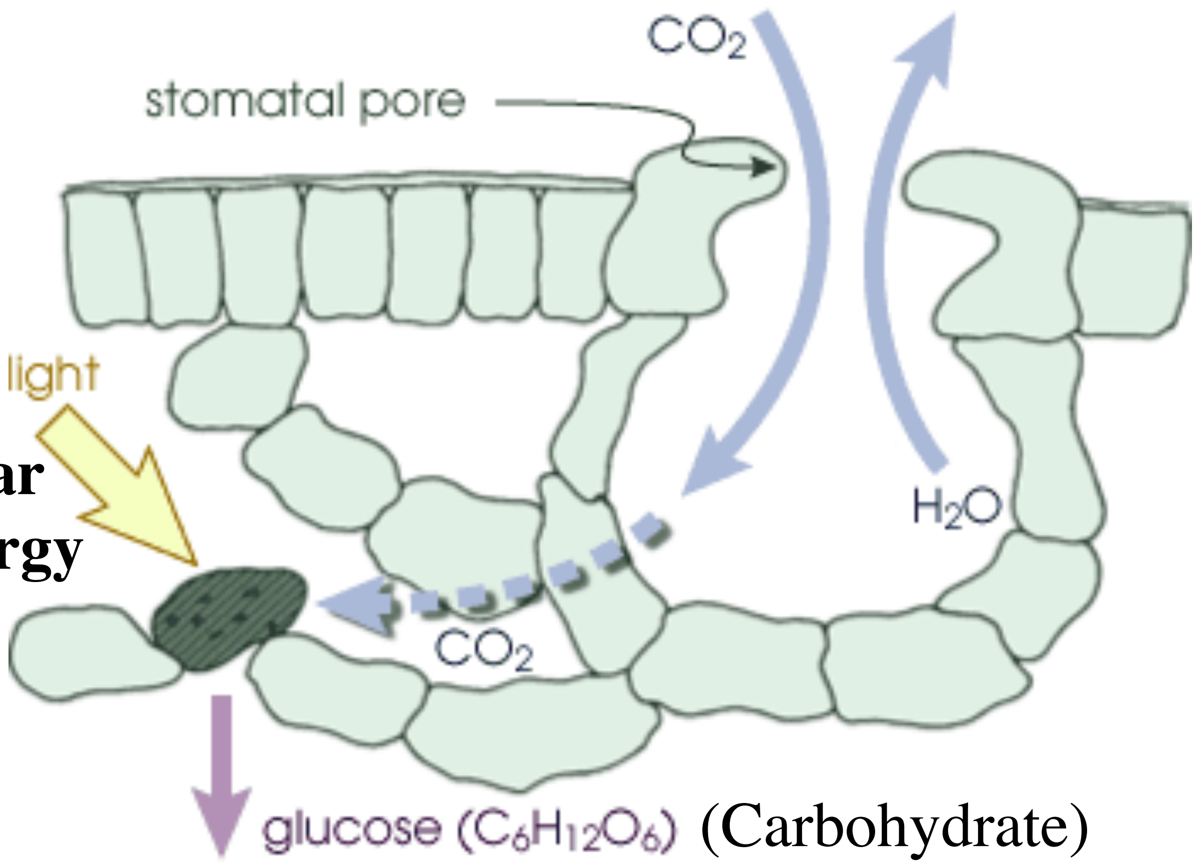
Fig. 8-7

Short-term terrestrial organic C cycle

1. Inorganic C (atm. CO_2) --> organic C by photosynthesis:

$$CO_2 + H_2O = CH_2O + O_2$$

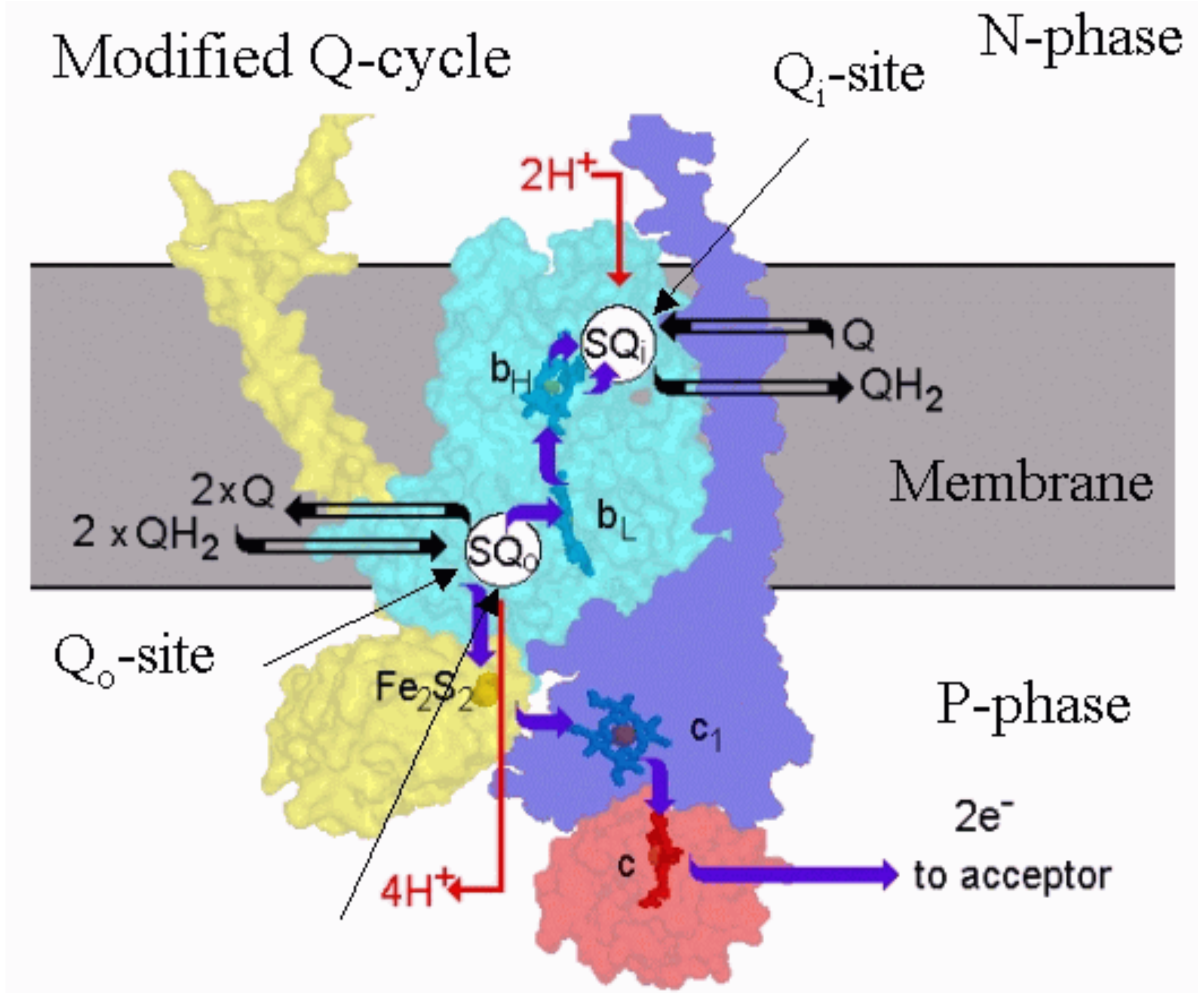
Solar energy



(Carbohydrate)

Primary productivity: amount of organic matter made by photosynthesis in a unit time in a unit area of Earth surface

Ubiquinol:cytochrome c oxidoreductase (bc1 complex)



This group of electron transfer enzymes (known as bc1 complexes in mitochondria, bacterial respiratory chains and photosynthetic bacteria, or b6f complexes in the photosynthetic chains of photosynthesis) carries the main flux of energy through the biosphere. The annual synthesis (and consumption) of biomass in the biosphere represents a storage of energy 20–100 fold greater than all human energy usage, including fossil fuels and nuclear power. Because of inefficiencies in energy conversion, the flux in the biosphere is about 1000–fold greater than that through all anthropogenic processes.

Photosynthesis leads to formation of ***biomass***: organic C in living organisms. Includes ***primary producers*** and ***consumers***. (*What parts of plants store most terrestrial plant biomass? What is their residence time? How does consumer biomass compare to primary producer biomass?)*

2. Ways of consuming/decomposing carbohydrate:

a. Respiration: process releasing E for metabolism

$$CH_2O + O_2 \dashrightarrow CO_2 + H_2O$$

Happens slowly abiotically, is catalyzed by enzymes biotically

Reaction occurs in plants, animals and aerobic bacteria

2. Ways of consuming/decomposing carbohydrate:
b. Methanogenesis: anaerobic metabolism (below surface)

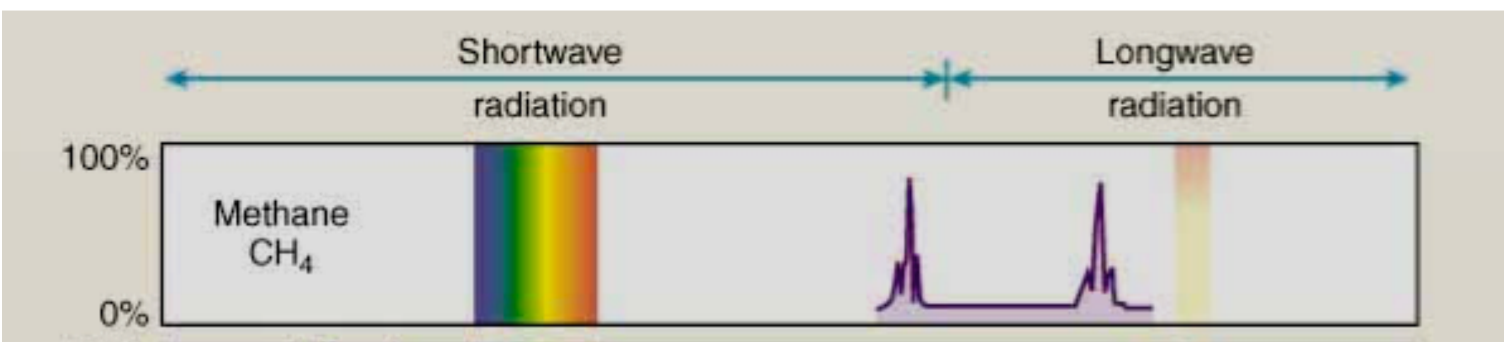
$$CH_2O \dashrightarrow CO_2 + CH_4$$

Methane is unstable in air: it combines with O_2 to make CO_2
(mostly by reaction with photochemically produced OH radicals)

What is the residence time of methane in the atmosphere?

amount of methane in atm = 5 Gton C

amount supplied by methanogenesis = 0.5 Gton C/yr



wavelength

Marine organic carbon cycle (short time scale)

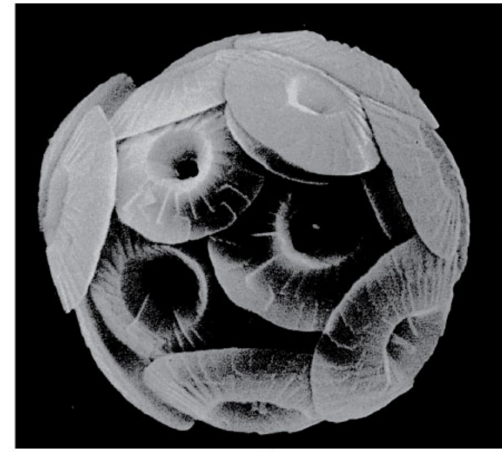
Primary producers: Phytoplankton, including diatoms, coccolithophorids, other plankton living in photic zone (top ~100 m, surface ocean)

Consumers: Zooplankton, including foraminifera, radiolarians, consume phytoplankton, produce fecal pellets. This, other organic matter settles, decomposes as it settles.

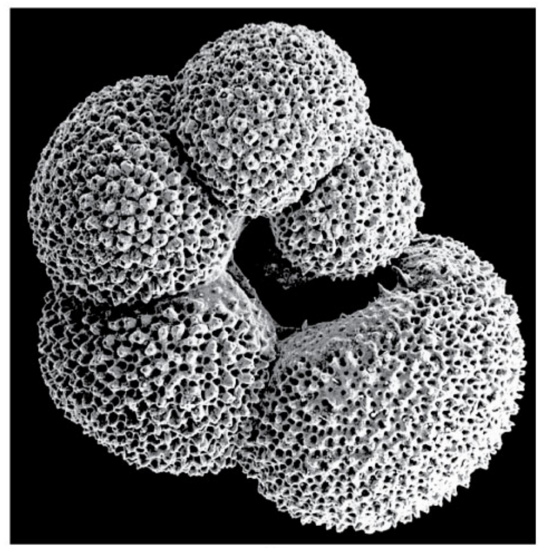
Diatom

(a)

Coccolith

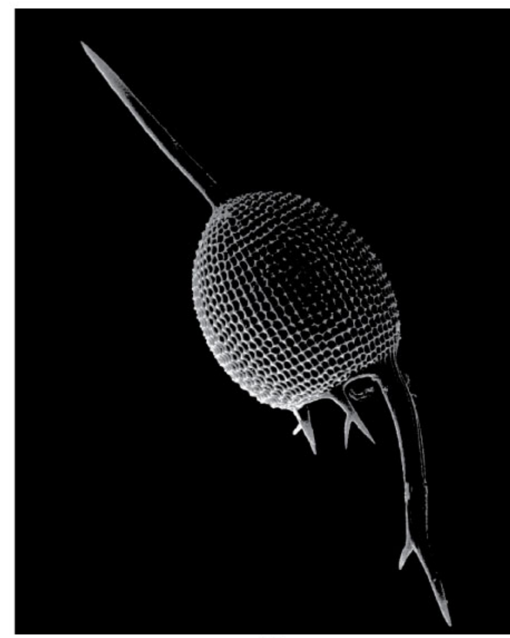


(b)



(c)

Foram (carbonate)

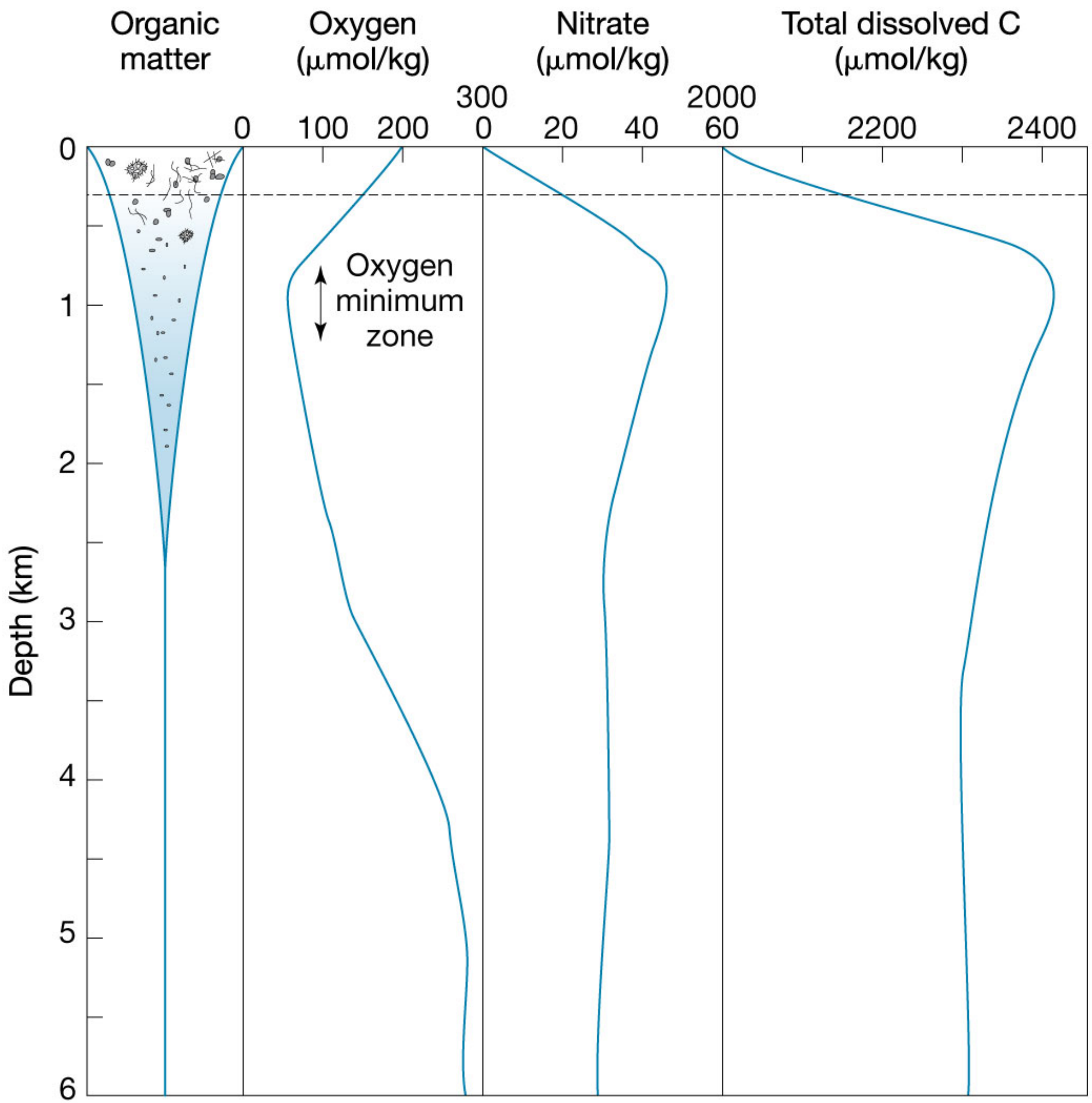


(d)

Radiolarian (silica)

Ocean circulation again!

- O rich surface waters
- Decomposition increases nutrients
- Aerobic decomposers use O, produce CO_2
- Deep cold water dissolves more O_2 than warm water where it originates as polar surface water
- Only about 0.1% of org. matter that settles gets preserved in marine sediments



Box 8-1

Biological pump:

Surface waters:
Depleted in C, N, P nutrients

Phytoplankton need
C:N:P in 106:16:1 ratio
Redfield ratios! Stray to far from these ratios, biological productivity falls.

Seawater has close to this ratio

(Iron is 0.01 in above ratio scheme - and is sometimes the limiting nutrient!)

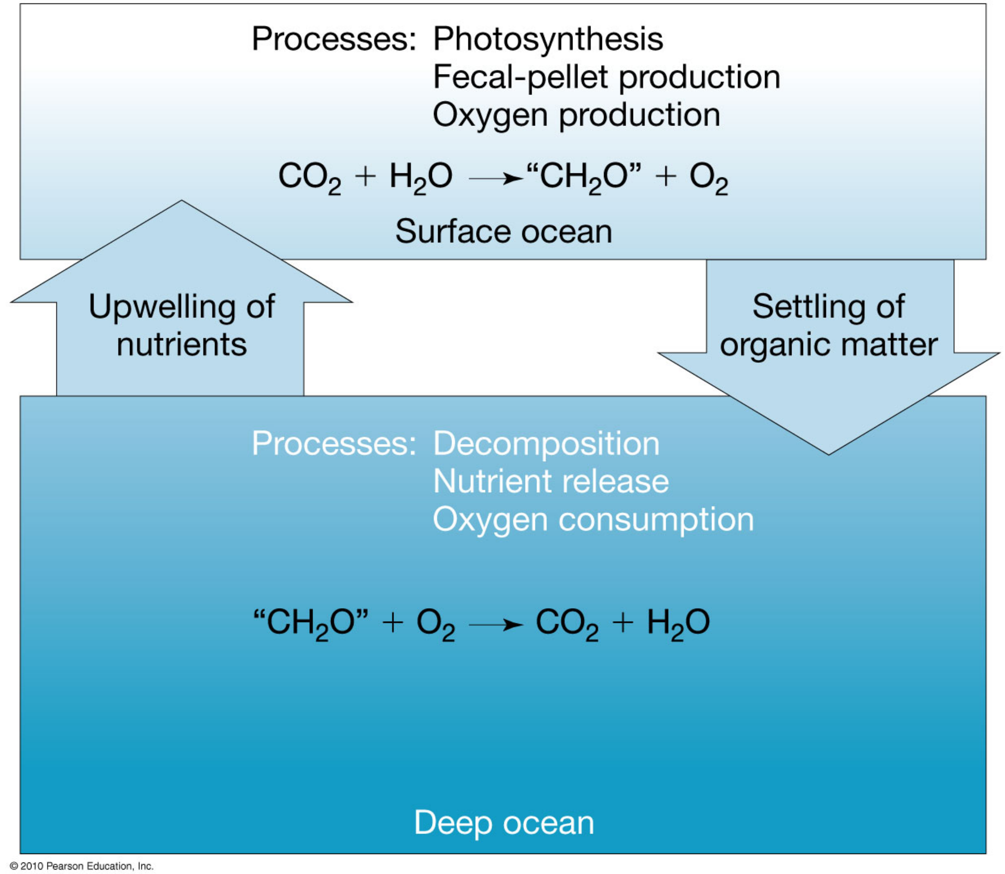
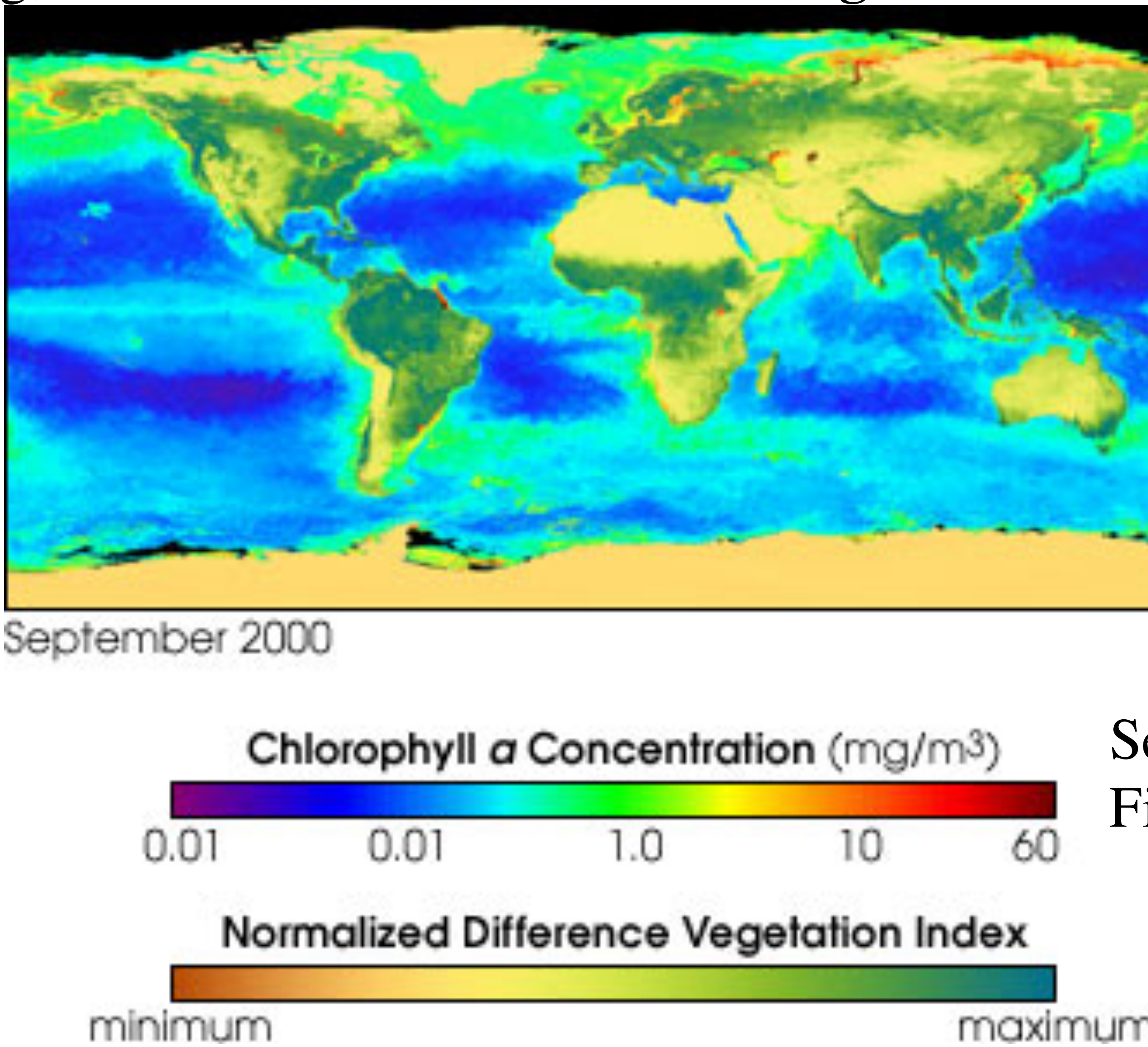


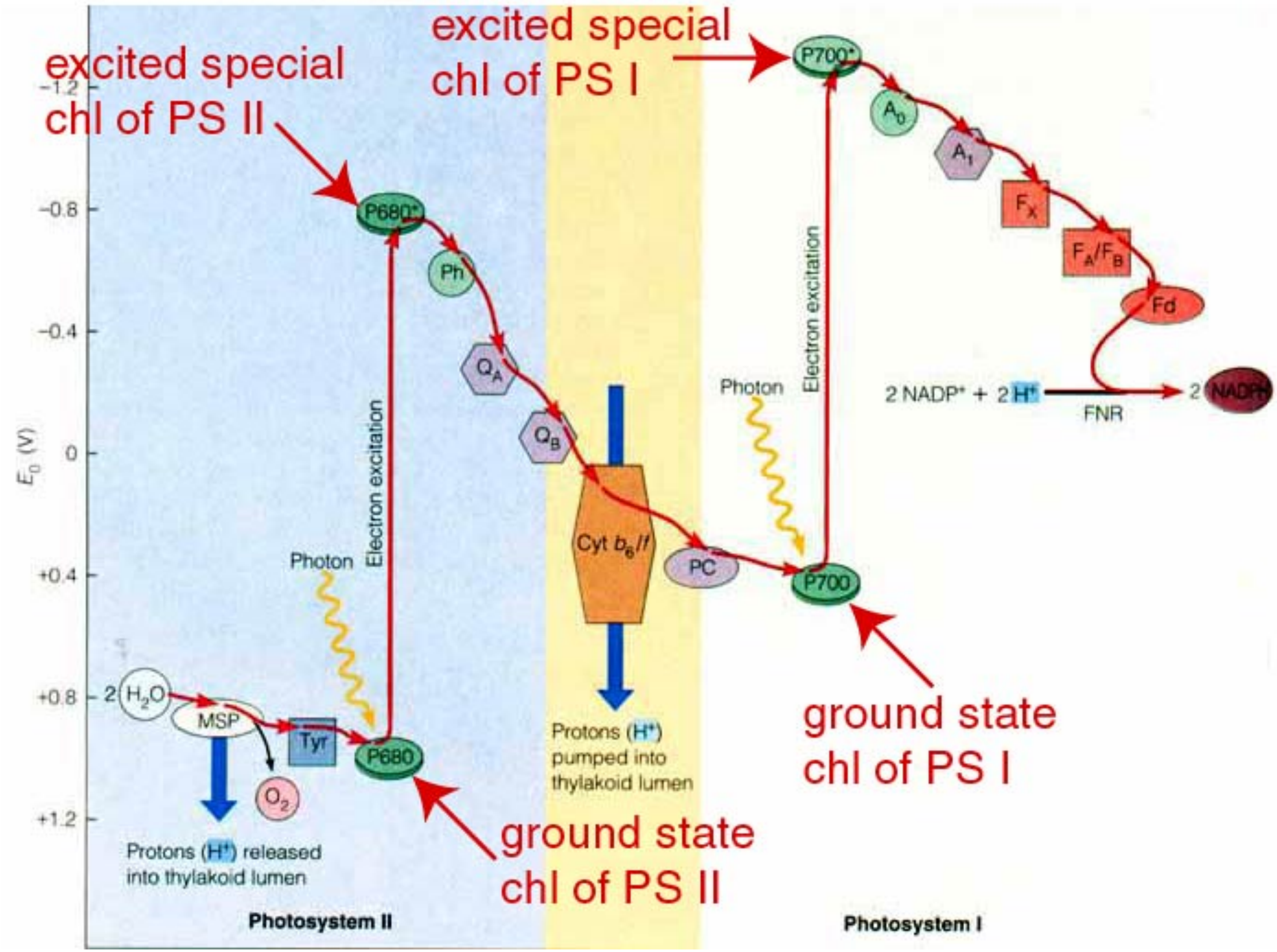
Fig. 8-9

Ocean color is a function of density of phytoplankton. Plankton are most abundant in high-latitude oceans, regions of upwelling, off river mouths. **What is limiting? Sun? *Nutrients*? T?**



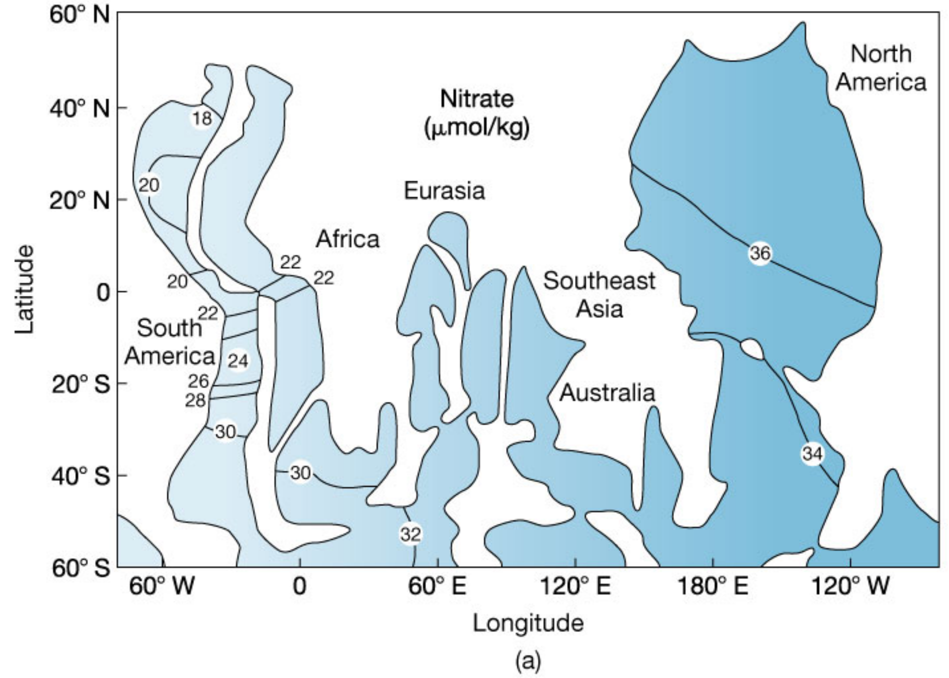
See Fig. 5-13, Fig. 8-10

Plants also take a "tandem" approach:



Which ocean has highest nutrients? Why?

Deep ocean (4 km) nitrate



Why is Pacific so depleted in O_2?

What equation expresses this?

Deep ocean (4 km) O_2

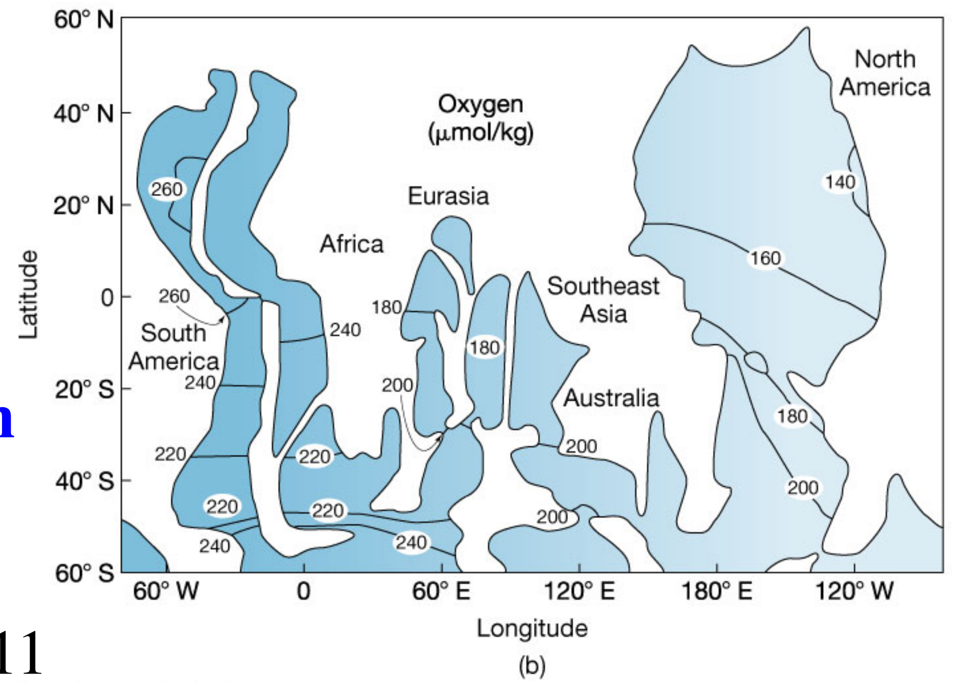


Fig. 8-11

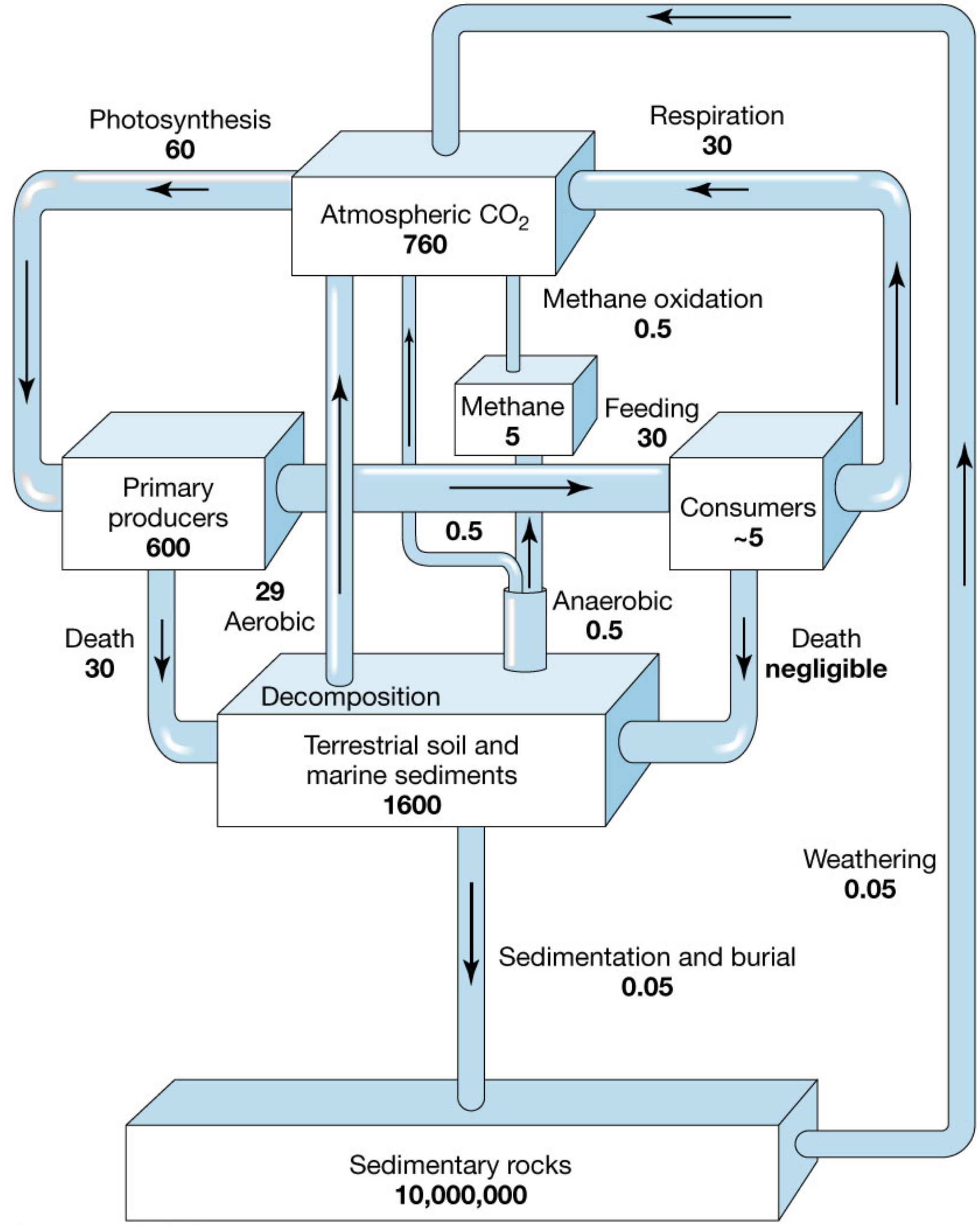
Long-term organic C cycle

Organic C is buried in sedimentary basins

Buried and lithified

Coal, petroleum forms
(<0.1% buried C is economic)
(<1% of avg. sed. Rock is organic matter)

Weathering
oxidation by air, water
CO_2 produced
(same as respiration)



Inorganic C cycle involves atmosphere, oceans, sediments, sed. rocks.

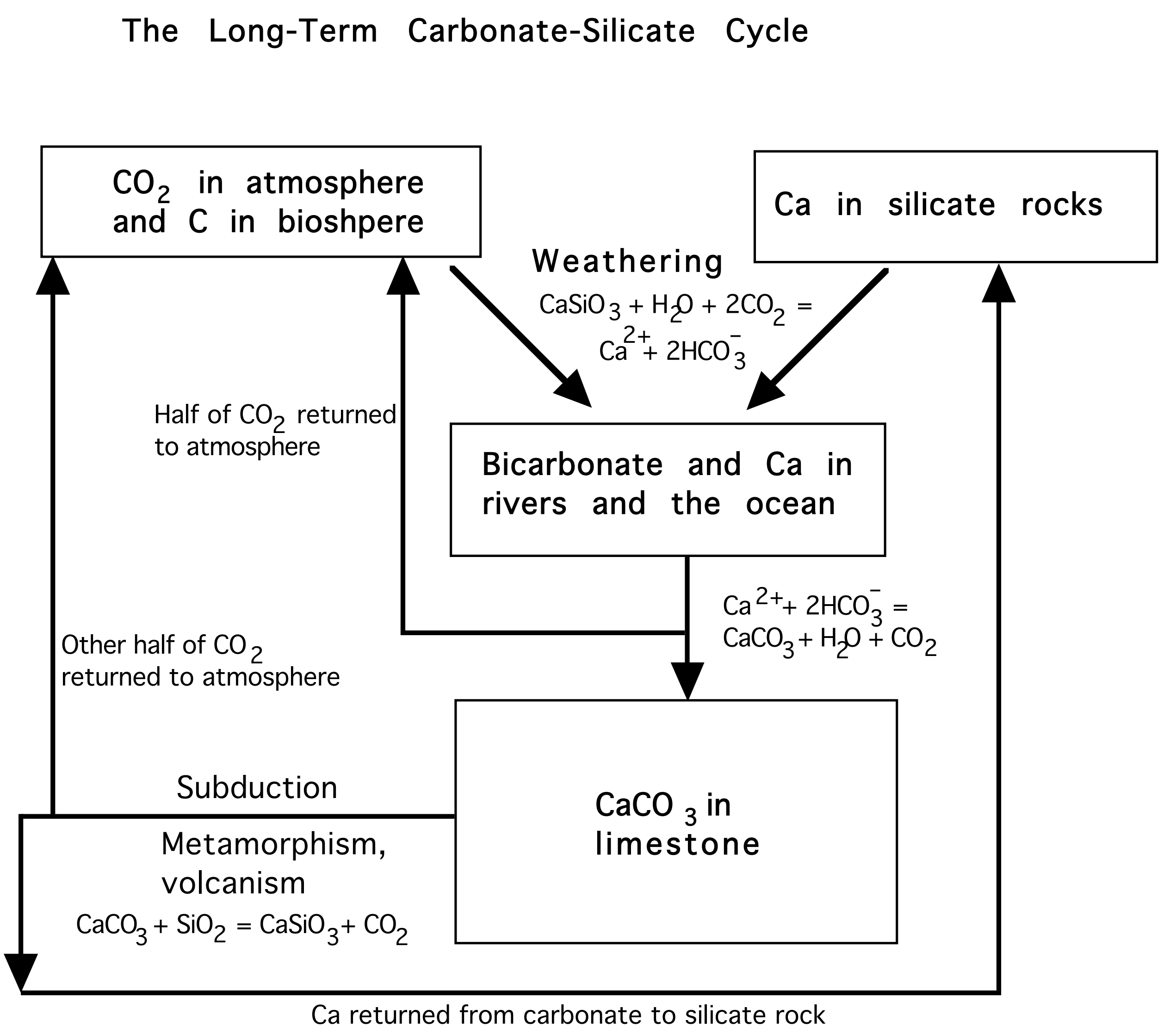
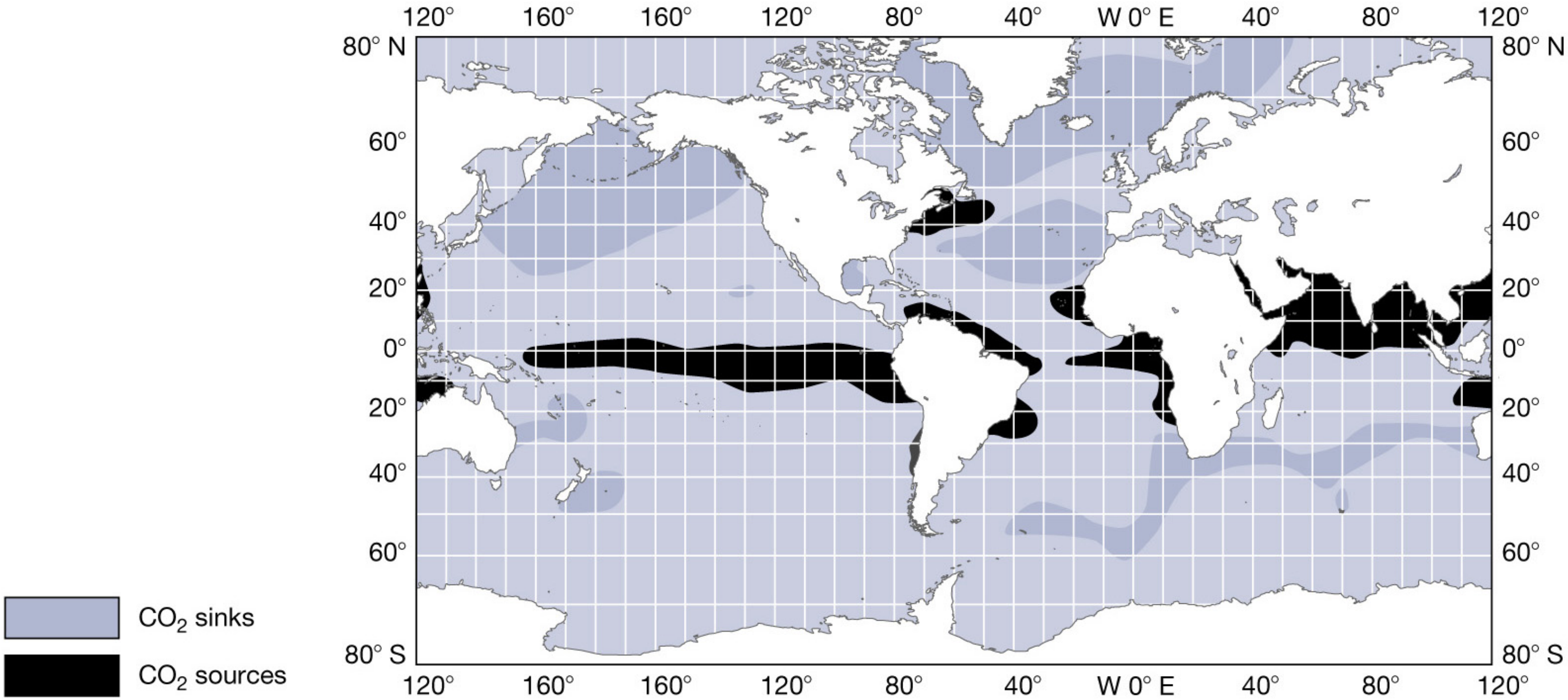


Fig. 8-16

Inorganic C cycle

involves ocean, sediments, & sedimentary rocks, mainly limestone

1. Exchange between ocean and atmosphere



2. Dissolution of CO_2 in water:

$CO_2 + H_2O <--> H_2CO_3$

$H_2CO_3 <--> H^+ + HCO_3^-$

$HCO_3^- <--> H^+ + CO_3^{2-}$

Vocab: reactants, products
anions, cations
chemical equilibrium
carbonate ion, bicarbonate ion

What do these reactions have to do with pH?

3. Perturbations of the system by addition of atm. CO_2:

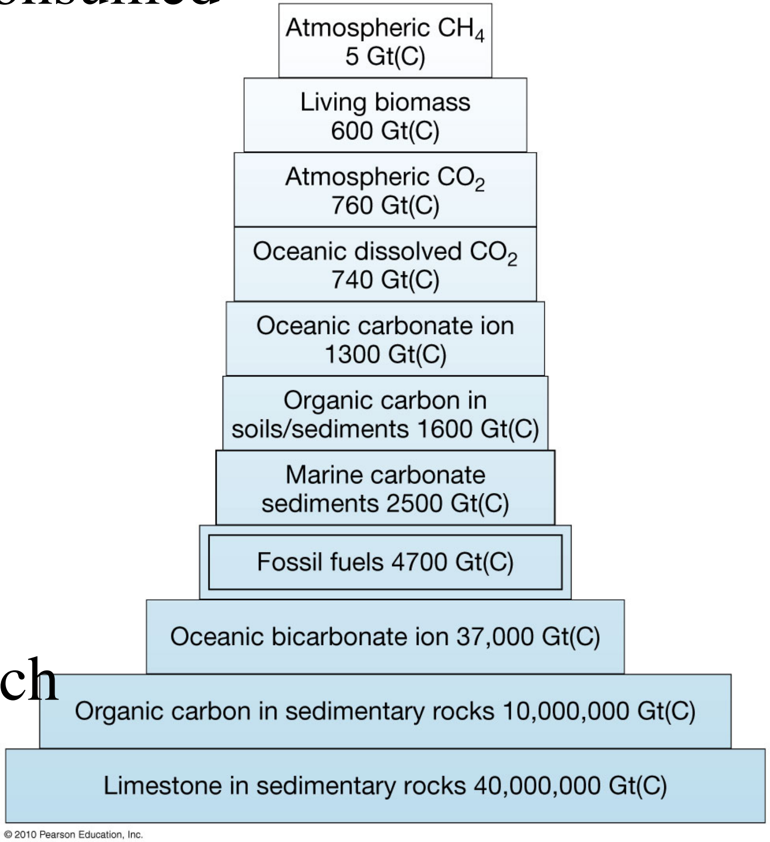
$CO_2 + H_2O \rightarrow H_2CO_3$ more carbonic acid is made

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ carbonic acid dissociates, H^+ produced

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$ excess H^+ consumed

Overall,
$CO_2 + H_2O + CO_3^{2-} \rightarrow 2\ HCO_3^-$

Ocean can take up some CO_2 simply by equilibration with atm.
and take up more by converting CO_2 to other forms of inorganic carbon (bicarbonate ion). But there is only so much CO_3^{2-} in the oceans (see Fig. 8-3).



Chemical weathering

Carbonate rock weathering:

$$CaCO_3 + H_2CO_3 \text{ ---> } Ca^{2+} + 2HCO_3^-$$

Silicate rock weathering:

$$CaSiO_3 + 2H_2CO_3 \text{ --> } Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$$

Dissolved ions from weathering are carried to the oceans, where carbonate mineral deposition takes place:

$2Ca^{2+} + 2HCO_3^- \dashrightarrow CaCO_3 + H_2CO_3$

(happens mainly biotically, also abiotically)

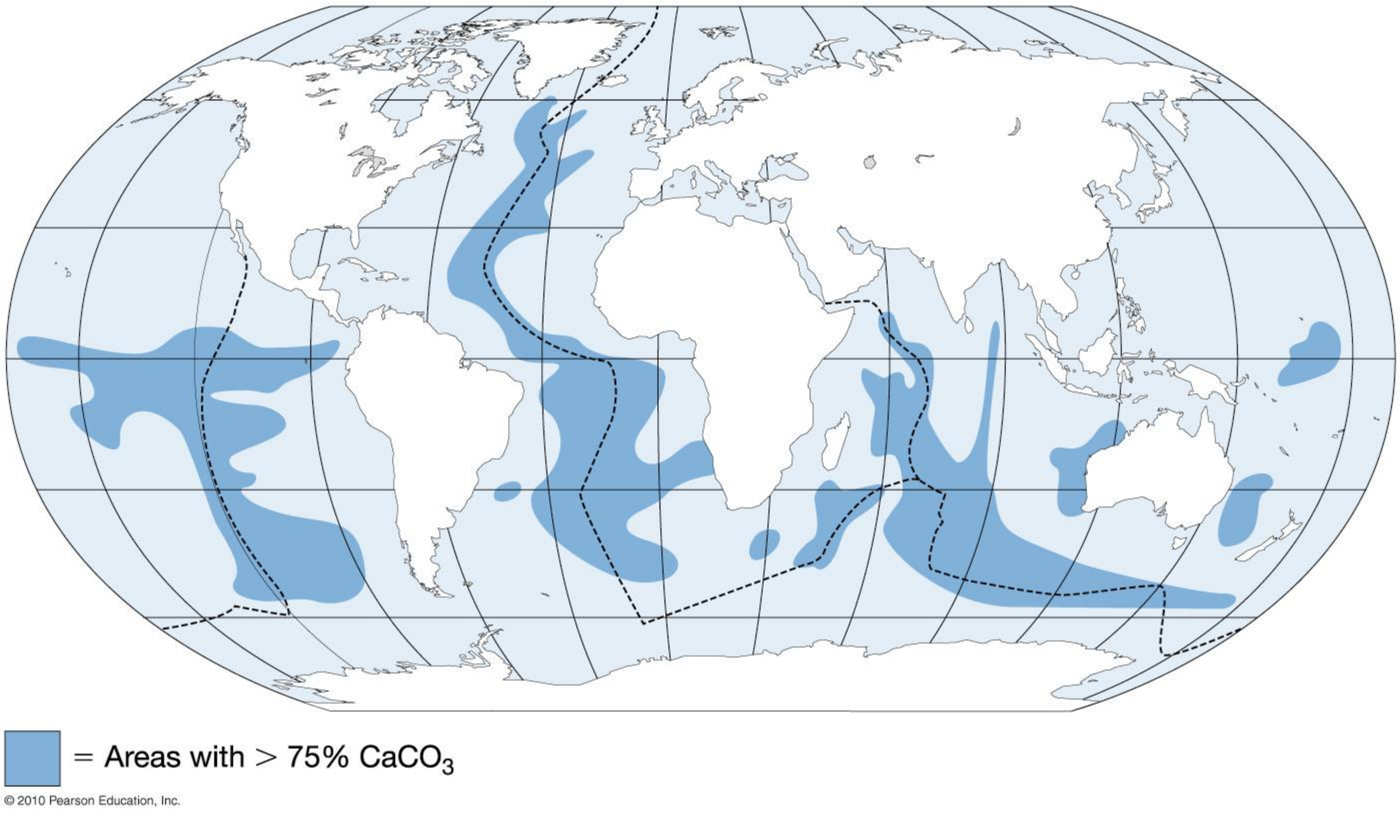


Fig. 8-15

Where does carbonate accumulate? Why?

Silicate rock weathering:

$$CaSiO_3 + 3H_2O + 2CO_2 \text{ --> } Ca^{2+} + 2HCO_3^- + + H_4SiO_4$$

A wollastonite crust is a literary device that captures the essentials of silicate weathering. Wollastonite breakdown yields:

calcium ions
bicarbonate ions
dissolved silica (in the form of silicic acid, H_4SiO_4)

Later these materials end up in the oceans where organisms use these materials to make shells:

$$Ca^{2+} + 2HCO_3^- \text{ --> } CaCO_3 + H_2O + CO_2$$

$$H_4SiO_4 \text{ --> } SiO_2 + 2H_2O$$

Eventually the calcite and quartz are returned to sea-floor sediment, and can be subducted:

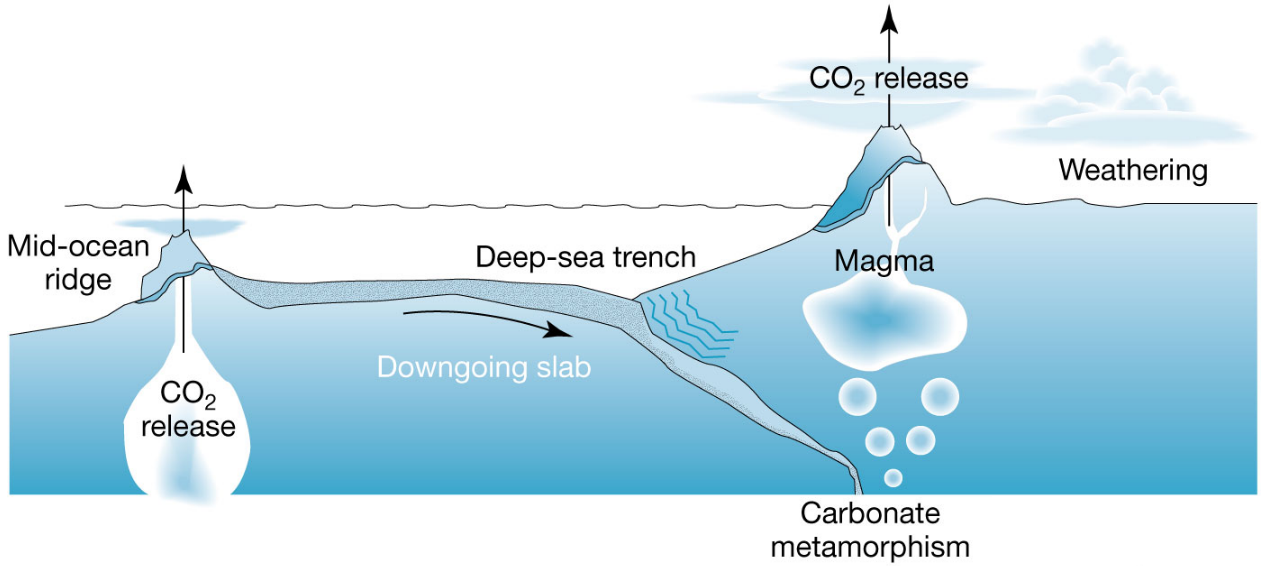


Fig. 8-17

Plate tectonics returns CO_2 to atm:

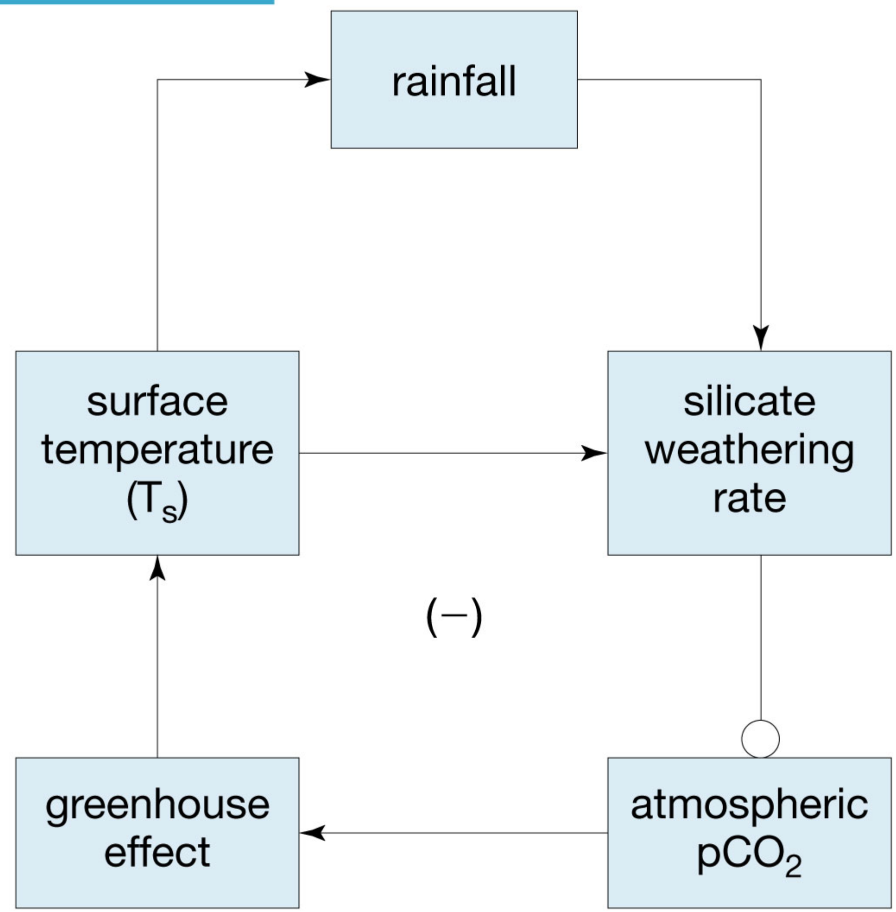
$CaCO_3 + SiO_2$-->

$CaSiO_3 + CO_2$

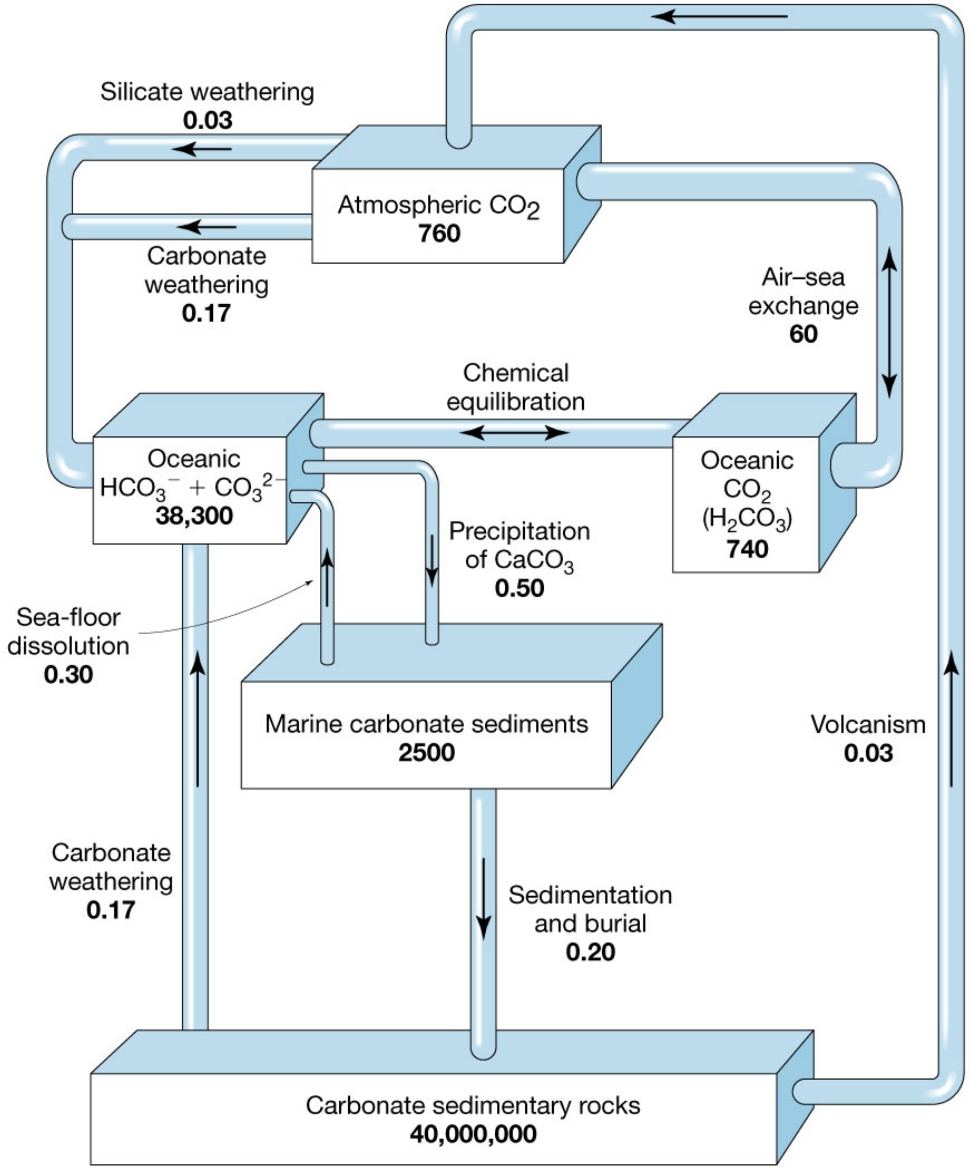
Rate of volcanism is insensitive to climate, but chemical weathering rate is:

$CaSiO_3 + 2H_2O + 2CO_2$ -->

$Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$



Large reservoirs, small fluxes: Long residence and response times



Which is a better way to remove CO_2 and lock it into rocks?

1. Weather carbonate rocks:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

2. Weather silicate rocks:

$$CaSiO_3 + H_2O + 2CO_2 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$$

3. Doesn't matter--both consume CO_2

Need to consider what happens next:

1. Weather carbonate rocks:

$$CaCO_3 + H_2O + CO_2 \text{ --> } Ca^{2+} + 2HCO_3^-$$

Then carbonate precipitates:

$$Ca^{2+} + 2HCO_3^- \text{ --> } CaCO_3 + H_2O + CO_2$$

Net result = 0

2. Weather silicate rocks:

$$CaSiO_3 + H_2O + 2CO_2 \text{ --> } Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$$

Then carbonate precipitates:

$$Ca^{2+} + 2HCO_3^- \text{ --> } CaCO_3 + H_2O + CO_2$$

Net result =

$$CaSiO_3 + CO_2 \text{ --> } CaCO_3 + SiO_2$$

(Uptake of CO_2 has a characteristic response time of ~1 My)

We don't have a wollastonite Earth…so how does silicate weathering really work?

1. Dissolution (ex. forsterite)

$Mg_2SiO_4 + 4CO_2 + 2H_2O = 2Mg^{2+} + 4HCO_3^- + (SiO_2)_{dissolved}$

2. Dissolution and oxidation (ex. forsterite)

$Fe_2SiO_4 + 0.5O_2 + 3H_2O = 2Fe(OH)_3 + (SiO_2)_{dissolved}$

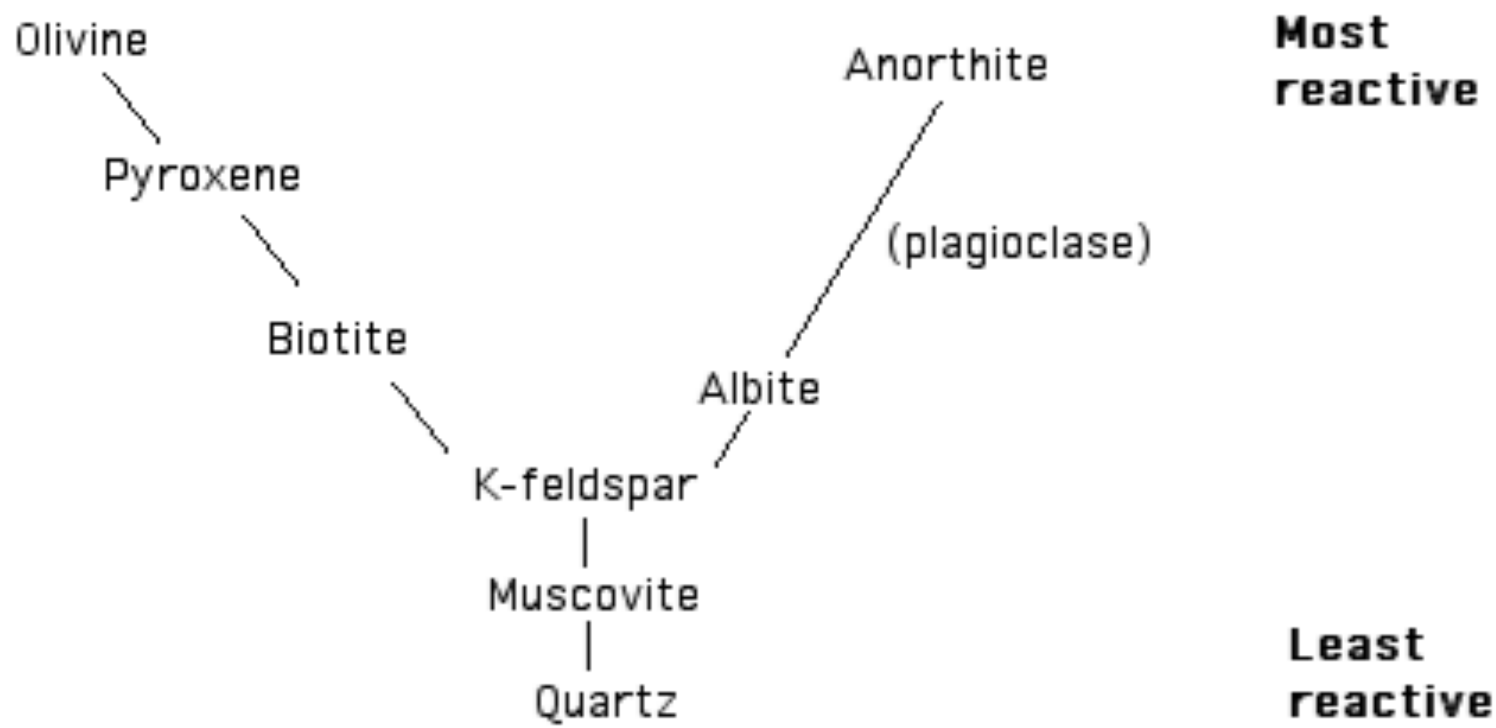
3. Dissolution plus ppt of a secondary mineral (ex. plagioclase)

$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 = Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$;

anorthite kaolinite

Cations (Ca, Na, Mg) go into solution,

Al, Fe, SiO_2 are retained as clay minerals or oxides



The products of weathering are:

- Unaltered primary minerals--dominantly quartz, plus some feldspars and micas.
- Clay minerals (and iron oxides) formed by alteration of primary minerals.
- Dissolved ions, notably calcium and bicarbonate, but also sodium, magnesium, sulfate and silica.

What rocks are formed from weathering products?

- Unaltered primary minerals (quartz) become sandstone.
- Clay minerals become shale.
- Dissolved calcium and bicarbonate become limestone.
- Sulfate and chloride (together with calcium and sodium) become evaporites. The common minerals of evaporites are gypsum ($CaSO_4 \bullet 2H_2O$) and halite (NaCl).
- Dissolved silica becomes chert (at least in part).

- Primary minerals (quartz) tend to be large and transported only where there are strong currents to move them, for example in a river channel or a beach environment.

- Clay minerals tend to form very fine particles, which remain in suspension where currents are strong. They are deposited where currents are weak (for example deep water).

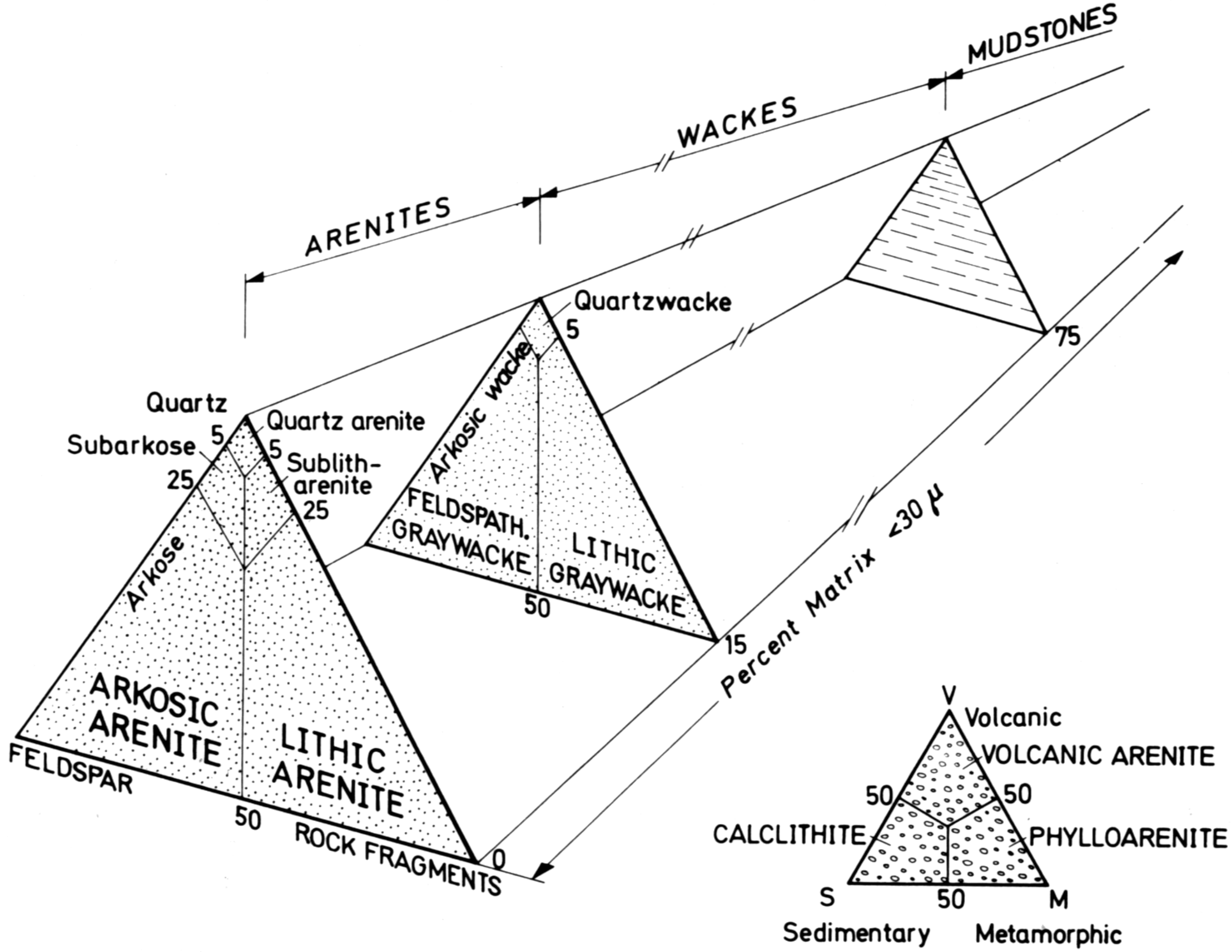
- Limestones are deposited where conditions favor the growth of organisms that secrete calcium carbonate shells. These are typically tropical shallow-water environments where there is little input of clastic sediment (clastic = from the mechanical breakup of other rocks), or planktonic (open ocean away from coasts) environments worldwide.

- Evaporites are deposited only where a suitable environment (semi-isolated basin or supratidal flat) is present in an arid tropical environment.

- Chert forms where silica skeletons of organisms accumulate

Products of weathering:

1. Primary minerals that survived weathering (sandstones)
2. Secondary minerals formed during weathering (shales)
3. Precipitates formed from the solutes released by weathering (limestones and evaporites)



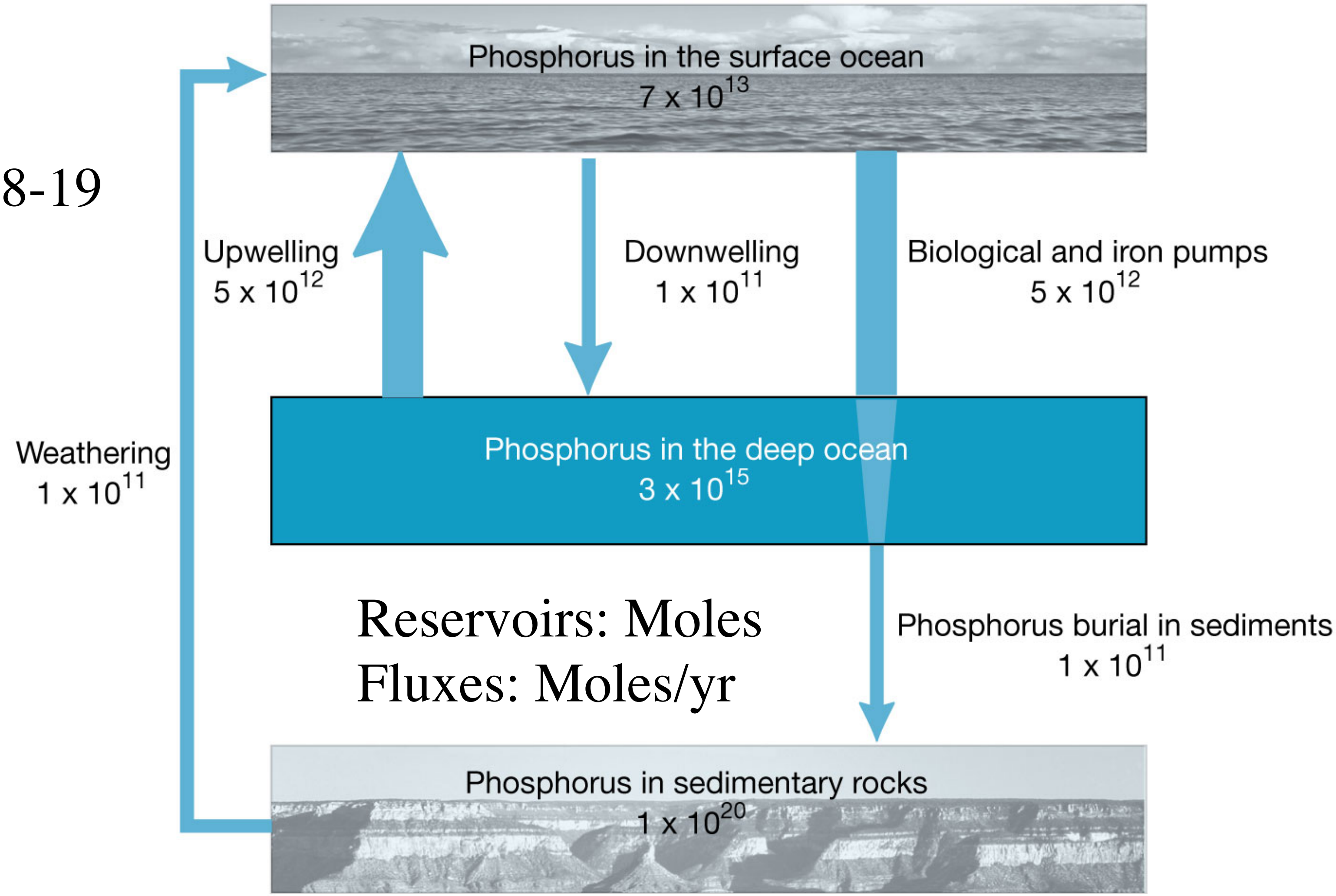
The relative proportions of sandstone:shale:limestone:evaporite in all the sedimentary rocks of the world is about **11:73:15:2**.

What determines these proportions?

Do you think these numbers correspond to what you see driving around the state? If not, why not?

Phosphorus cycle

Fig. 8-19



Reservoirs: Moles
Fluxes: Moles/yr

Strongly coupled to organic carbon cycle!

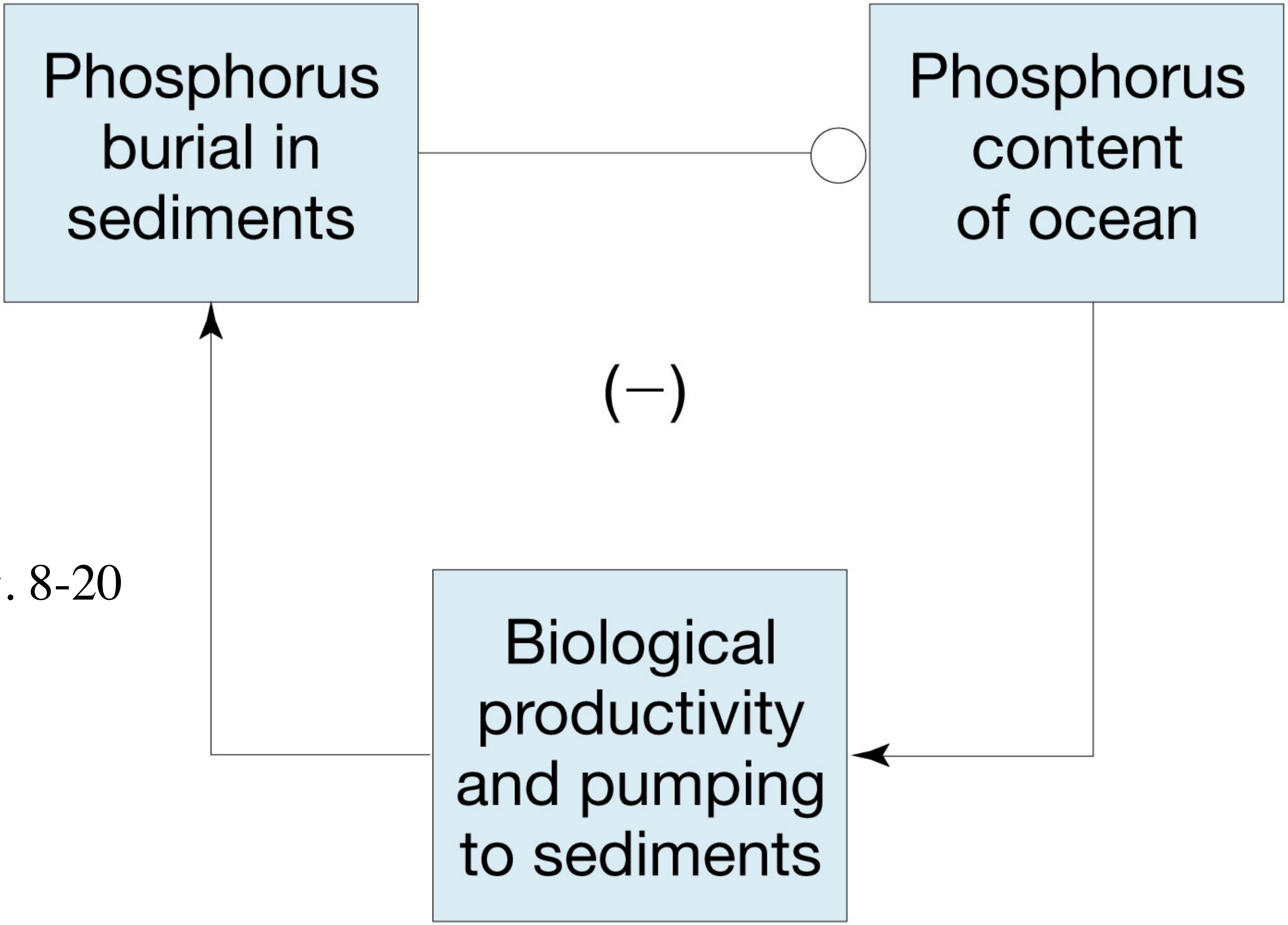

Phosphorus burial in sediments
Phosphorus content of ocean
(−)
Biological productivity and pumping to sediments

Fig. 8-20

Nitrogen cycle

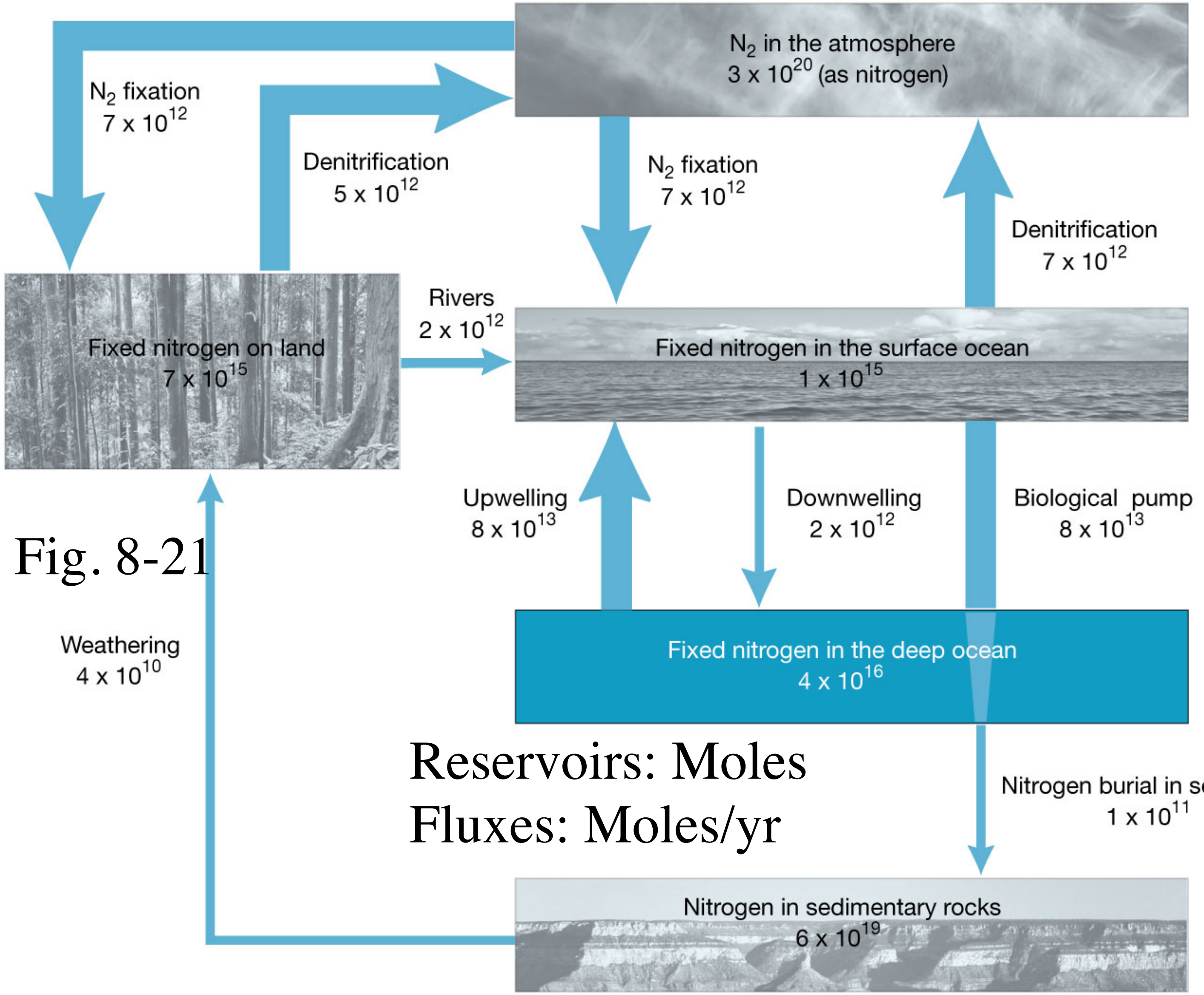
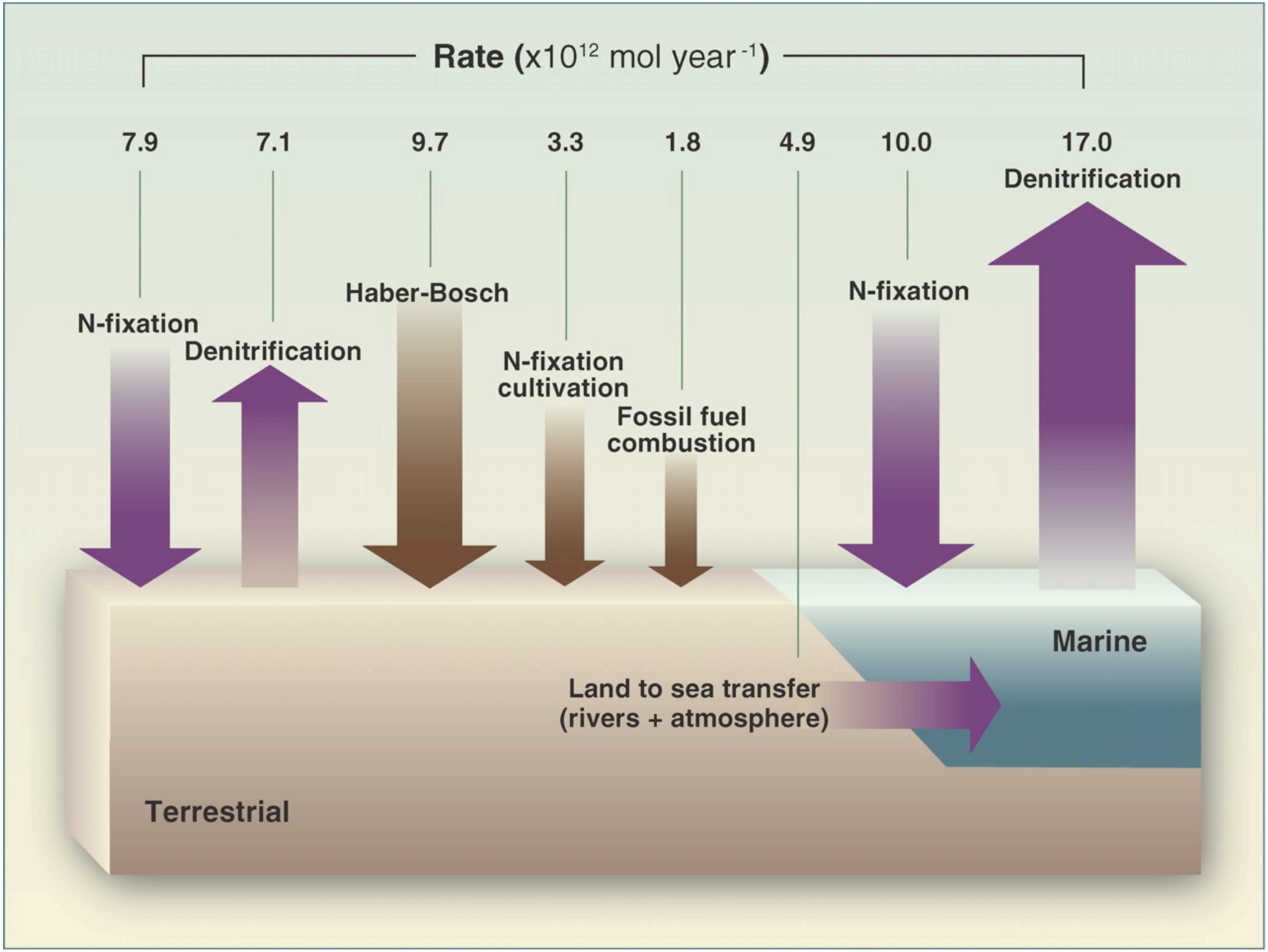


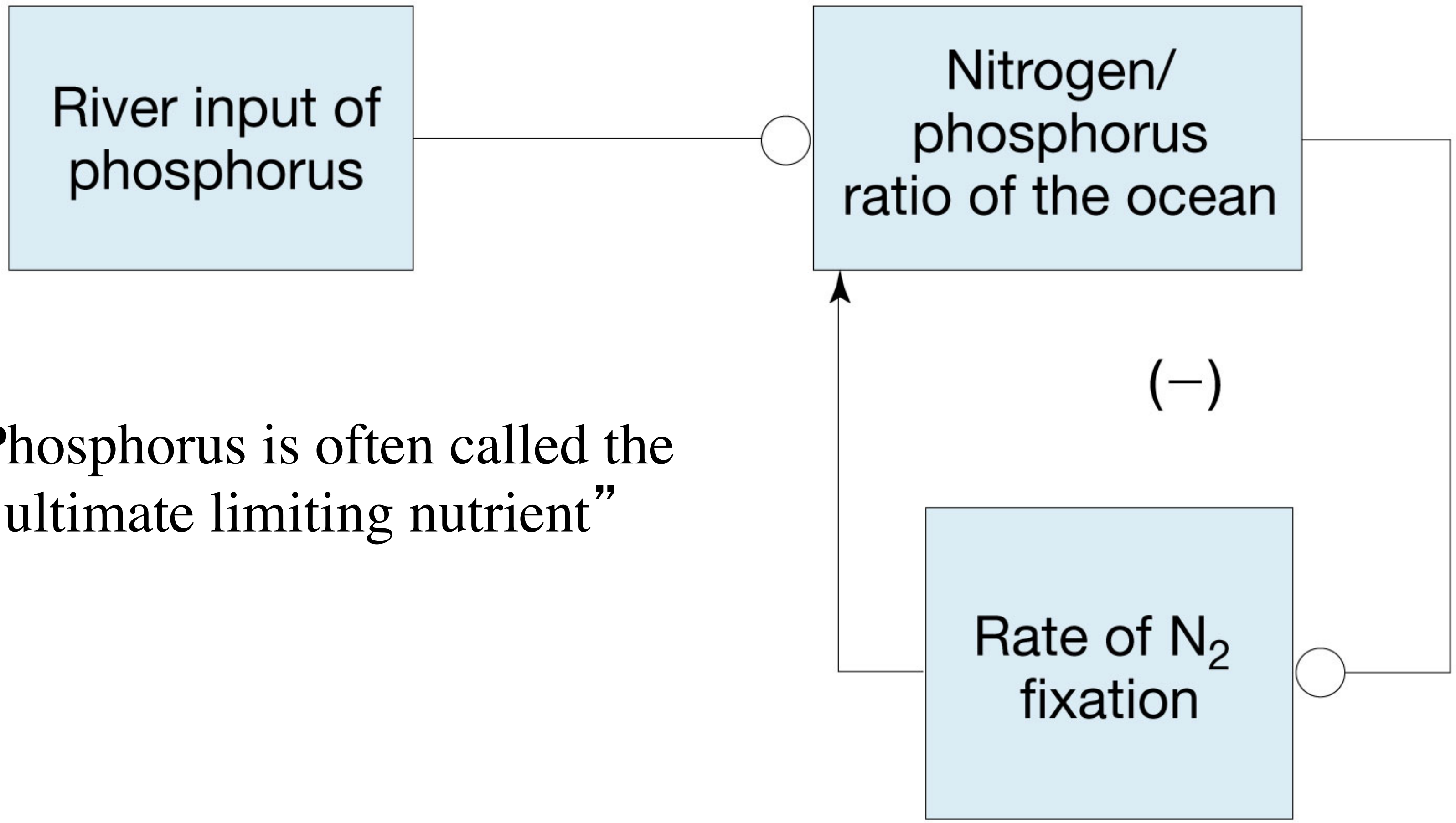
Fig. 8-21

Reservoirs: Moles
Fluxes: Moles/yr

N_2 is inert- It needs to be "fixed" in order to used by living things: e.g., nitrate (NO_3^-) or ammonium (NH_4^+). Nitrogen fixation is one of the main biochemical problems life had to evolve early on!!

Nitrogen cycle





Phosphorus is often called the "ultimate limiting nutrient"