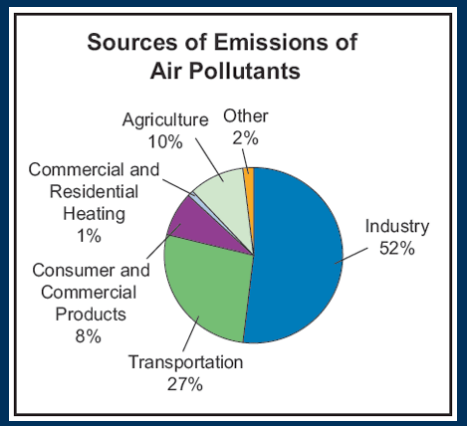
# GGS 319
# Part 1: Air Pollution Fundamentals

- ✓ The atmosphere and its components
- ✓ ***How air pollutants are categorized***
- ✓ ***The source/cycle of air pollutants***
- ✓ How pollution affects health and welfare
- ✓ Clean air acts
- ✓ Air quality management & standards



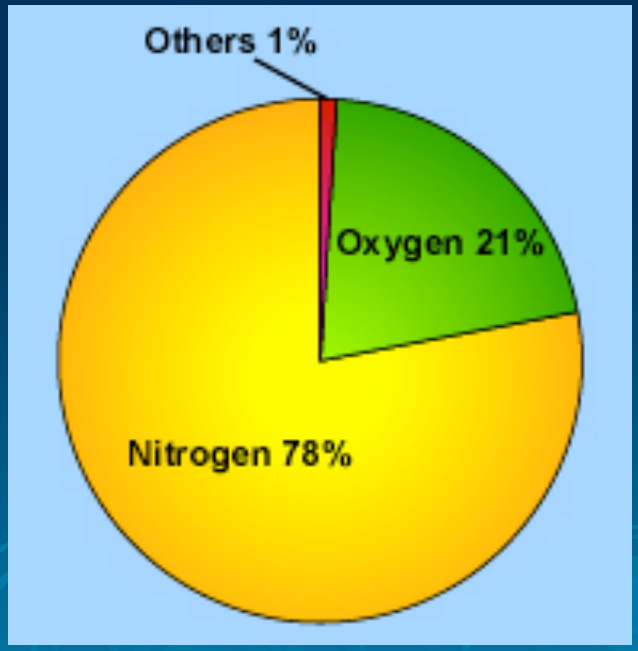





# Atmospheric Composition

- ✓ The composition of the atmosphere is controlled by the exchange of elements between the different reservoirs of the Earth

- ✓ Let us examine this broader perspective and specifically;
  - ✓ Cycle of nitrogen, oxygen, and carbon dioxide
  - ✓ Humans effect on nitrogen, oxygen, and carbon dioxide



# Earth System

- ✓ Is there anything in this picture that is not influenced by water?
- ✓ Is there anything in this picture not influenced by life?
- ✓ Is there anything in this picture not influenced by the atmosphere?



# Characteristics of Earth System

- Cyclical flow in a closed Earth system

- In this closed system Lithosphere, Hydrosphere, Atmosphere, and Biosphere are interacting



# Earth System (Geochemical) Cycles

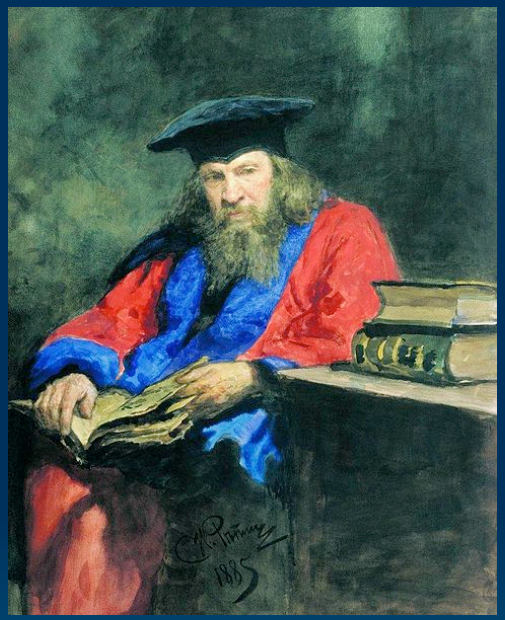
- From an Earth system perspective
  - The composition of the atmosphere is controlled by the exchange of elements between the different reservoirs ("spheres") of the Earth such as
  - Reservoirs on Earth
    - Atmosphere
    - Biosphere (vegetation, animals)
    - Hydrosphere (oceans, lakes, rivers, ground water)
    - Lithosphere (Earth's crust)

# Earth System Cycles (Natural Elements)

- Natural elements
  - There are 92 natural elements
  - About 25 of the 92 natural elements are known to be essential to life
    - Approximately 96% of living material are made from
      - Carbon (C) 18.5 %
      - Hydrogen (H) 9.5%
      - Nitrogen (N) 3.3%
      - Oxygen (O) 65%
    - Approximately 4% of living material are made from
      - Calcium (Ca) 1.5%
      - Phosphorus (P) 1.0%
      - Potassium (K) 0.4%
      - Sulfur (S) 0.3%
      - Sodium (Na) 0.2
      - Chlorine (Cl) 0.2%
      - Magnesium (Mg) 0.1%

# Earth System Cycles (Chemical Elements)

- Chemical elements



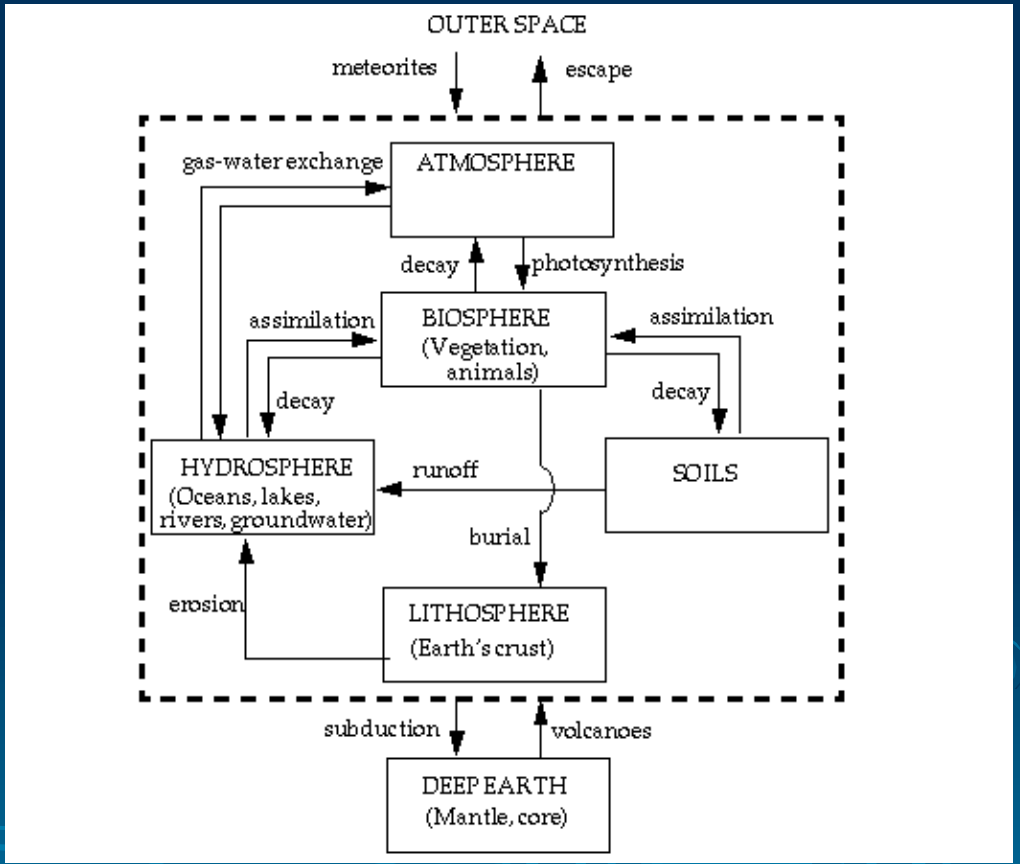
| Group → / ↓ Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 H | | | | | | | | | | | | | | | | | 2 He |
| 2 | 3 Li | 4 Be | | | | | | | | | | | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne |
| 3 | 11 Na | 12 Mg | | | | | | | | | | | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 4 | 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 5 | 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 6 | 55 Cs | 56 Ba | | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 7 | 87 Fr | 88 Ra | | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 Cn | 113 Uut | 114 Fl | 115 Uup | 116 Lv | 117 Uus | 118 Uuo |
| Lanthanides | | | | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu |
| Actinides | | | | 89 Ac | 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | 103 Lr |

Russian chemistry professor Dmitri Mendeleev published the first periodic table in 1869

# Earth System Cycles

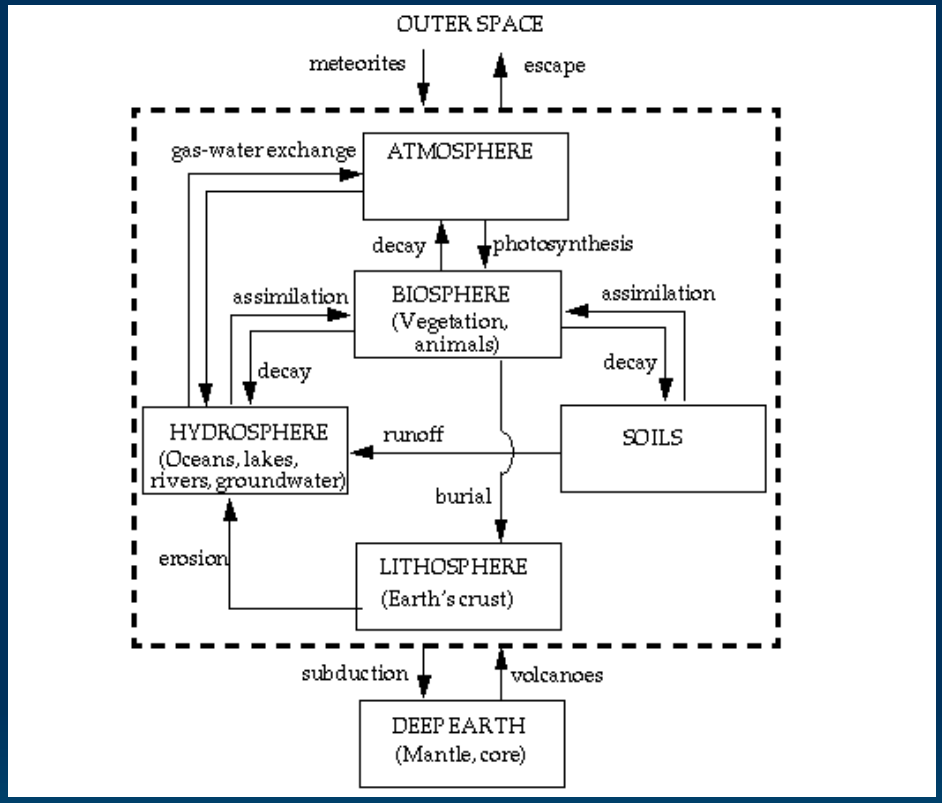
- The Earth system is an assemblage of atoms of the 92 natural elements
- Almost all of these atoms have been present in the Earth system since the formation of the Earth 4.5 billion years ago by gravitational accretion of a cloud of gases and dust
- Extraterrestrial sources (meteors) are relatively unimportant
- Escape of atoms to outer space is prevented by gravity except for the lightest atoms (Hydrogen & Helium)

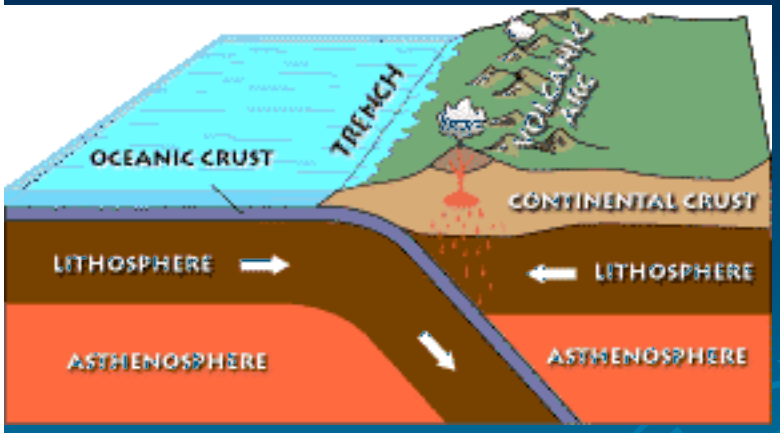
The Earth System mass is conserved!

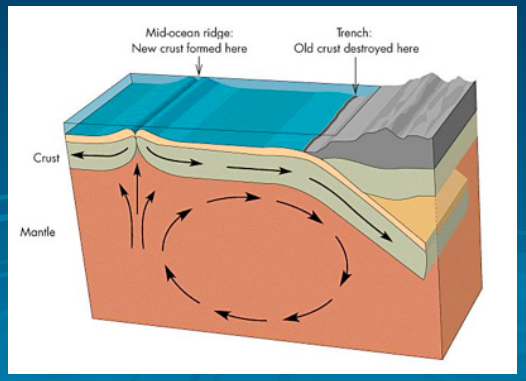


# Earth System Cycles

- Most of the mass of the Earth is present in the deep Earth (but isolated)
- Communication between the deep Earth and the Lithosphere takes place by
  - Volcanism
  - Subduction of tectonic plates



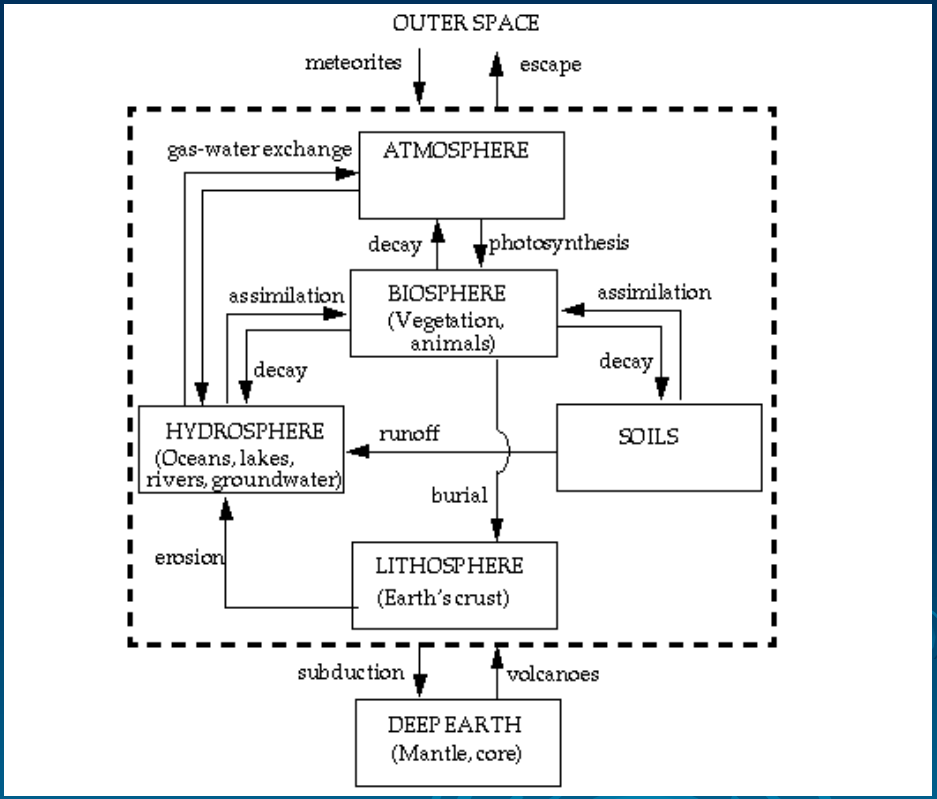






# Earth System Cycles

- The abundance of an element in the atmosphere can then be determined by two factors
  - The total abundance of the element in lithosphere
  - The partitioning of the element between the atmosphere and other spheres

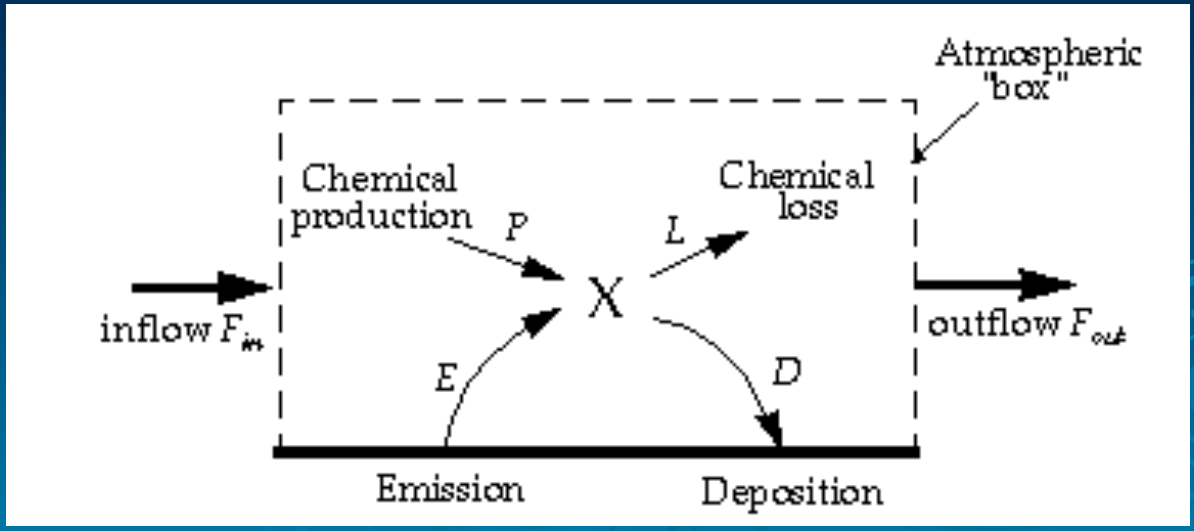


# The Simplest Model: One Box Model (cycling of elements between the earth's reservoirs)

- The concentration of chemical species in the atmosphere are controlled by four types of processes:
  - Emissions
    - Anthropogenic (e.g., fossil fuel combustion)
    - (Biogenic (e.g., photosynthesis of oxygen)
    - Natural (e.g., volcanoes)
  - Chemistry
  - Transport
  - Deposition
    - Dry deposition (gravity, uptake of CO2 by photosynthesis)
    - Wet deposition (scavenging by precipitation)
- We will discuss these processes mathematically later

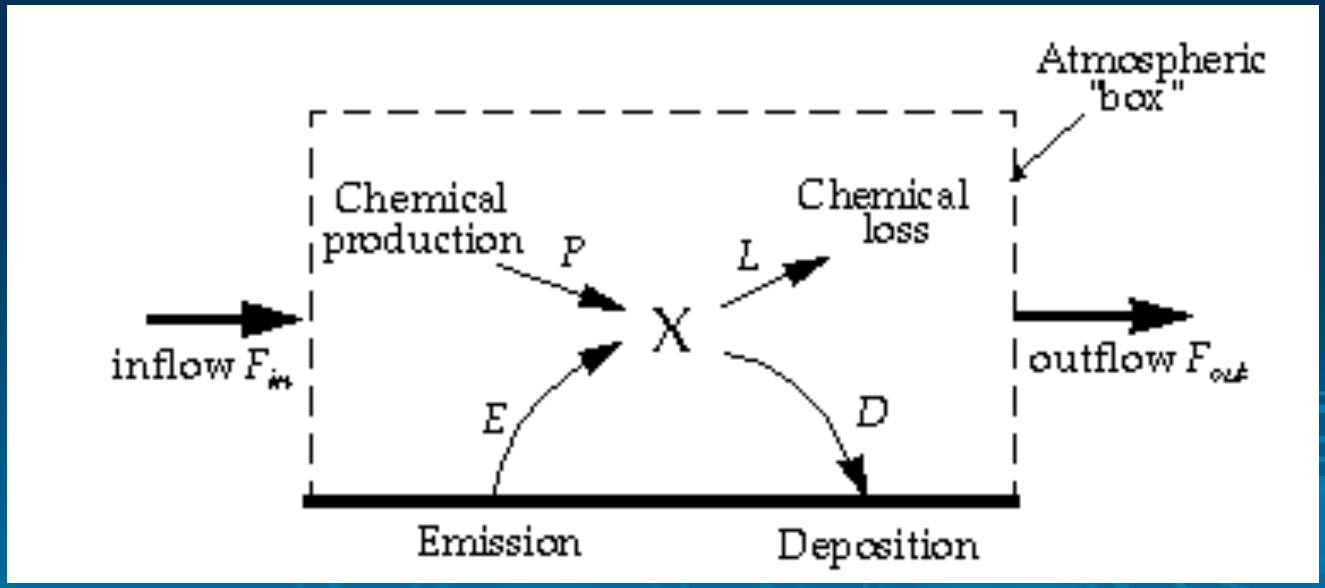
# The Simplest Model: One Box Model

- Atmospheric species, X
- The mass of X is called an inventory
- The box itself is called a reservoir
- Inflow + Outflow = Transport
- Inflow + E + P = Sources
- Outflow + L + D = Sinks
- Often the box is assumed will-mixed in order to facilitate computation of sources and sinks



# The Simplest Model: One Box Model

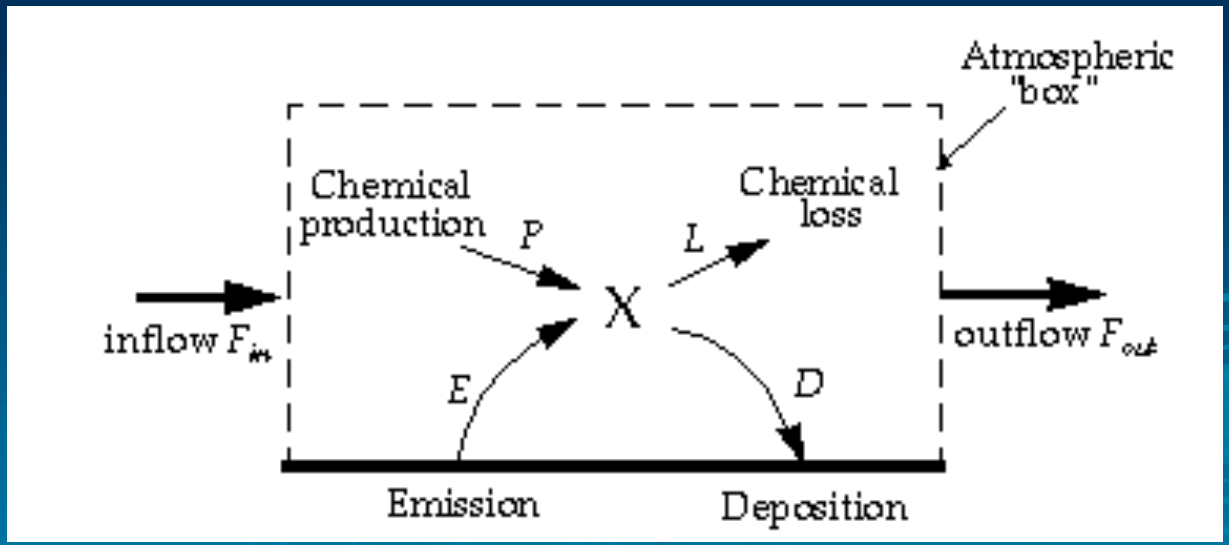
- The box can represent a selected atmospheric domain
  - An urban area
  - The United States
  - The Global atmosphere
- If the box is the global atmosphere, then Fin=Fout=0



# The Simplest Model: Concept of Lifetime

- The lifetime (t) of X in the box is defined as the average time that a molecule of X remains in the box
- Often called the residence time
- The ratio of the mass m (kg) of X in the box to the removal rate (kg/s)

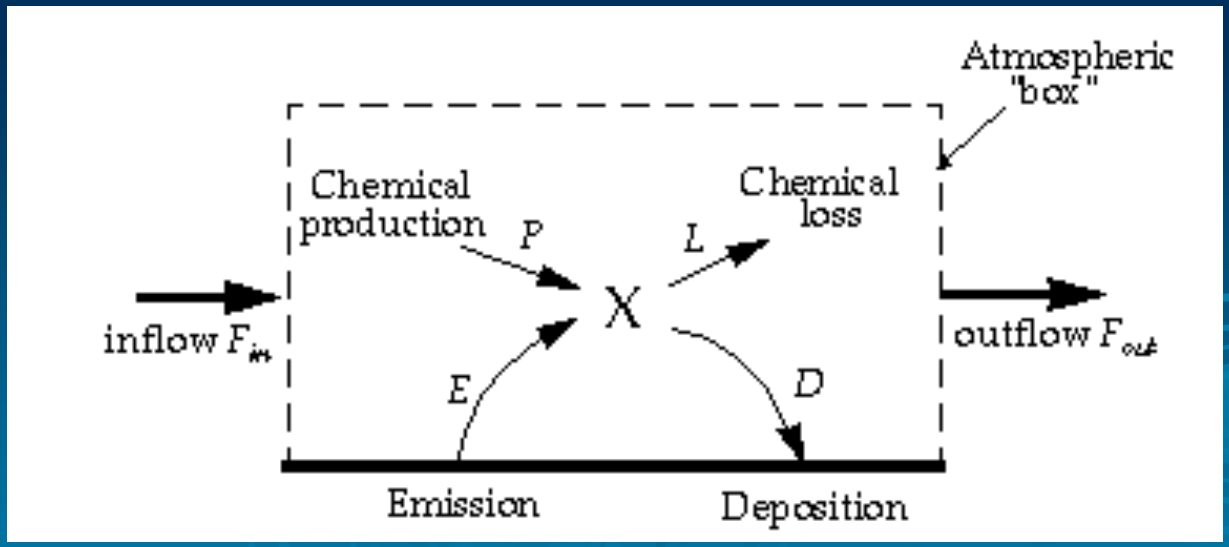
$$t = \frac{m}{F_{out} + L + D} \quad \rightarrow \quad \frac{kg}{kg\,s^{-1}} = s$$



# The Simplest Model: Concept of Lifetime

- The sinks (Fout, L, and D) are often first-order
  - Meaning that they are proportional to the mass inside the box (i.e., "the more you have, the more you can lose")
- So, the lifetime is independent of the inventory of X in the box

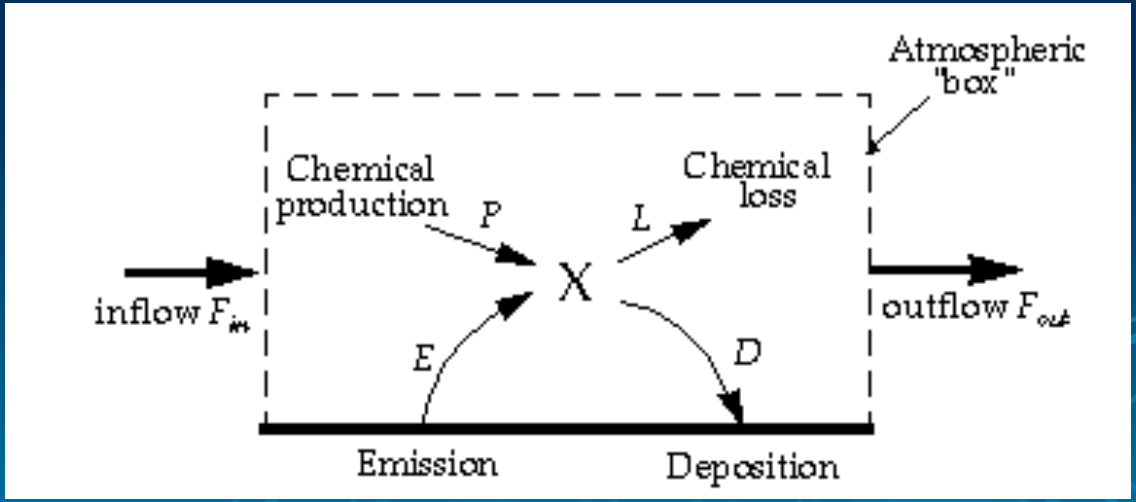
$$t = \frac{m}{F_{out} + L + D} \quad \rightarrow \quad \frac{kg}{kg\,s^{-1}} = s$$



# The Simplest Model: Concept of Lifetime

- Consider a first-order chemical loss for X with rate constant k
- We can then generalize the overall loss rate constant

$$t = \frac{m}{F_{out} + L + D} = \frac{m}{(k_{out} + k_L + k_D)m} = \frac{1}{k}$$



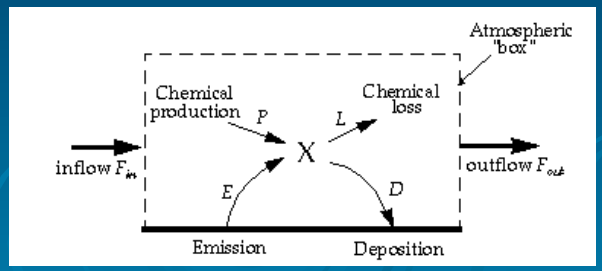
# The Simplest Model: Mass balance

- By mass balance, the change with time in the abundance of a species X inside the box must be equal to the difference between source and sinks
- This mass balance equation can solved for m(t) if all terms on the right-hand-side are known

$$\frac{dm}{dt} = \sum sources - \sum \sin ks = F_{in} + E + P - F_{out} - L - D = S - km$$

$$S = F_{in} + E + P \qquad km = F_{out} - L - D$$

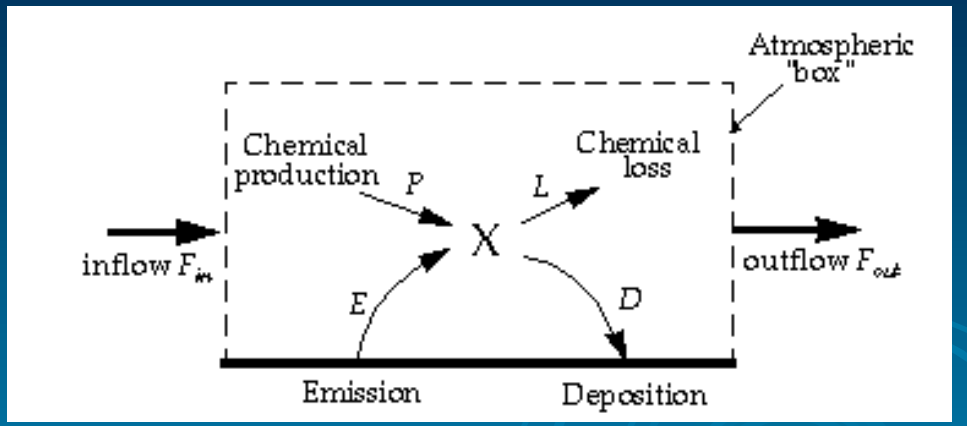
$$m(t) = m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt})$$

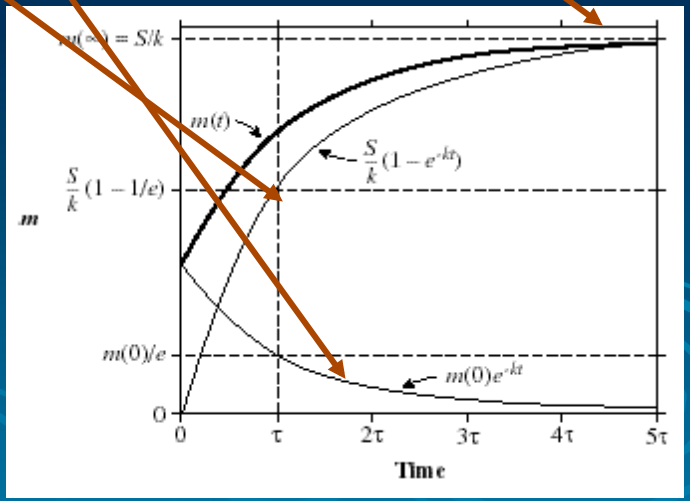


# The Simplest Model: Mass balance

- Evolution of species mass with time in a box model with first-order loss
- The mass, m(t) eventually approaches a steady-state value by a balance between sources and sinks
- Decay of the initial condition
- Approach to steady state

$$m(t) = m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt})$$

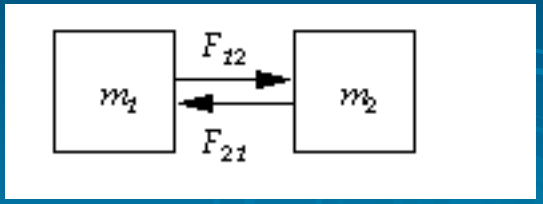


# Multi-Box Models

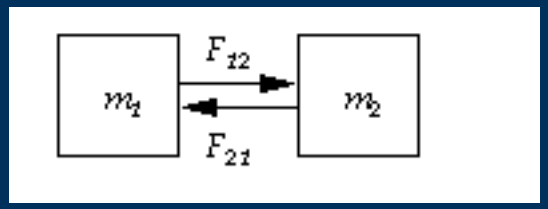
- The one-box model is a simple tool for describing the chemical evolution of species in the atmosphere
- However, the drastic simplification of transport is often unacceptable. Also the model offers no information on variation of concentration within the box (i.e., well mixed)
- Multi-box model is an assemblage of N boxes exchanging mass with each other
- The mass balance equation is the same, but the equations are coupled through the Fin and Fout terms

$$\frac{dm}{dt} = \sum sources - \sum \sin ks = F_{in} + E + P - F_{out} - L - D$$

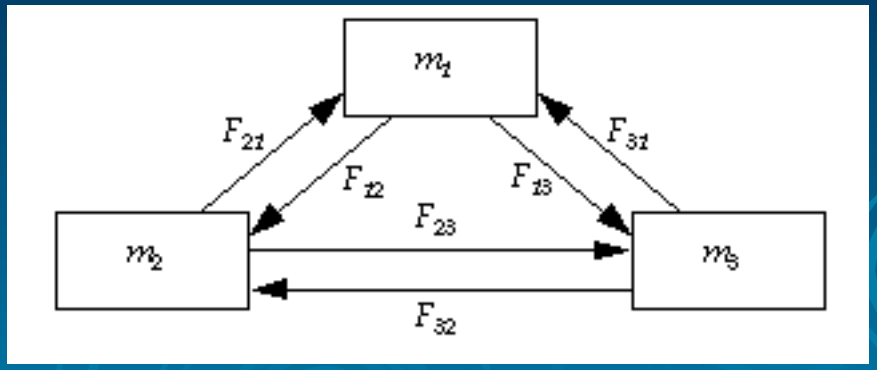


# Multi-Box Models

- For example, m1
- Similar equation can be written for m2




$$\frac{dm_1}{dt} = \sum sources - \sum \sin ks = F_{21} + E_1 + P_1 - F_{12} - L_1 - D_1$$



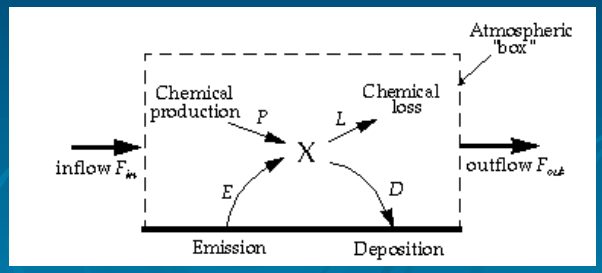
# The Simplest Model: Mass balance

- By mass balance, the change with time in the abundance of a species X inside the box must be equal to the difference between source and sinks
- This mass balance equation can solved for m(t) if all terms on the right-hand-side are known

$$\frac{dm}{dt} = \sum sources - \sum \sin ks = F_{in} + E + P - F_{out} - L - D = S - km$$

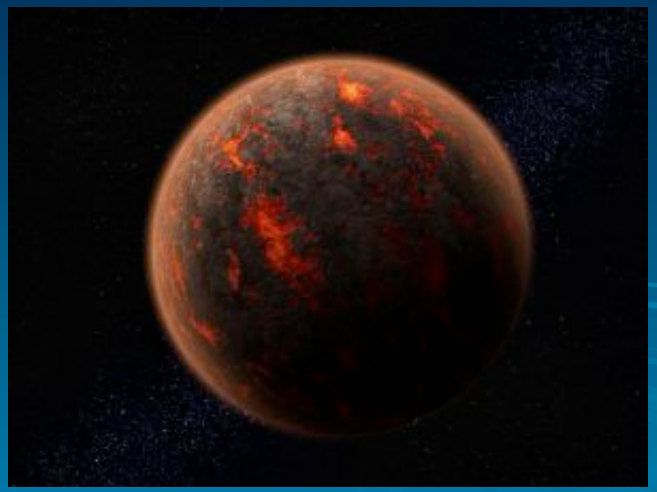
$$S = F_{in} + E + P \qquad km = F_{out} - L - D$$

$$m(t) = m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt})$$



# Early Evolution of The Atmosphere

- Supply of elements to the surface reservoirs was set in the earliest stages of Earth's history when the crust formed and volcanic outgassing transferred material from the deep Earth to the atmosphere
- Early atmosphere = Volcanic gases
  - It was mostly $H_2O$ (~95%), $CO_2$, $N_2$, and sulfur gases (No free $O_2$)
- The outgassed water precipitated to form oceans
- $CO_2$, and sulfur gases then dissolved in the oceans, leaving $N_2$ as the dominant gas in the atmosphere

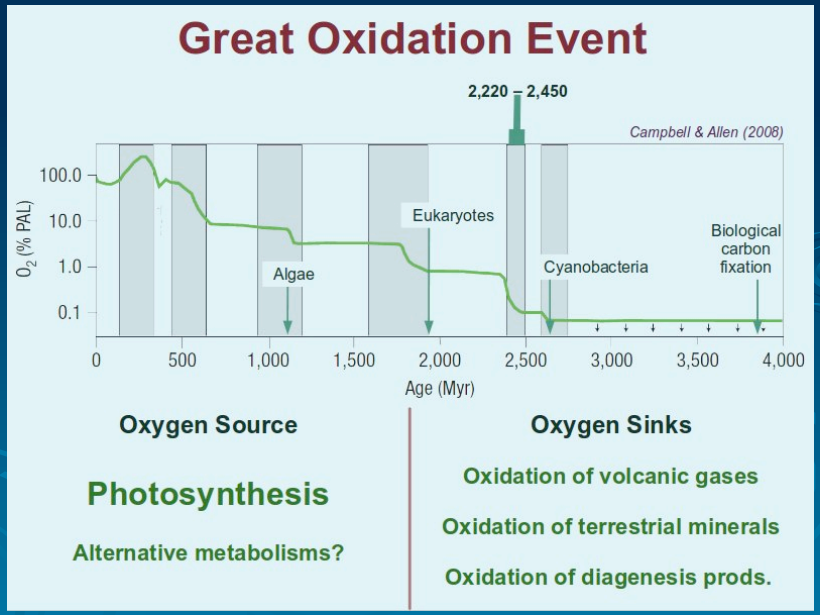




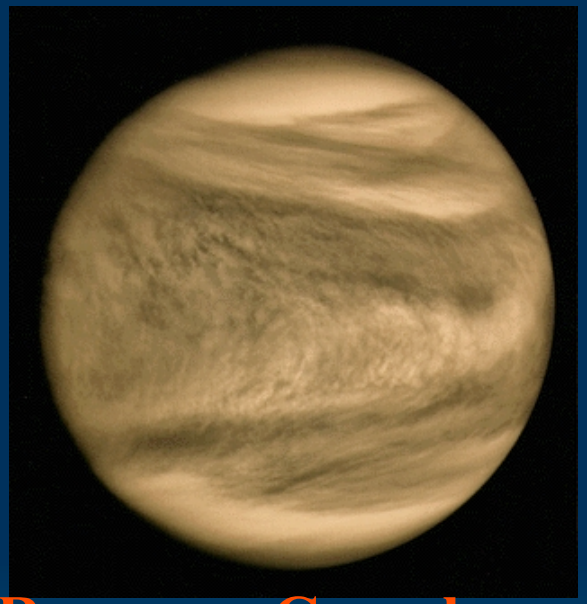
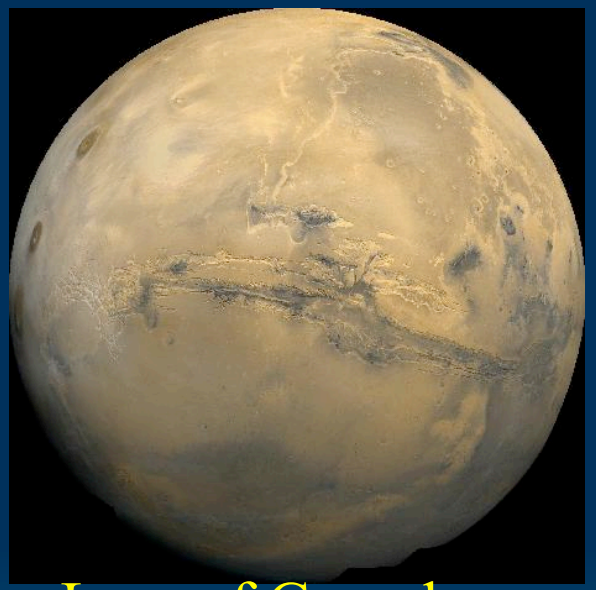
# Early Evolution of The Atmosphere

- The presence of liquid water allowed the development of living organisms.
- About 3.5 billion years ago, some organisms developed the capacity to convert $CO_2$ to organic carbon by photosynthesis
- This process released $O_2$ which gradually accumulated in the atmosphere, reaching its current atmospheric concentration about 400 million years ago





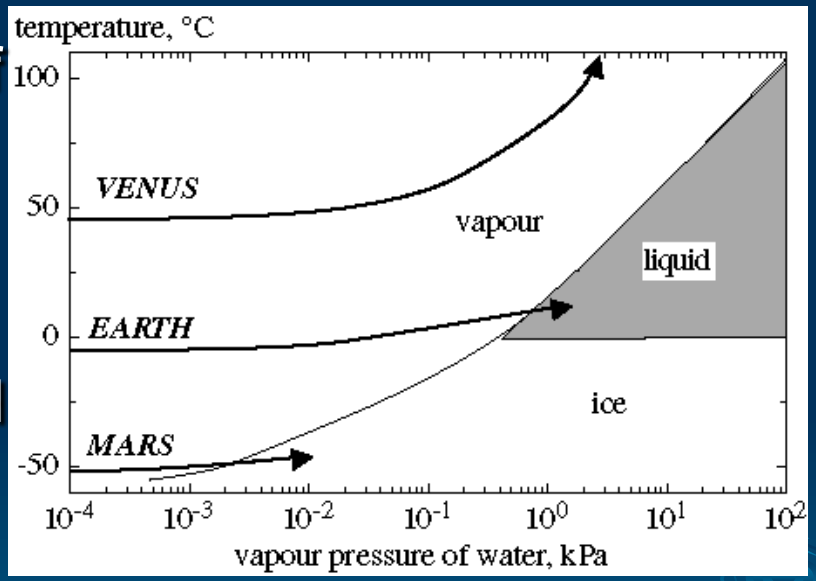
# Early Evolution of The Atmosphere

| Venus | Earth | Mars |
|---|---|---|
|  |  |  |
| **Runaway Greenhouse** | Robust Biosphere | Loss of Greenhouse gases $CO_2$ & $H_2O$ |

- It is instructive to compare the evolution of the Earth's atmosphere to that of its neighbor planes Venus and Mars
- All three planets presumably formed with similar assemblages of elements but their present-day atmospheric compositions are vastly different

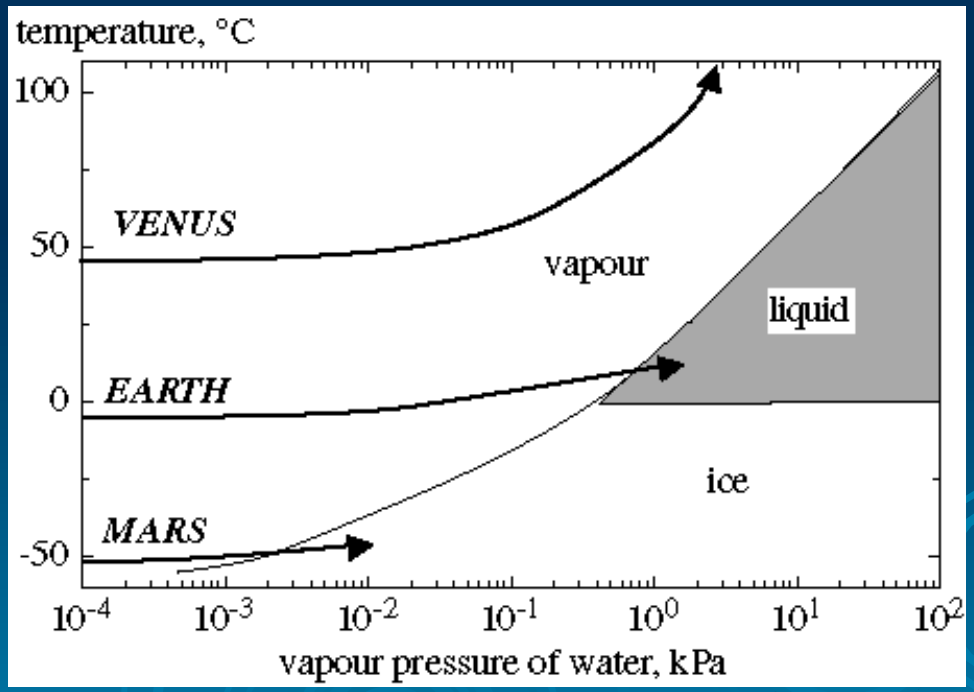
# Early Evolution of The Atmosphere

- Venus has an atmosphere ~100 times thicker than that of Earth and consisting mostly $CO_2$
- Because of the greater proximity of Venus to the Sun, the temperature of the early Venus was too high for the outgassed water to condense and form oceans
- Water vapor in Venus's upper atmosphere photolyzed to produce H atoms that escaped the planet's gravitational field and the O atoms left behind were removed by oxidation of rocks
- This mechanism is thought to explain the low $H_2O$ concentration in the Venusian atmosphere



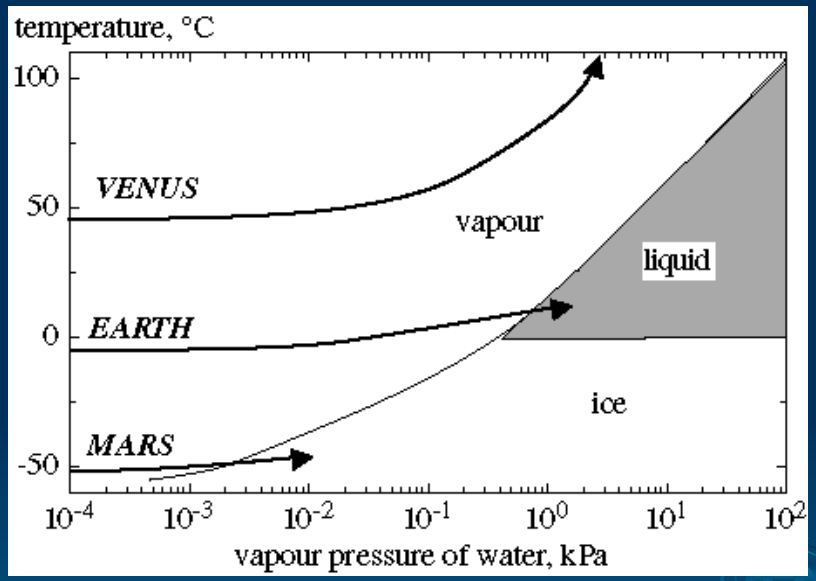
# Early Evolution of The Atmosphere

- On Earth, by contrast, the atmosphere contains only $10^{-5}$ of all water in the surface reservoirs (the bulk is in the oceans) so that loss of water to outer space is extremely slow and is compensated by evaporation from the oceans



# Early Evolution of The Atmosphere

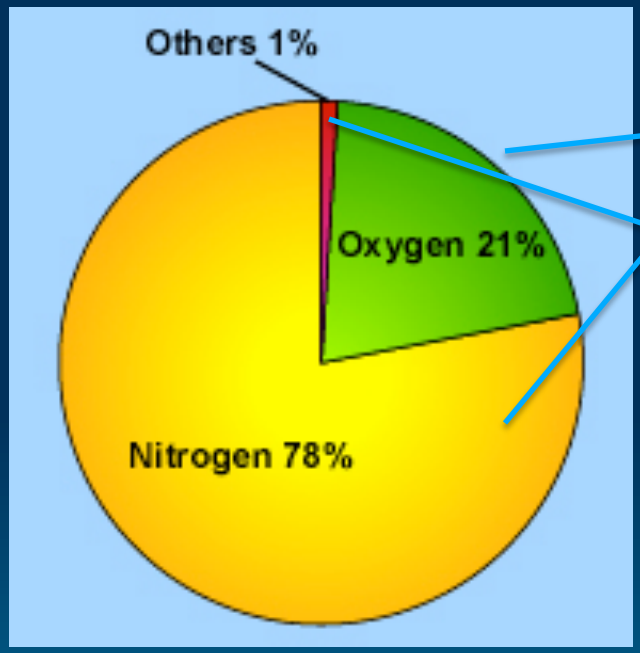
- The atmosphere of Mars is much thinner than that of the Earth and consists principally of $CO_2$
- The smaller size and hence weaker gravitational field of Mars allows easier escape of H atoms to outer space
- Although the mixing ratio of $CO_2$ in the Martian atmosphere is high, its total abundance is in fact extremely low compared to that of Venus
- It is thought that $CO_2$ has been removed from the Martian atmosphere by surface reactions producing carbonate rocks



# Early Evolution of The Atmosphere

| | Venus | Earth | Mars |
|---|---|---|---|
| Radius (km) | 6100 | 6400 | 3400 |
| Mass of planet (1023 kg) | 49 | 60 | 6.4 |
| Gravity (m $s^{-2}$) | 8.9 | 9.8 | 3.7 |
| Surface temperature (K) | 730 | 290 | 220 |
| Surface pressure (mb) | 9100 | 1000 | 7 |
| Atmospheric composition (mol/mol) | | | |
| $CO_2$ | 0.96 | $4X10^{-4}$ | 0.95 |
| $N_2$ | $3.4X10^{-2}$ | 0.78 | $2.7X10^{-2}$ |
| $O_2$ | $6.9X10^{-5}$ | 0.21 | $1.3X10^{-3}$ |
| $H_2O$ | $3X10^{-3}$ | $1X10^{-2}$ | $3X10^{-4}$ |

# Cycle of Atmospheric Composition




## Atmospheric Composition

| Constituent[a] | Molecular weight | Fractional concentration by volume |
|---|---|---|
| Nitrogen ($N_2$) | 28.013 | 78.08% |
| Oxygen ($O_2$) | 32.000 | 20.95% |
| Argon (Ar) | 39.95 | 0.93% |
| **Water vapor ($H_2O$)** | 18.02 | 0–5% |
| **Carbon dioxide ($CO_2$)** | 44.01 | 380 ppm |
| Neon (Ne) | 20.18 | 18 ppm |
| Helium (He) | 4.00 | 5 ppm |
| **Methane ($CH_4$)** | 16.04 | 1.75 ppm |
| Krypton (Kr) | 83.80 | 1 ppm |
| Hydrogen ($H_2$) | 2.02 | 0.5 ppm |
| **Nitrous oxide ($N_2O$)** | 56.03 | 0.3 ppm |
| **Ozone ($O_3$)** | 48.00 | 0–0.1 ppm |

[a] So called *greenhouse gases* are indicated by bold-faced type. For more detailed information on minor constituents, see Table 5.1.

# Measures of Atmospheric Composition

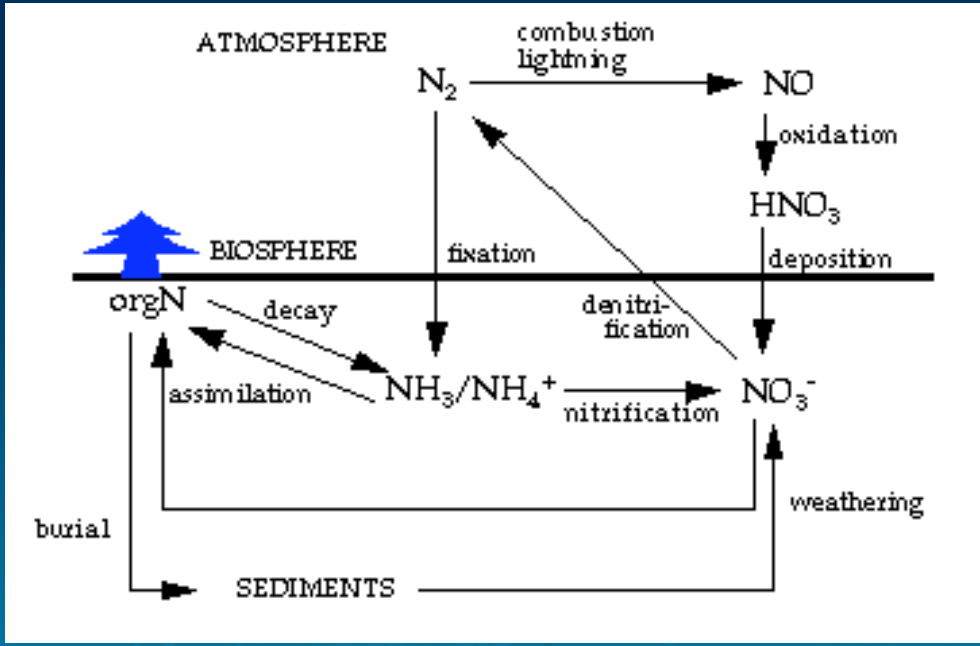
- The objective of atmospheric chemistry is to understand the factors that control the concentration of chemical species in the atmosphere
- Three principal measures
  - Mixing ratio
  - Number density
  - Partial pressure

# Measures of Atmospheric Composition

- The objective of atmospheric chemistry is to understand the factors that control the concentration of chemical species in the atmosphere
- Three principal measures
  - Mixing ratio
    - The mixing ratio of a gas X is defined as the number of moles of X per mole of air
  - Number density
    - The number of density of a gas X is defined as the number of molecules of X per unit volume of air (e.g., molecules of air per $cm^3$)
  - Partial pressure
    - The partial pressure of a gas X in a mixture of gases of total pressure P is defined as the pressure that would be exerted by the molecules of X if all the other gases were removed from the mixture

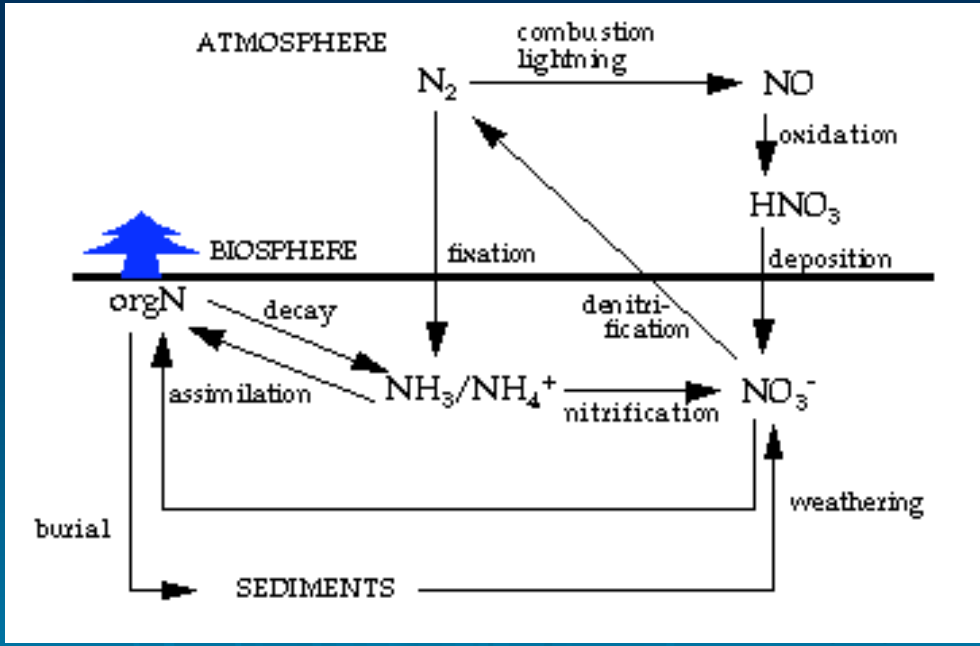
# The Nitrogen ($N_2$) Cycle

- Nitrogen accounts for 78% of air on a molar basis
- Highly stable
- It is an essential component of the biosphere (think of the amino acids)
- The atmosphere is an obvious source for this nitrogen



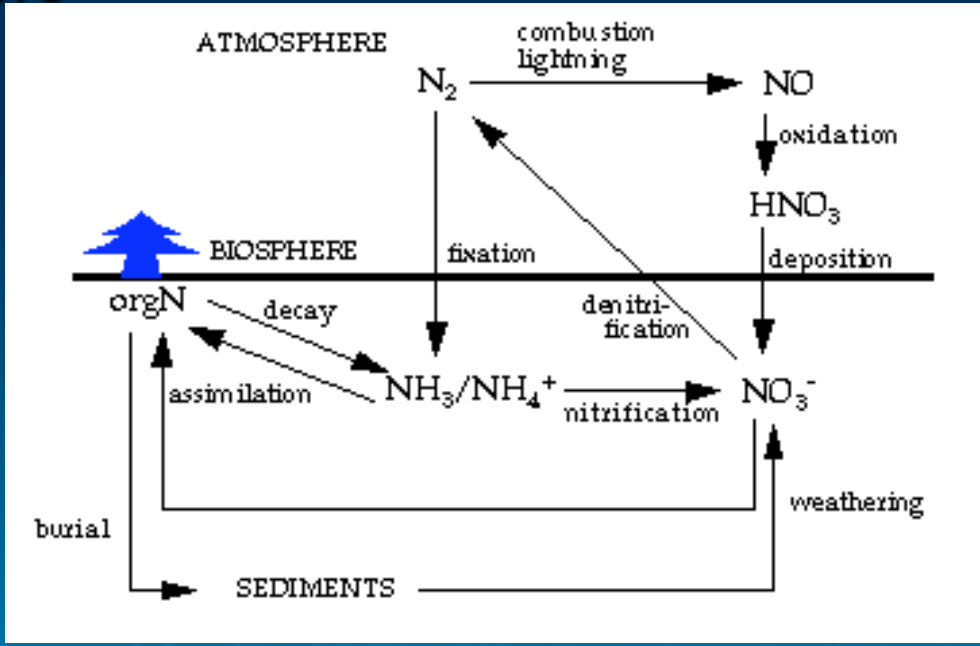
# The Nitrogen ($N_2$) Cycle

- A process called fixation converts $N_2$ molecule to biologically available nitrogen (this is achieved in ecosystems by bacteria which reduce $N_2$ to ammonia $NH_3$ and ammonium $NH_4$)
- The $NH_3$ is assimilated as organic nitrogen by the bacteria or by their host plants, which may in turn be consumed by animals



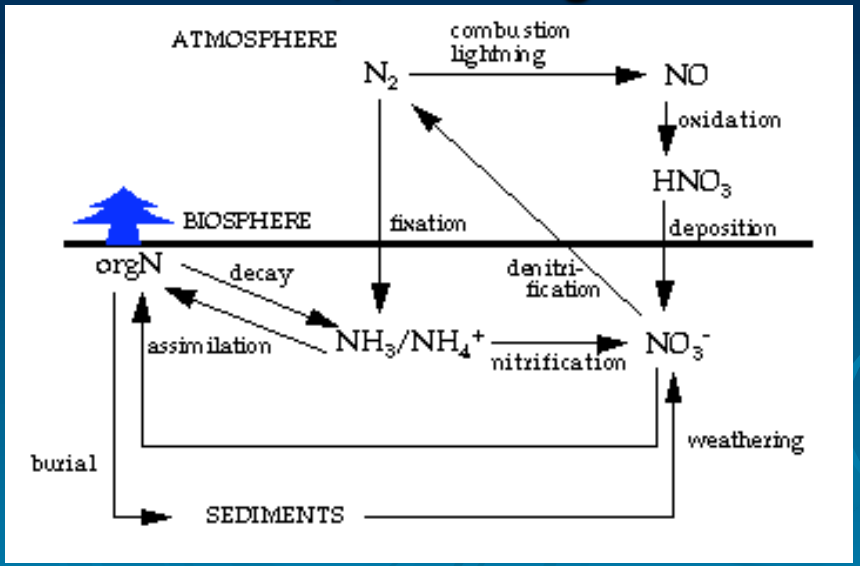
# The Nitrogen ($N_2$) Cycle

- A process called nitrification converts $NH_4$ to nitrate, $NO_3$
- Nitrate is highly mobile in soil and is readly assimilated by plant and bacteria, proving another route for formation of organic nitrogen
- A process called denitrification converts $NO_3$ to $N_2$, thus nitrogen can be returned from the biosphere to the atmosphere



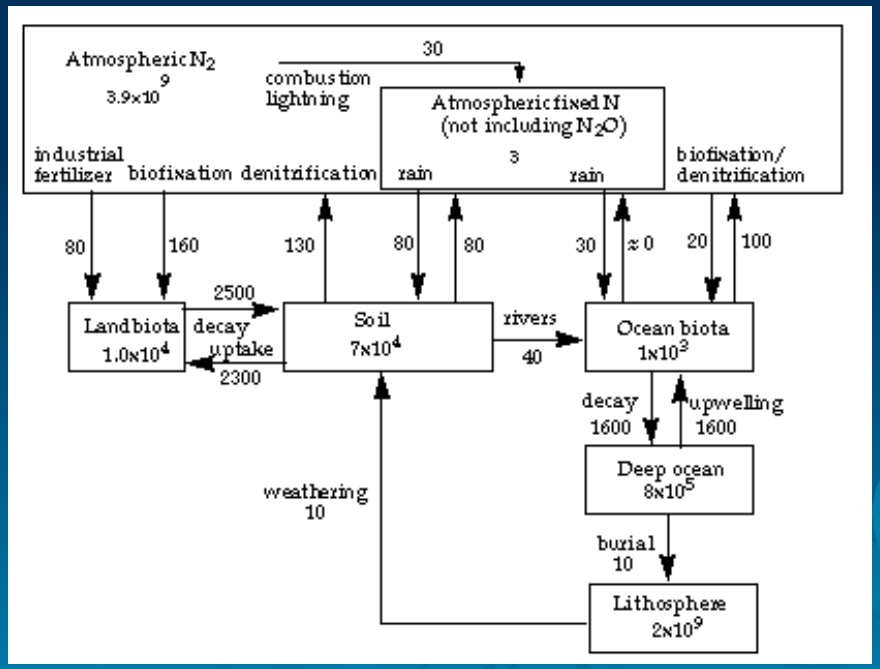
# The Nitrogen ($N_2$) Cycle

- High temperature oxidation of $N_2$ to NO during combustion or lightning, followed by atmospheric oxidation of NO to HNO3 which is water soluble and scavenged by rain
- Transfer of nitrogen to the lithosphere takes place by burial of dead organisms in the bottom of the ocean
- These dead organisms are then incorporated into sedimentary rock
- Eventually the sedimentary rock is brought up to the surface of the continents and eroded, returning to the biosphere



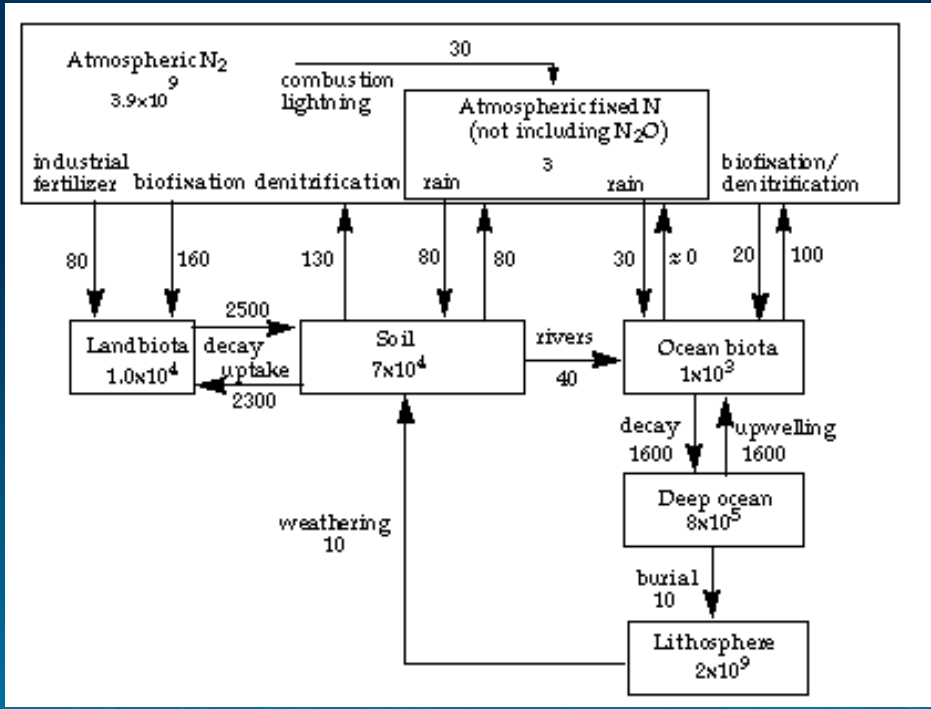
# Box Model of the Nitrogen ($N_2$) Cycle

- This model gives estimates of total nitrogen inventories in the major surface reservoirs and the flows of nitrogen between different reservoirs
- The most accurate by far of all these numbers is the mass of nitrogen ($3.9 \times 10^9$ Tg) in air which is calculated from the uniform mixing ratio 0.78 mol/mol
- Where 1 teragram (Tg)=1x1012 g



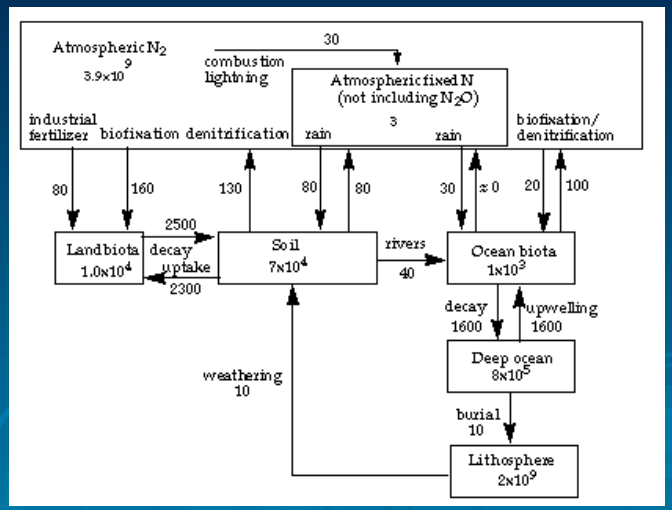
# Box Model of the Nitrogen ($N_2$) Cycle

- An important observation from this model is that human activity has greatly increased the rate of transfer of nitrogen to the biosphere (industrial manufacture of fertilizer, fossil fuel combustion, etc), resulting possibly in a global fertilization of the biosphere



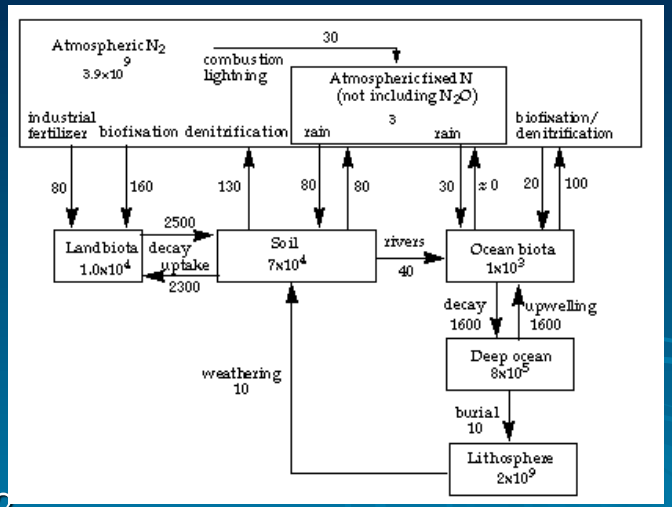
# Box Model of the Nitrogen ($N_2$) Cycle

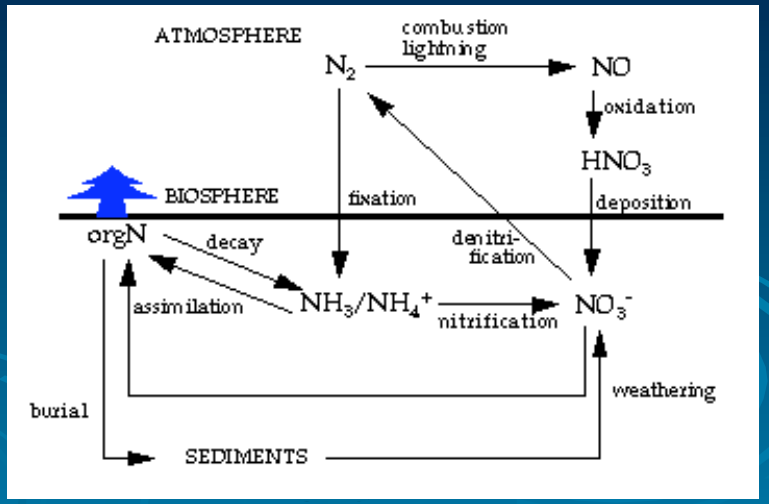
- Let us focus on the factors controlling the abundance of atmospheric nitrogen
- The atmosphere contains most of the nitrogen present in the surface reservoirs of the Earth
- Based on the inventories, the nitrogen content of the atmosphere could not possibly be more than 50% higher than today even if all the nitrogen in the lithosphere were transferred to the atmosphere so that the amount of nitrogen in the atmosphere is constrained by the total amount of nitrogen present in the surface revoirs of the Earth



# Box Model of the Nitrogen ($N_2$) Cycle

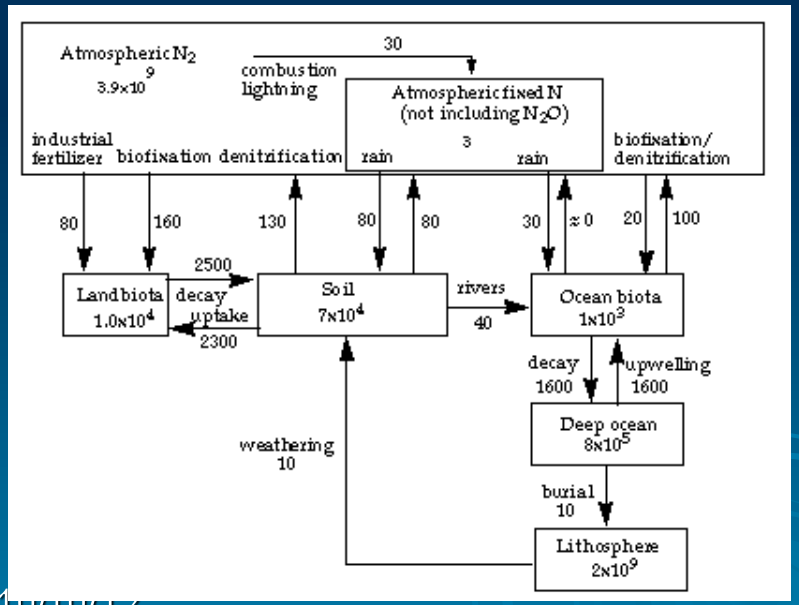
- What about the possibility of depleting atmospheric nitrogen by transferring the nitrogen to the other surface reservoirs?
- Imagine a scenario where denitrification were to shut off while N2 fixation still operated
  - Atmospheric nitrogen would be eventually depleted accumulation NO3 in the oceans
- The time scale of such depletion is 13 million years
- We can then safely conclude that human activity will never affect atmospheric nitrogen level significantly

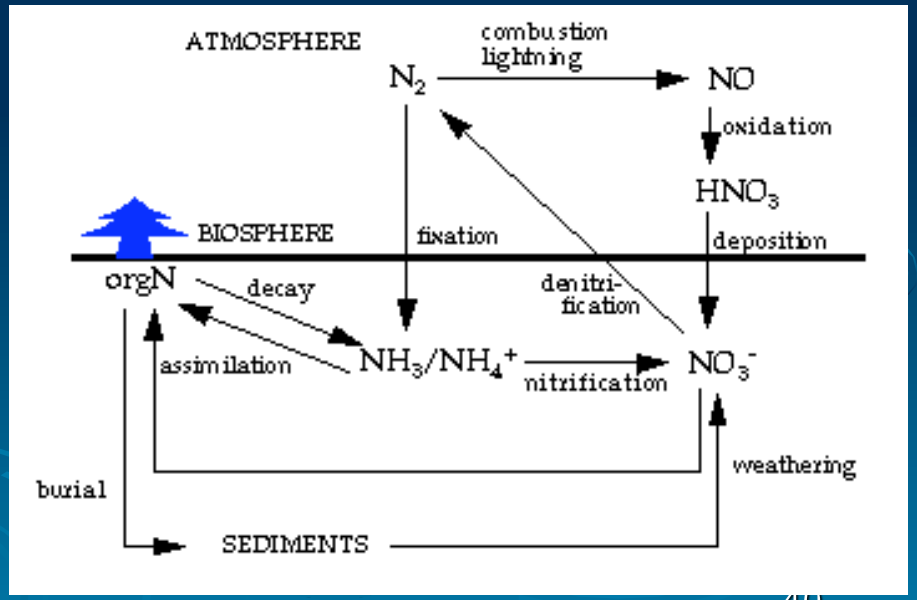


# Box Model of the Nitrogen ($N_2$) Cycle

- On a geological time scale, however, we see that denitrification is critical for maintaining atmospheric nitrogen
- If nitrogen were depleted from the atmosphere, thus shutting off nitrogen fixation, life on Earth outside of the oceans would be greatly restricted.



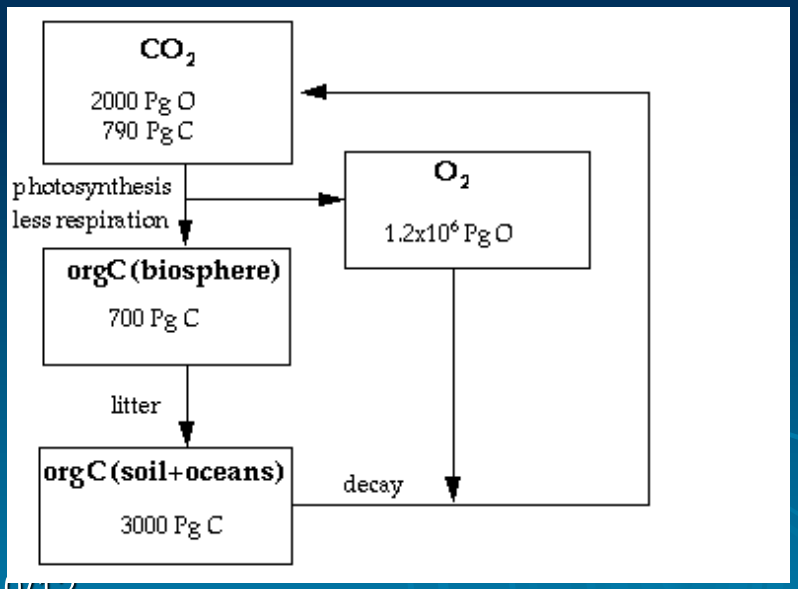



# The Oxygen ($O_2$) Cycle

- Atmospheric oxygen is produced by photosynthesis
- Closely coupled to C cycle by photosynthesis/respiration cycle
  - Green-plant photosynthesis (Gross Primary Production)

    $CO_2 + H_2O \ ===> \ CH_2O + O_2$ (1) (generation)
  - Green-plan respiration and litter/microbial decay of dead biomass

    $CH_2O + O_2 ===> CO_2 + H_2O$ (2) (destruction)
- NPP = (1) – (2) on global basis, NPP ~ 0.5 GPP



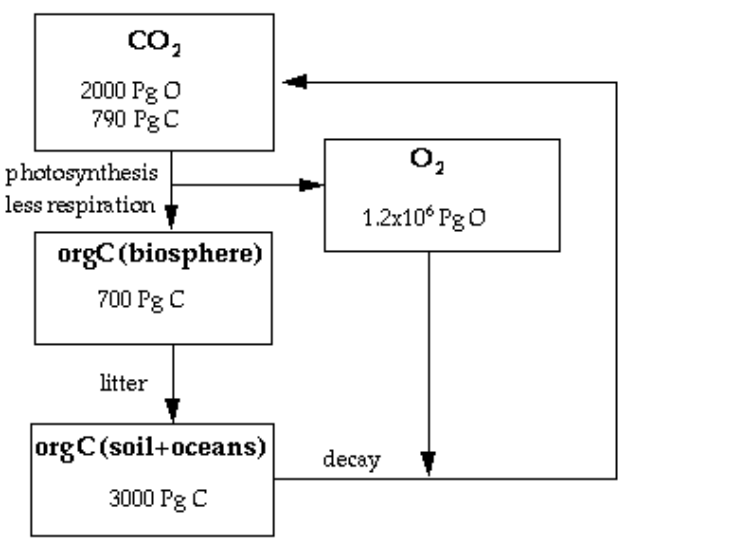

1 kilogram (kg) = $10^3$ grams (g)
1 megagram (Mg) = $10^6$ g = $10^3$ kg
1 gigagram (Gg) = $10^9$ g = $10^6$ kg
1 tertagram (Tg) = $10^{12}$ g = $10^9$ kg
1 petagram (Pg) = $10^{15}$ g = $10^{12}$ kg

$CH_2O$ represents most common form of organic matter (carbohydrate)

# The Oxygen ($O_2$) Cycle

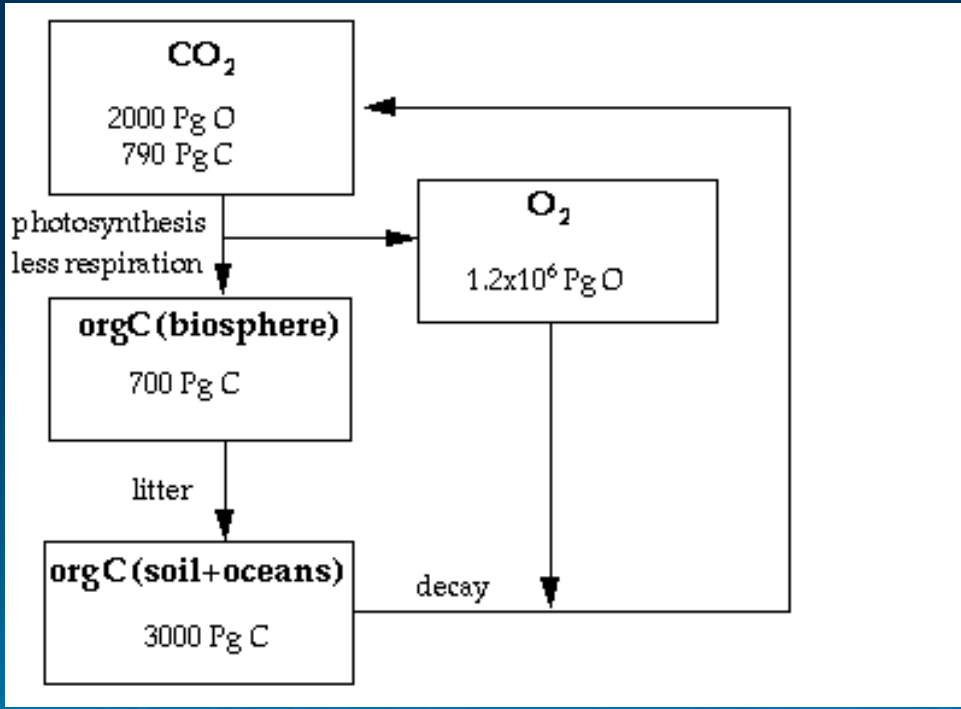
- The oxygen cycle provides insights into how $CO_2$ content of atmosphere is maintained
- Comparison of the inventories tells us that cycling with the biosphere cannot control the abundance of $O_2$ in the atmosphere

  $O_2$ >> $CO_2$ or OrgC
- If photosynthesis were for some reason to stop, oxidation of the entire organic carbon reservoir would consume less than 1% of O2 presently in the atmosphere and there would be no further O2 loss (since there would be no organic carbon left to oxidized)



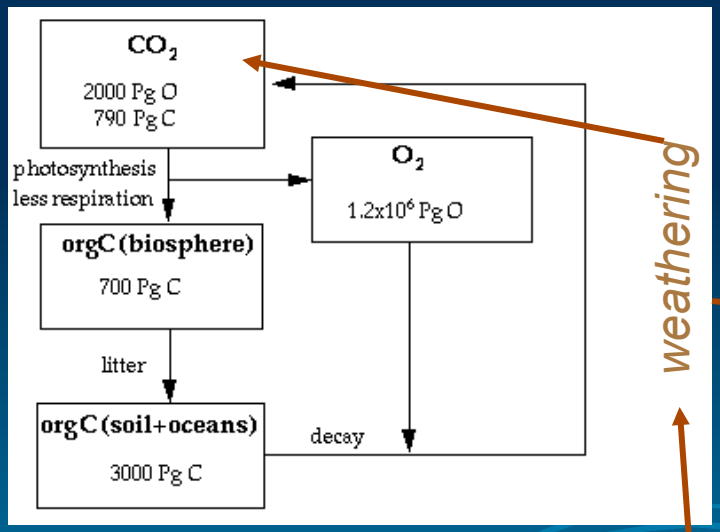
# The Oxygen ($O_2$) Cycle

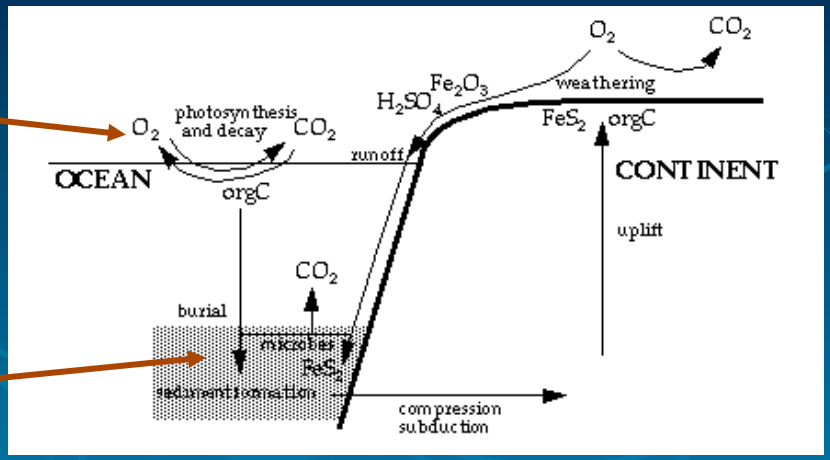
- Conversely, if respiration and decay were to stop, conversion of all atmospheric CO2 to O2 by photosynthesis would increase O2 levels by only 0.2%
- So, what, then, controls atmospheric oxygen?



# The Oxygen ($O_2$) Cycle

- The answer is the lithosphere
- Rock material brought to the surface in a reduced state is weathered (oxidized) by atmospheric $O_2$.
- The amount of Lithospheric Org C are sufficiently large (**$1.2x10^7$ Pg**) that weathering of rocks would eventually deplete atmospheric $O_2$ if not compensated by an oxygen source

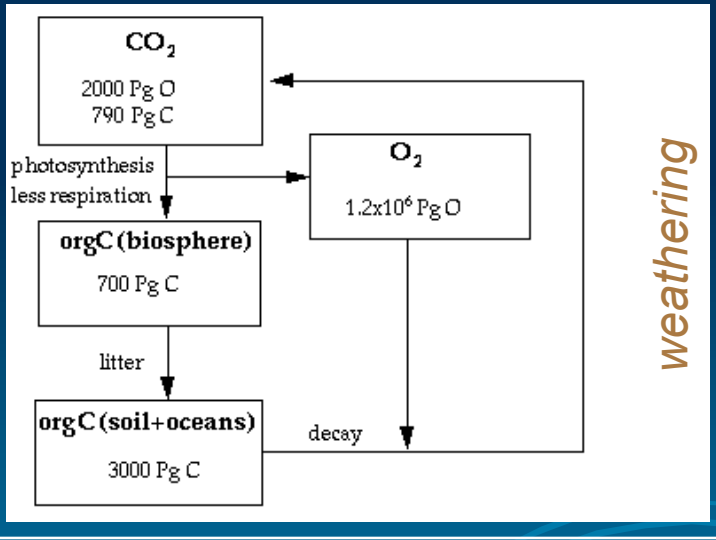


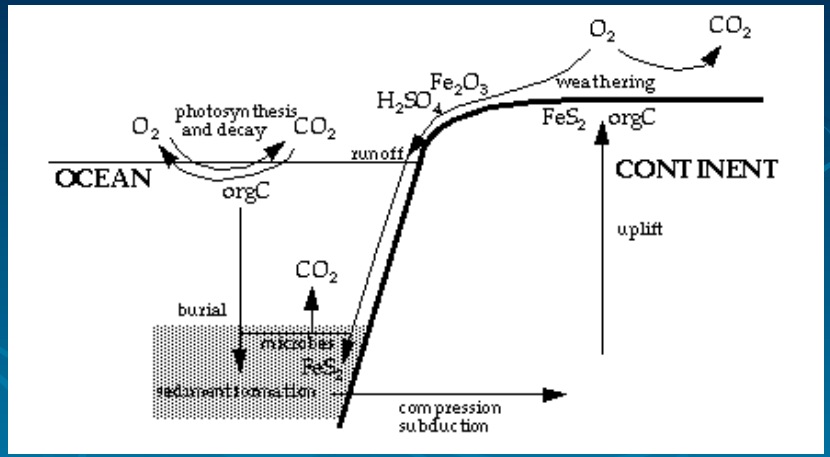

Ocean Bottom Carbon
**$1.2x10^7$ Pg**

# The Oxygen ($O_2$) Cycle

- Timescale of the sedimentary rock formation is 100 million years
- Lifetime of O2 is 3 million years
- But, fossil records show that atmospheric O2 levels have in fact not changed significantly over the past 400 million years, a time scale much longer than the lifetime of $O_2$ against loss by weathering




OCEAN BOTTOM C
**$1.2 \times 10^7$ Pg (C)**



# The Oxygen ($O_2$) Cycle

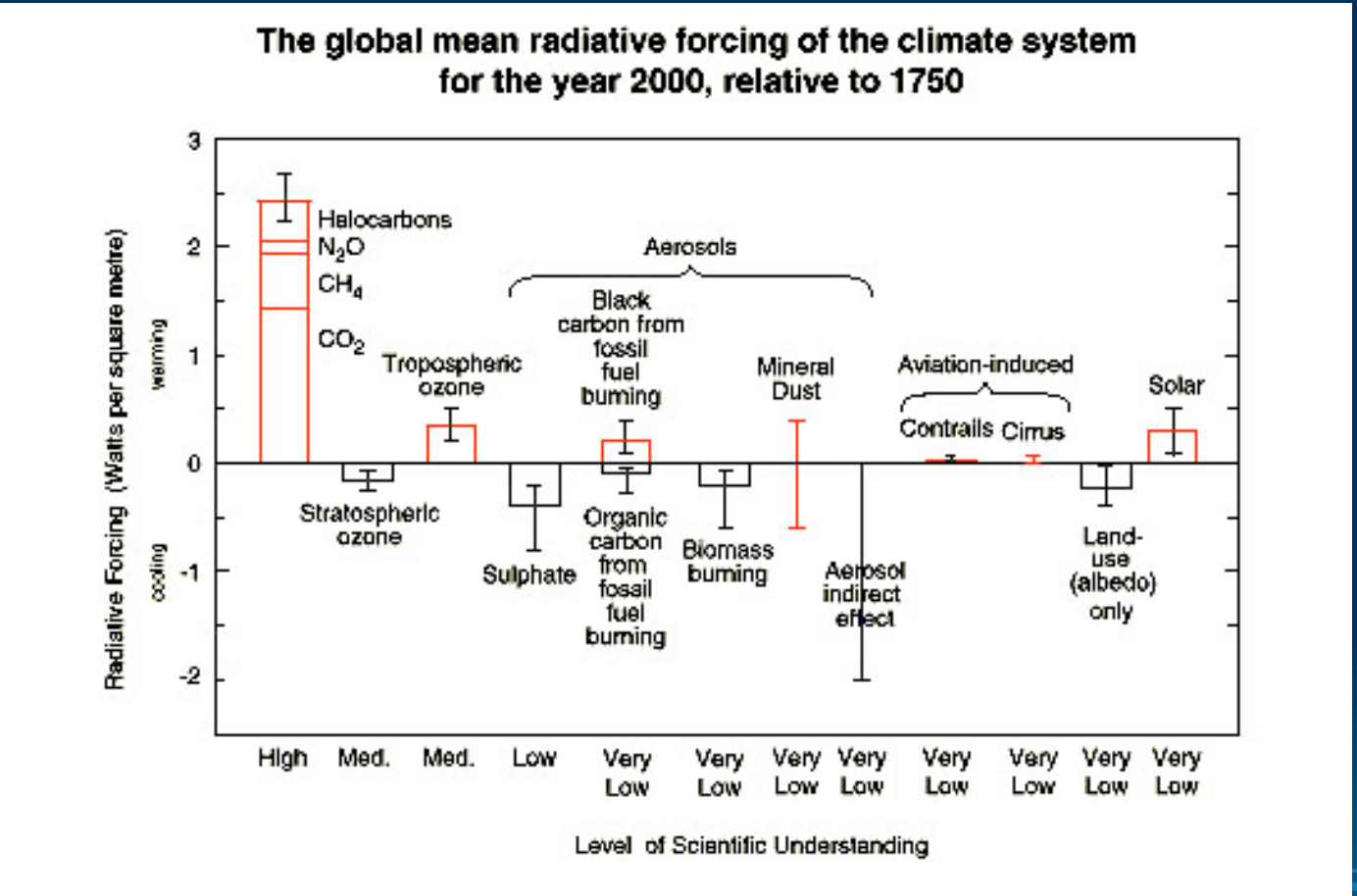
$\tau_{O2}$ (lifetime of O2) due to weathering
3.6 million years

If $O_2$ production halted & nothing else changed
4 million years to significantly change $O_2$

Atmosphere $O_2$ content has been stable for much longer, 400 million years
Then, there must be stabilizing feedbacks in the O2-lithosphere system. But this is poorly understood.

So, there is no human effect on $O_2$!

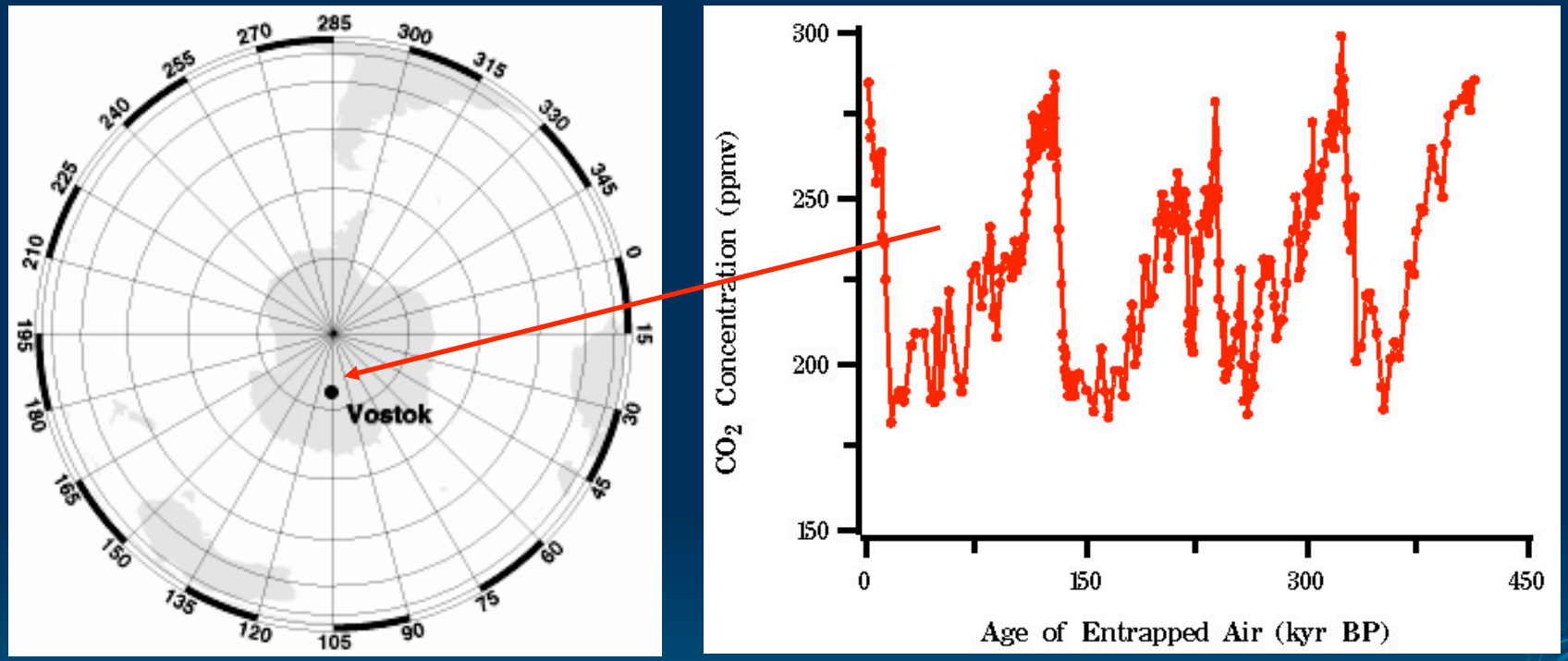
# The Carbon Dioxide ($CO_2$) Cycle




**THE IPCC THIRD ASSESSMENT**

- Radiative forcings of long-lived gases well quantified
- Large impact of $CO_2$

# ATMOSPHERIC $CO_2$ DURING THE LAST 450,000 YEARS




- Ice core measurements show that maximum concentration over the last 450,000 years is ~300 ppm

# ATMOSPHERIC $CO_2$ DURING THE LAST 1,000 YEARS

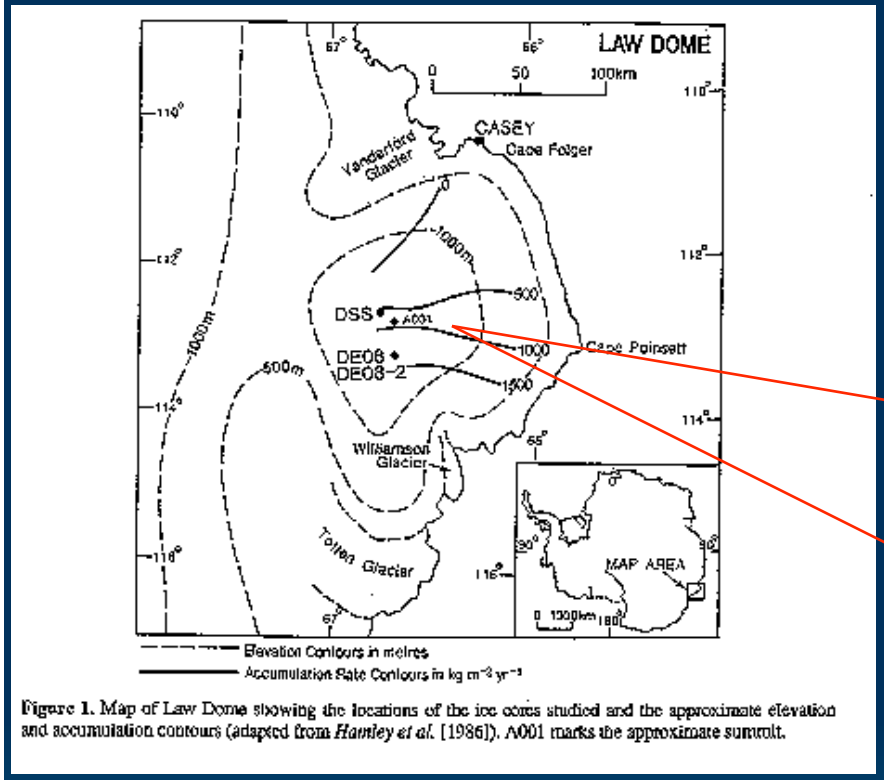
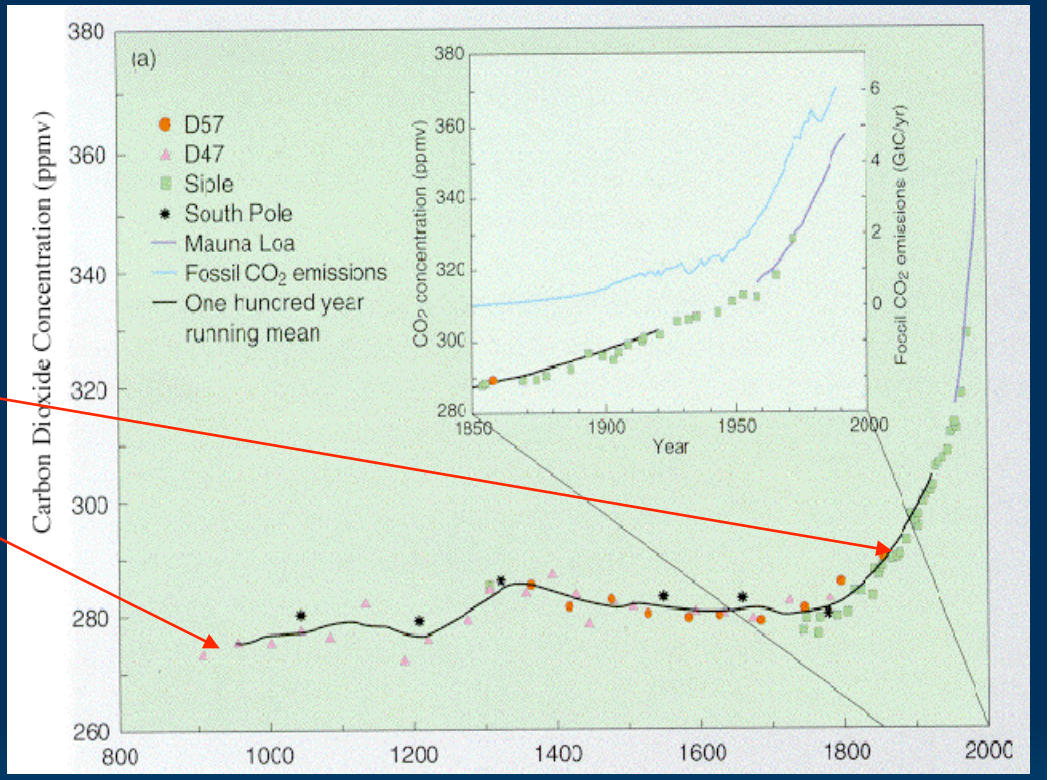


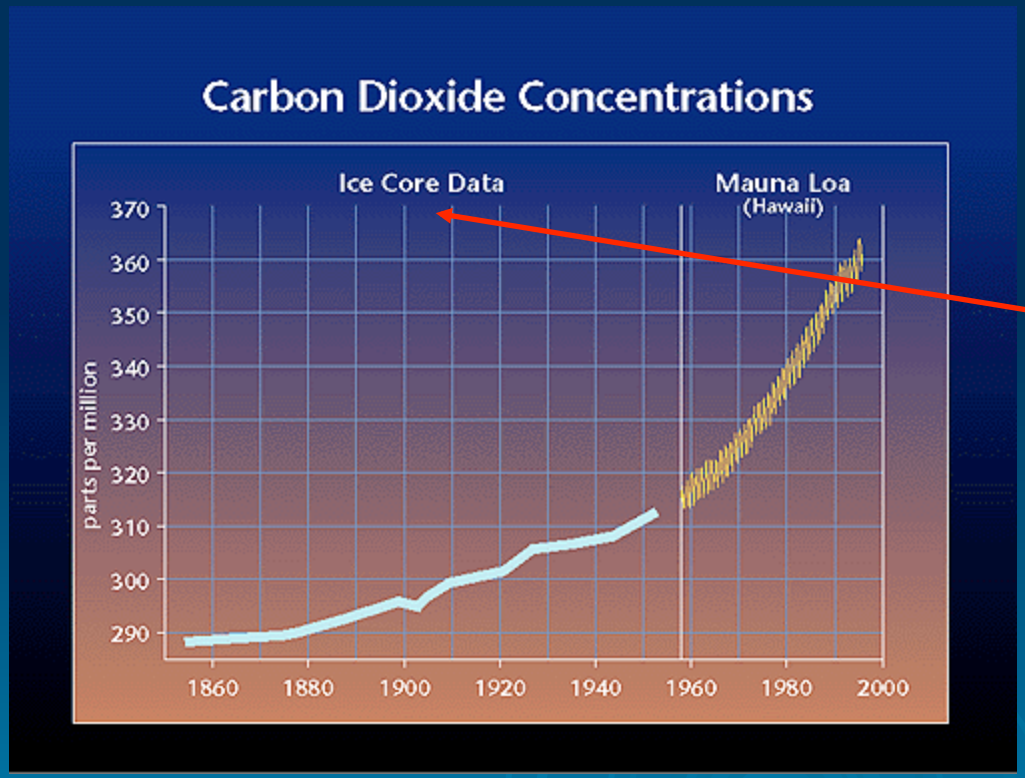

Figure 1. Map of Law Dome showing the locations of the ice cores studied and the approximate elevation and accumulation contours (adapted from *Hamley et al.* [1986]). A001 marks the approximate summit.

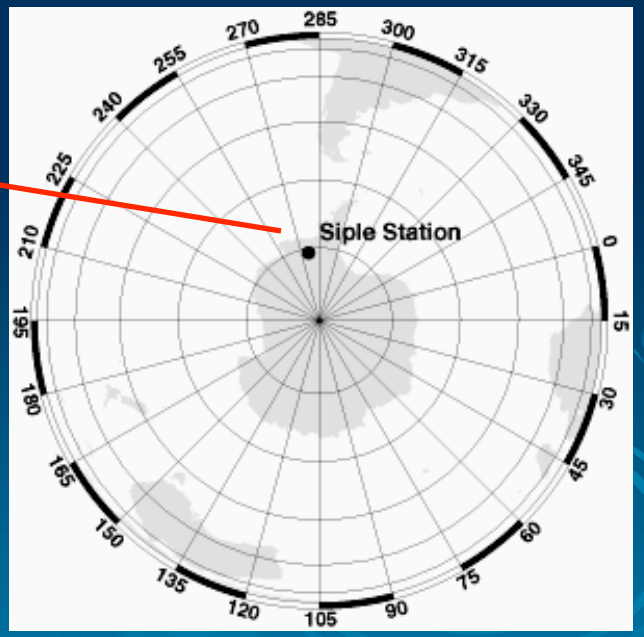



- Rise of atmospheric $CO_2$ over the last century has generally paralleled the rise in $CO_2$ emissions from fossil-fuel use
- The record of the last 1,000 years shows that natural variability is at most 10 ppm over 1,000 year time-scale

# ATMOSPHERIC $CO_2$ DURING THE LAST 140 YEARS

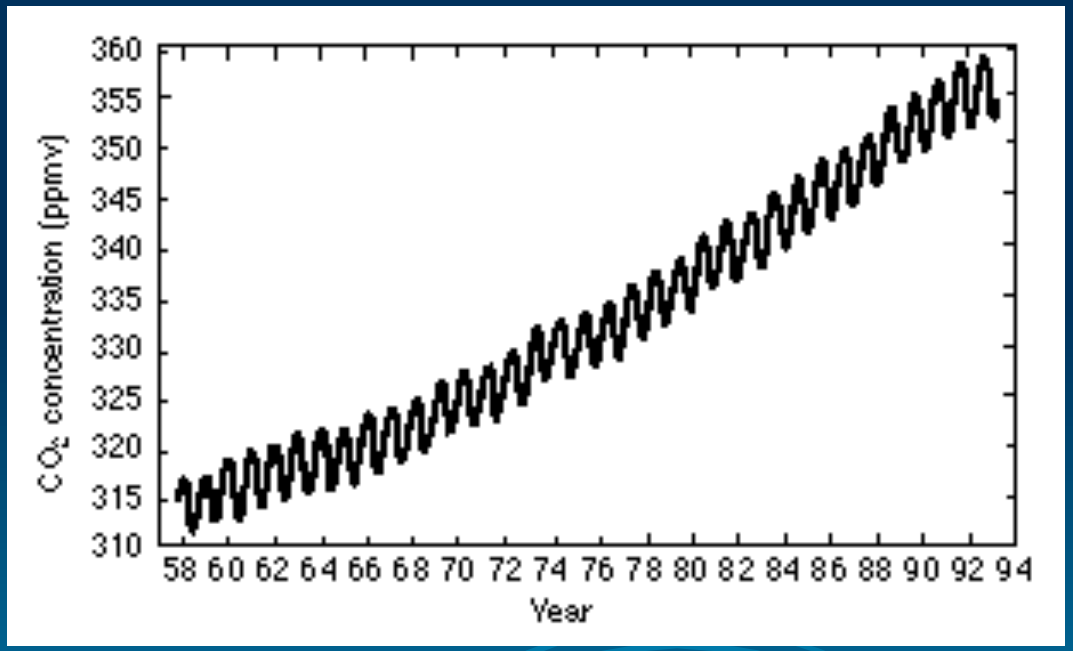
- Increase of ~90 ppm over last 140 years
- Is increase driven by anthropogenic $CO_2$ emmisions ?
- Winter maximum & summer minimum reflect the uptake of CO2 by vegetation during growing season, balanced by the net release of CO2 from the bisphere in Fall due to microbial decay



# Atmospheric $CO_2$ During The Last 60 Years

- Increase of ~40 ppm during the last 60 years
- This increase due mostly to fossil fuel combustion



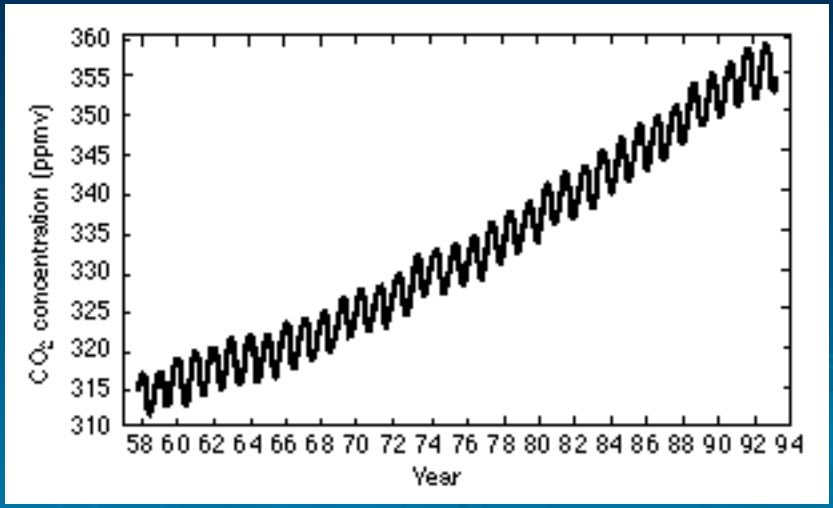

Measurements made at Mauna Loa in Hawaii

# The $CO_2$ Cycle

- The current global rate of increase of atmospheric CO2 is about 1.8 ppm a year

$$\frac{dm_{co_2}}{dt} = \frac{\Delta m_{co_2}}{\Delta t} = 1.8\,ppm$$

- This increase is due mostly fossil fuel combustion
- When fuel is burned, almost all of the carbon in the fuel is oxidized to CO2 and emitted to the atmosphere



# The $CO_2$ Cycle

- We can then use worldwide fuel use statistics to estimate the corresponding CO2 emission from

$$\frac{dm_{co_2}}{dt} = \sum sources - \sum \sin ks$$

1 kilogram (kg) = $10^3$ grams (g)
1 megagram (Mg) = $10^6$ g = $10^3$ kg
1 gigagram (Gg) = $10^9$ g = $10^6$ kg
1 tertagram (Tg) = $10^{12}$ g = $10^9$ kg
1 petagram (Pg) = $10^{15}$ g = $10^{12}$ kg

- Sources

| | |
|---|---|
| Fossil fuel combustion | 5.5 Pg/year |
| Deforestation in the tropics | 1.6 Pg/year |
| Total | 7.1 Pg/year |

- Sinks can be obtained as 3.3 Pg/year
- Sinks are the storage in the atmosphere
- So 46% of anthropogenic emissions are stored in the atmosphere, we need to understand the factors controlling these sinks

# The $CO_2$ Cycle

- Questions

  Where is the rest going?

  How will future anthropogenic emissions be distributed?

- The other half is transferred to other reservoirs (oceans, biosphere, and soils)

- We need to understand the factors controlling these processes

# The $CO_2$ Cycle

- Ocean-Atmosphere Exchange

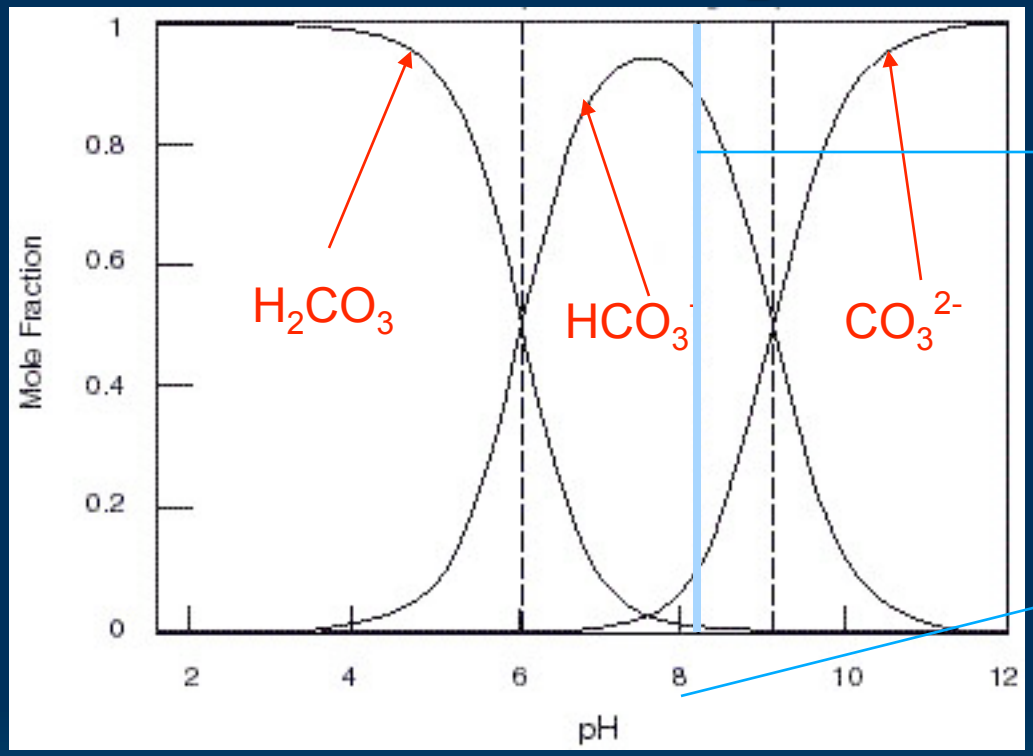
$CO_{2(g)} \Longleftrightarrow H_2CO_3$ (dissolved carbon dioxide)

- Ocean Carbonate Chemistry

$H_2CO_3 \Longleftrightarrow H^+ + HCO_3$ (bicarbonate ion)

$HCO_3^- \Longleftrightarrow H^+ + CO_3^{2-}$ (carbonate ion)

# The $CO_2$ Cycle




Ocean pH = 8.2

Most of the CO2 dissolved in the ocean in the form of HCO3

- Higher pH means lower $[H^+]$

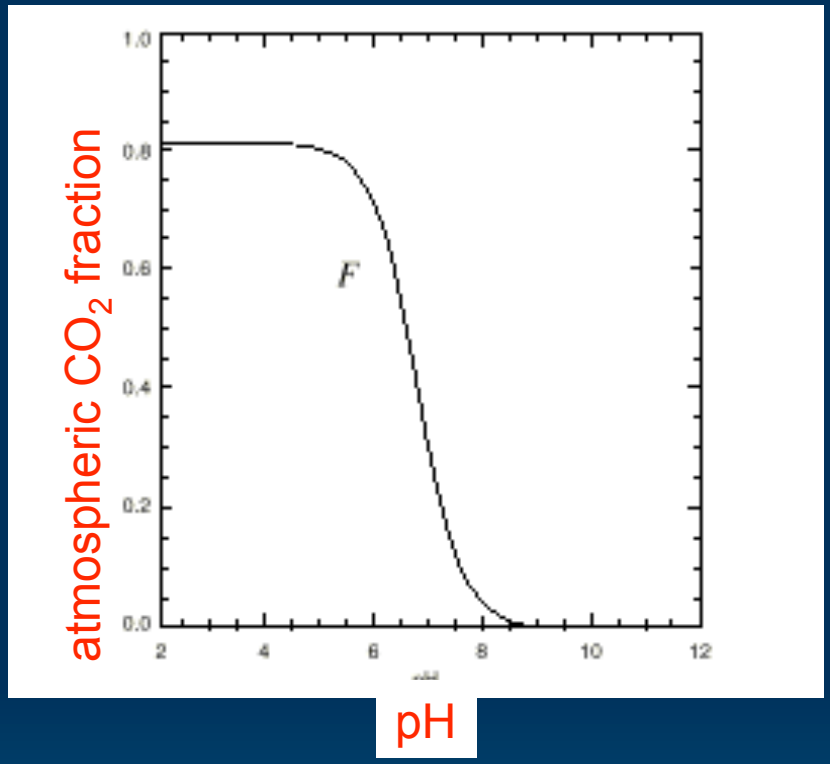
$$CO_{2(g)} \Longleftrightarrow H_2CO_3$$

$$H_2CO_3 \Longleftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \Longleftrightarrow H^+ + CO_3^{2-}$$

- The alkalinity of the ocean is maintained by weathering of rocks and river runoff

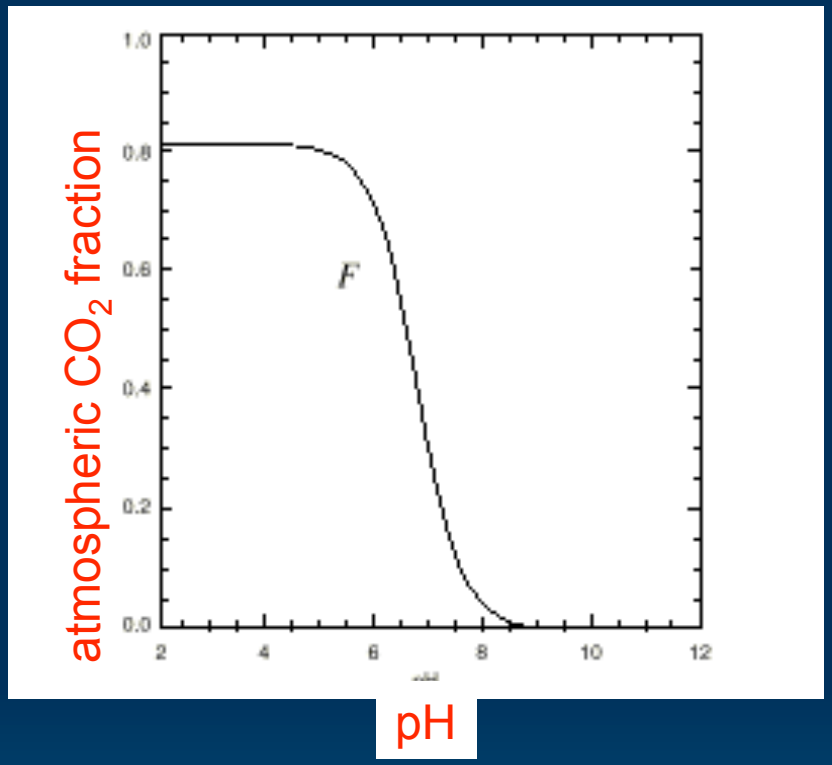
# The $CO_2$ Cycle




Key assumption: Atmosphere is in equil. with whole ocean, i.e ocean is mixed efficiently

- The concentration of CO2 in the atmosphere and in the ocean are related by equilibria
- Let F represent the atmospheric fraction of CO2 in the atmopshere-ocean system

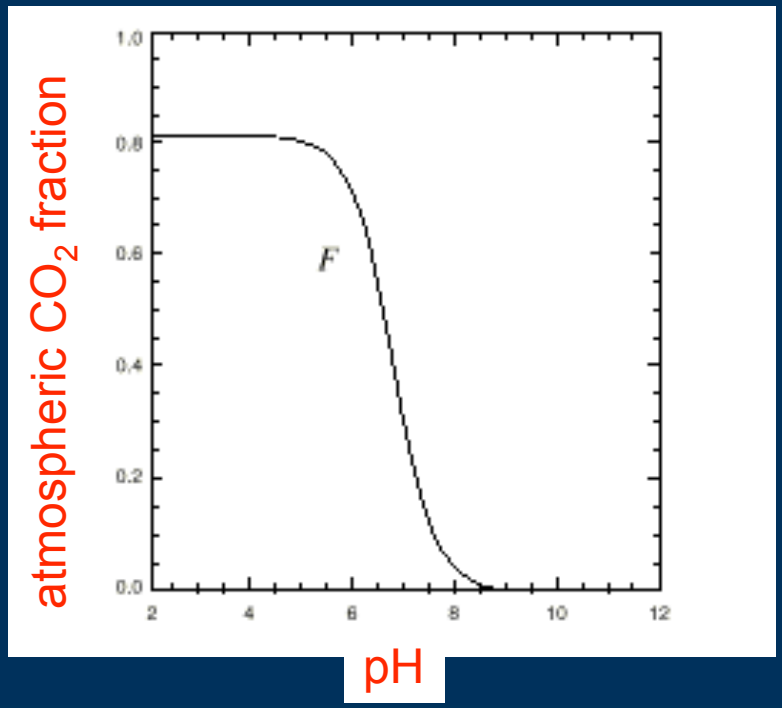
# The $CO_2$ Cycle




Key assumption: Atmosphere is in equil. with whole ocean, i.e ocean is mixed efficiently

- For an ocean pH of 8.2, the atmospheric fraction of CO2 in the atmosphere-ocean is equal to F=0.03
- So, at equilibrium, almost all of CO2 is dissolved in the ocean
- Only 3% is in the atmosphere

# The $CO_2$ Cycle

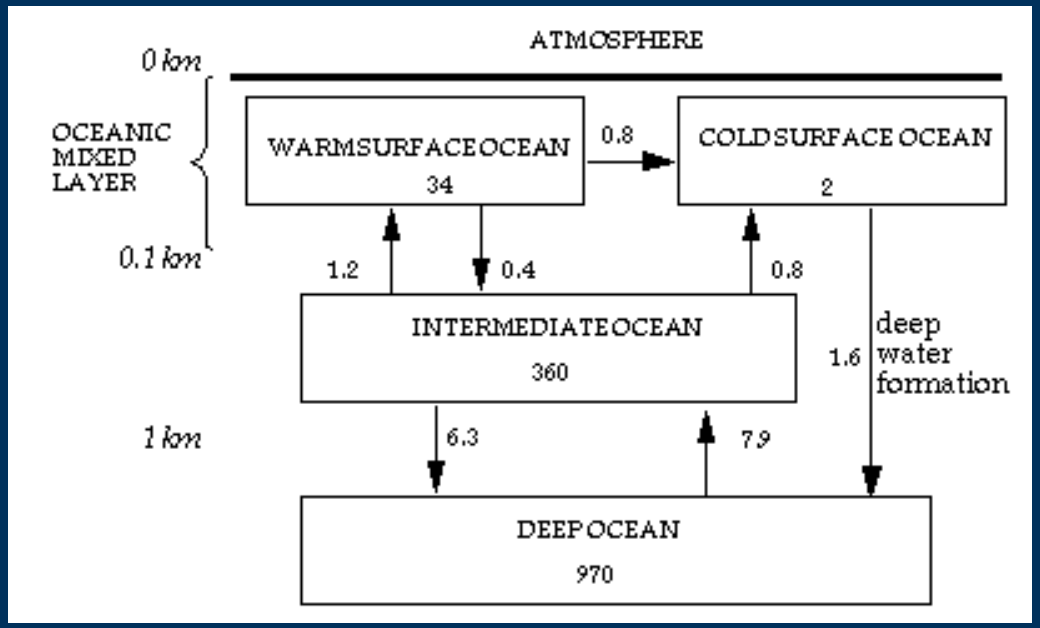



- However such an inference is flawed
- Because it ignores the acidification of the ocean resulting from added CO2
- As atmospheric CO2 increases, H increases and hence F increases
- This effect is a positive feedback to increases in the atmospheric CO2

# The $CO_2$ Cycle

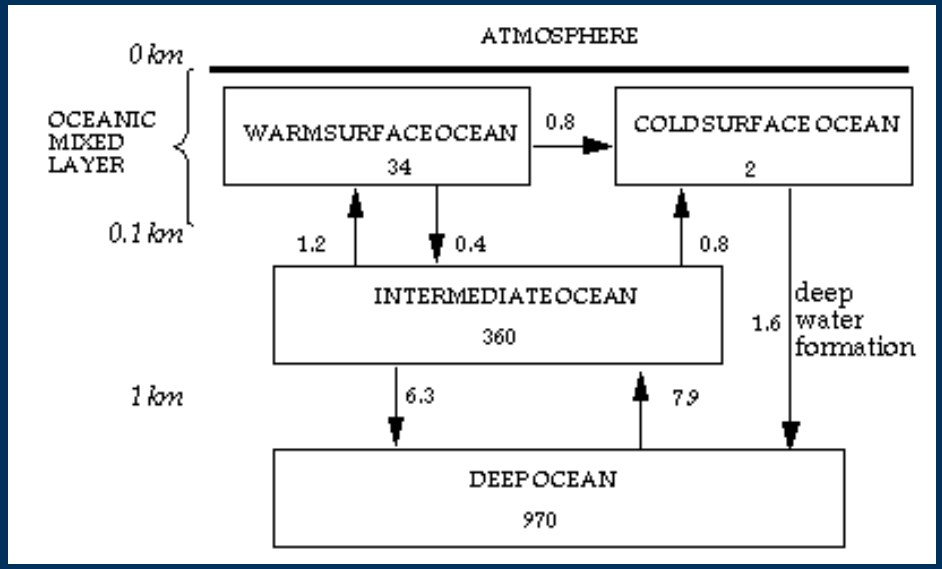
- However current estimated F= 0.30
- This means at equilibrium, 30% of CO2 emitted in the atmosphere remains in the atmosphere and the rest is incorporated into the ocean
- This assumes that atmosphere and ocean in equilibrium.
- But this is not correct due to the slow mixing of the ocean

# The $CO_2$ Cycle



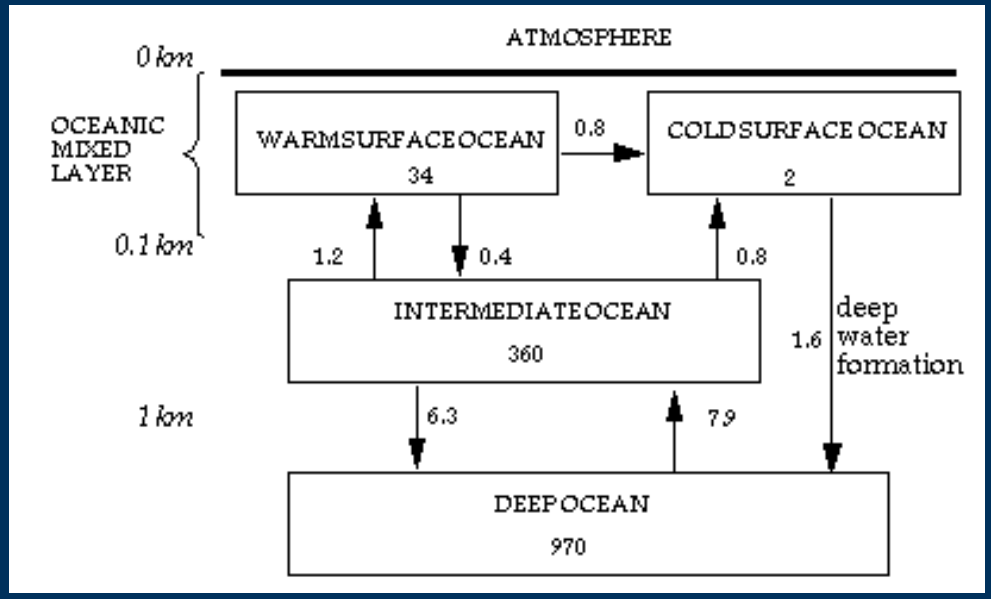

- Vertical mixing in the ocean is driven by buoyancy
- Two factors determine buoyancy; temperature and salinity
- Sinking of water takes place in polar regions; cold, salty and hence heavy
- In other regions, vertical mixing is suppressed; warmer temperatures
- Some mixing still takes place within ~100 m depth due to wind stress

# The $CO_2$ Cycle




- Residence times of water are 18 years for the oceanic mixed layer
- 40 years for the intermediate ocean
- 120 years for the deep ocean
- So, equilibrium of the whole ocean in response to a change in atmospheric CO2 therefore takes place on a time scale of the order of 200 years
- This means that CO2 released in the atmosphere over the past ceuntry has not had time to equilibrate with the whole ocean

# The $CO_2$ Cycle




- So the best current estimate from oceanic transport and chemistry models is that 30% of fossil fuel CO2 emitted to the atmosphere is incorporated in the oceans
- We discussed earlier that only 50% of emitted CO2 actually remains in the atmosphere
- That leaves a 20% missing sink
- We now turn our attention to the biosphere as a possible explanation for the missing sink, BIOSPHERE

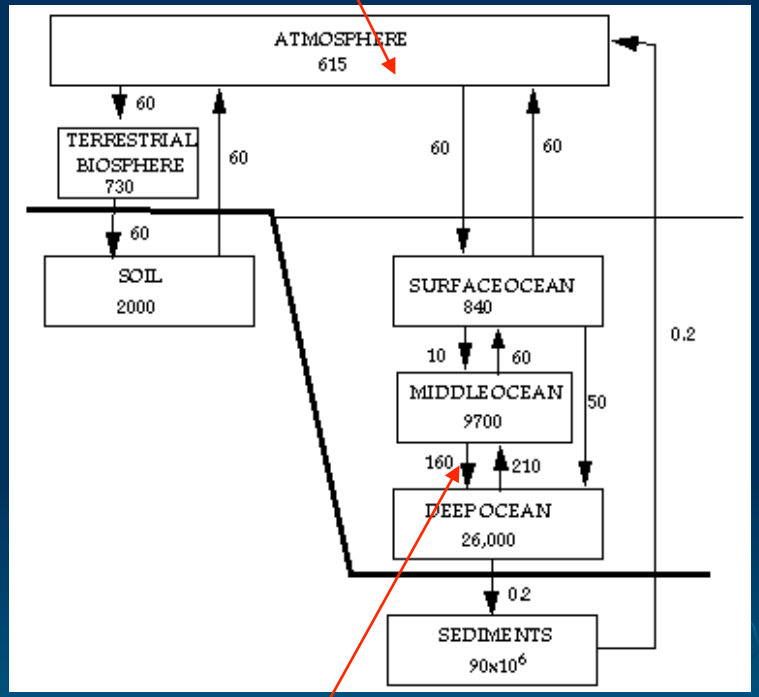
# The $CO_2$ Cycle

- Cycling of atmospheric CO2 with the biosphere involves processes of photosynhesis, respiration and microbial decay
- The lifetime of CO2 against net uptake by terrestrial plants is 9 years
- This thought to be 20% missing link of CO2 emitted by fossil fuel combustion.

# The $CO_2$ Cycle

- $CO_2$ added to the atmosphere partitions between the atmosphere, oceans, and terr. biosphere
- CO2 uptake by the biosphere is subject to limiting plant growth
- CO2 uptake by the ocean is limited by acidification and slow mixing
- Ultimate removal of the CO2 added to the atmosphere by fossil fuel combustion requires transfer of oceanic carbon to the lithosphere by formation of sedimentation
- The time scale for this transfer is estimated as 170,000 years
- One can conclude that fossil fuel combustion induces a very long-time perturbation to the global carbon cycle
- Humans effect this perturbation!

Inventories within the boxes are in Pg




Flows indicated by arrows in Pg/year