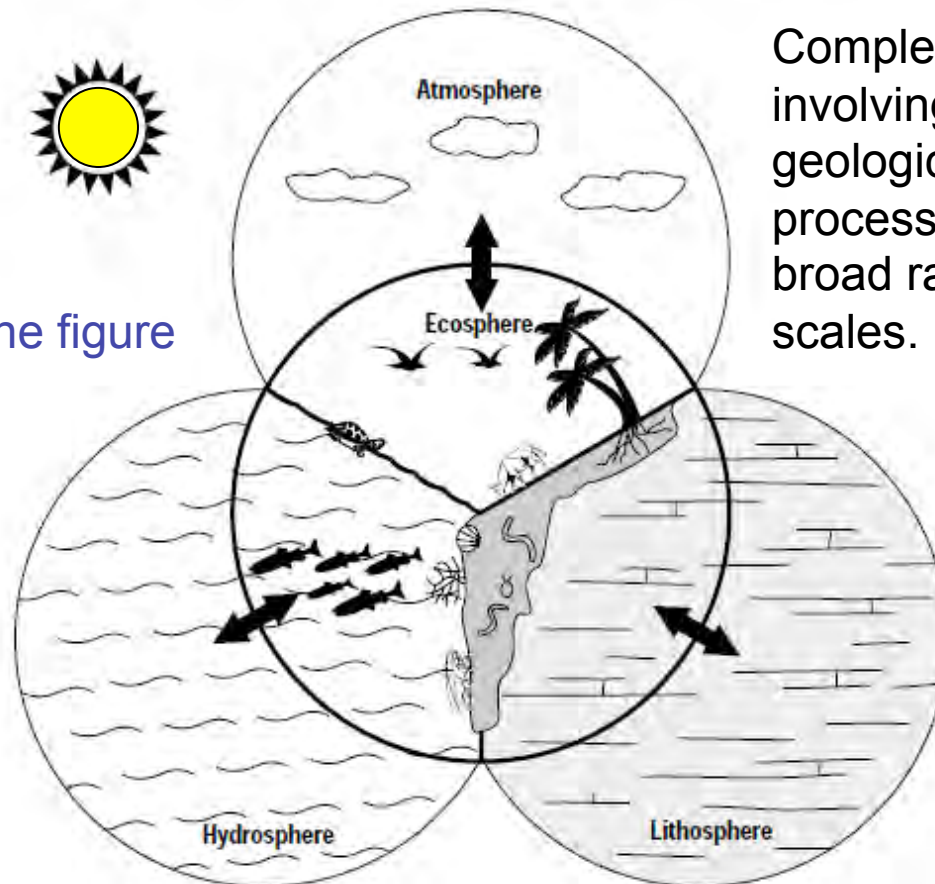


# Global Biogeochemical Cycles

**The interactions between the various spheres of the earth system**

*(after Christensen, 1991).*



Complex interactions involving biological, geological, and chemical processes operating on a broad range of time scales.

Place yourself on the figure

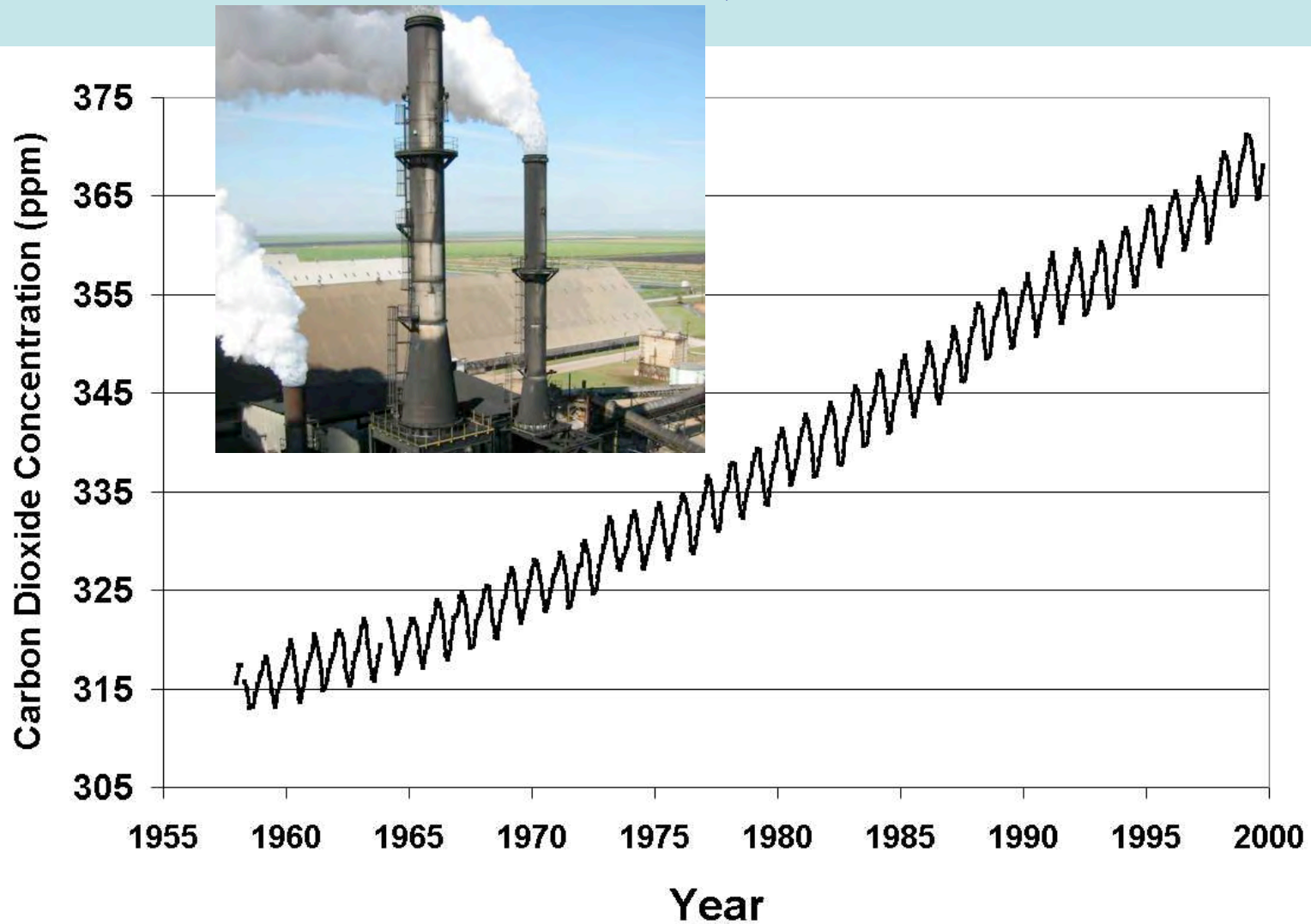
# Why Study Global Biogeochemical Cycles?

Understanding how the world works and how we are changing natural processes.



- Biogeochemical cycles provide the basic framework for investigating global change and its implications for life on earth.
- An understanding of biogeochemical cycles and anthropogenic impacts on them is fundamental for predicting impacts of global climate change.

# Atmospheric CO<sub>2</sub> concentrations at Mauna Loa, Hawaii



## The global biogeochemical cycles of many elements have been altered by human (anthropogenic) activity

Fossil fuel burning alone accounts for perhaps 80% of sulfur dioxide (SO<sub>2</sub>) emissions from the land surface to the atmosphere, 50% of carbon monoxide, 50% of NO<sub>x</sub>, 20% of methane, 5% of ammonia, and 4% of nitrous oxide. It is also responsible for 70–90% of anthropogenic CO<sub>2</sub> emissions to the atmosphere. CO<sub>2</sub> in the atmosphere increased by 30% since the industrial revolution.

# What do we try to understand in these studies?

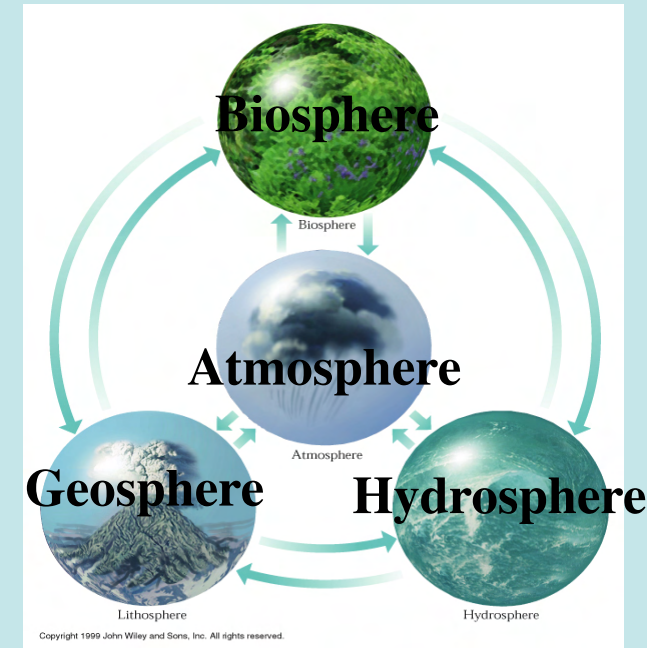
The present state of the Earth's surface environment.

What controls it.

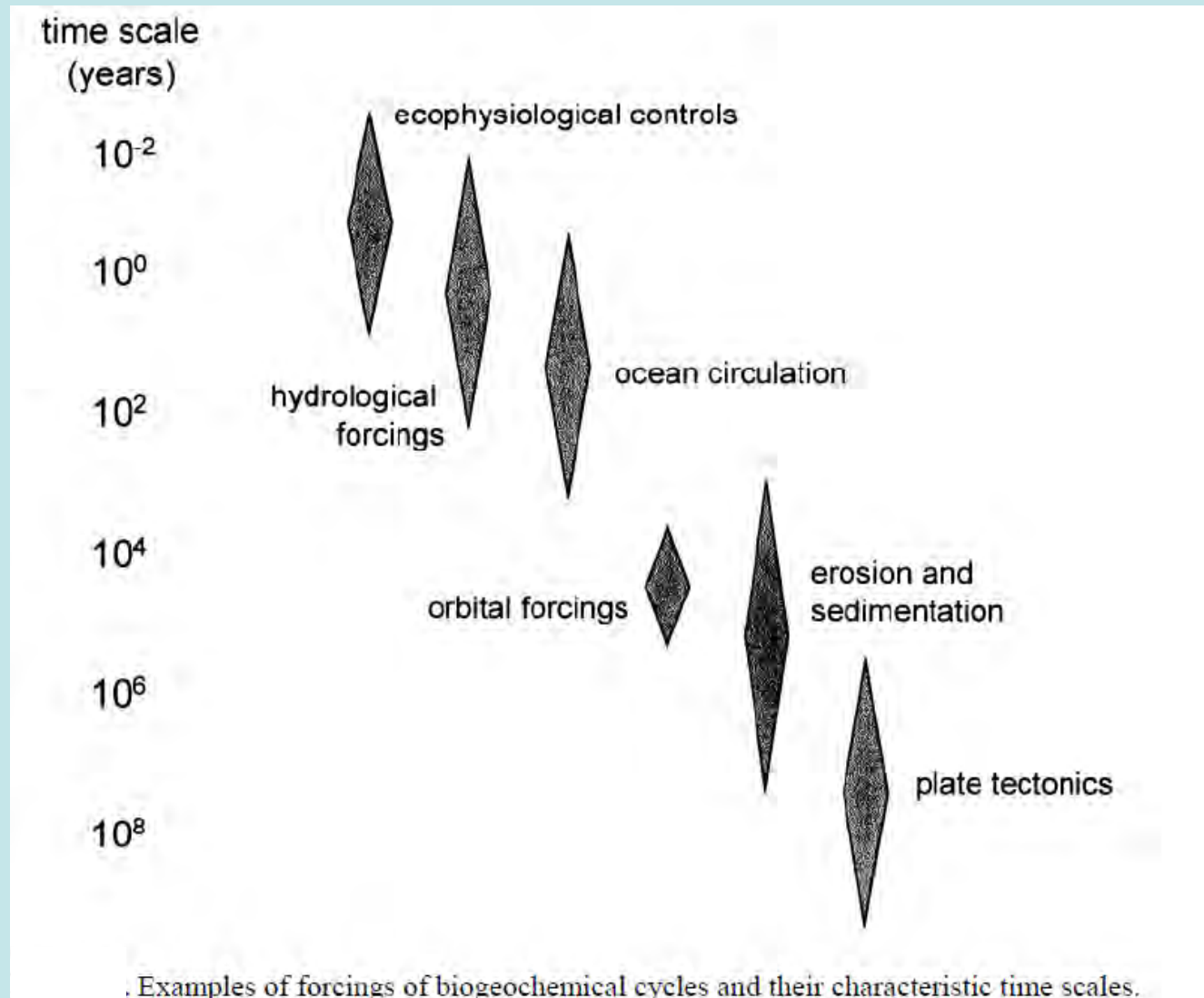
How it got to its present state.

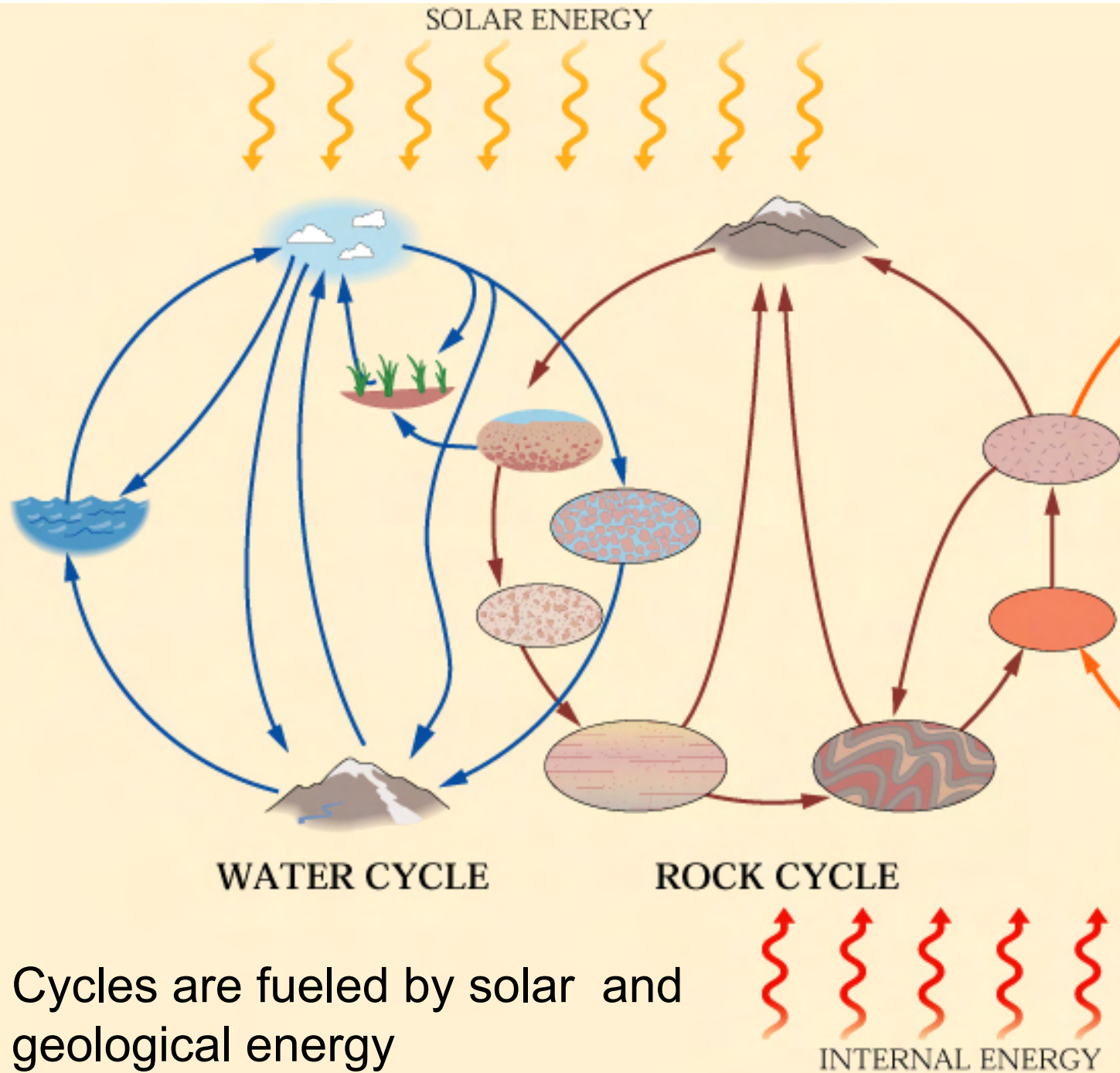
How did it change over Earth's history.

What are the processes/feedbacks that sustain a habitable planet.



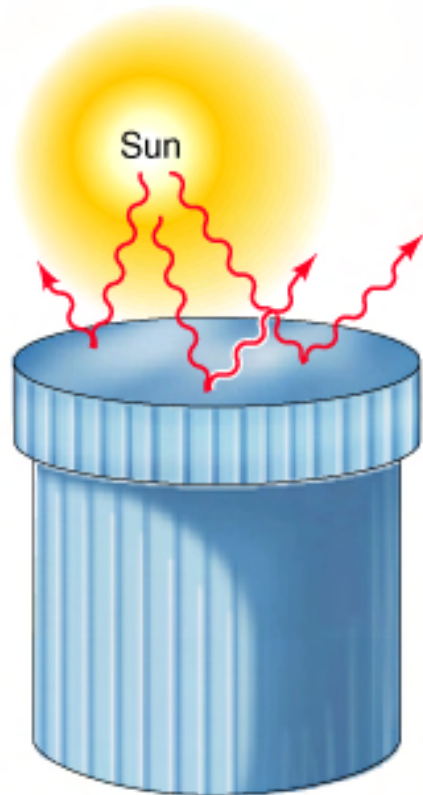
# Biogeochemical cycles operate on many different spatial and temporal scales



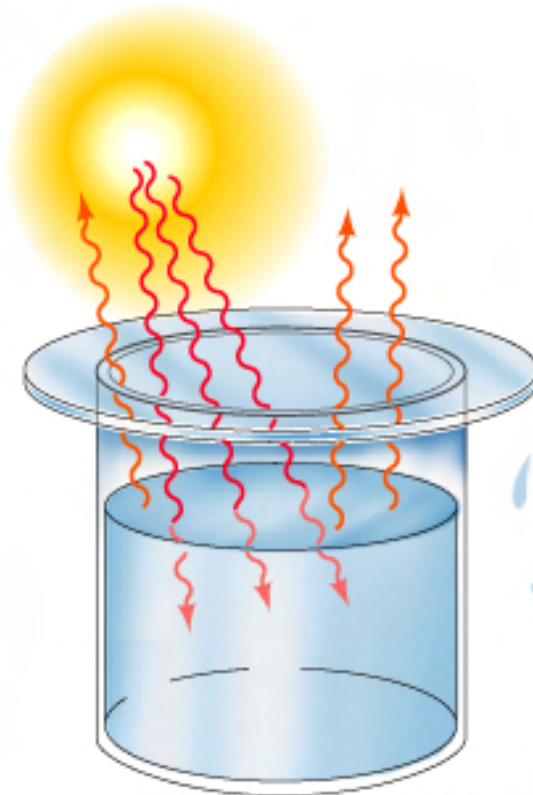


Cycles are fueled by solar and geological energy

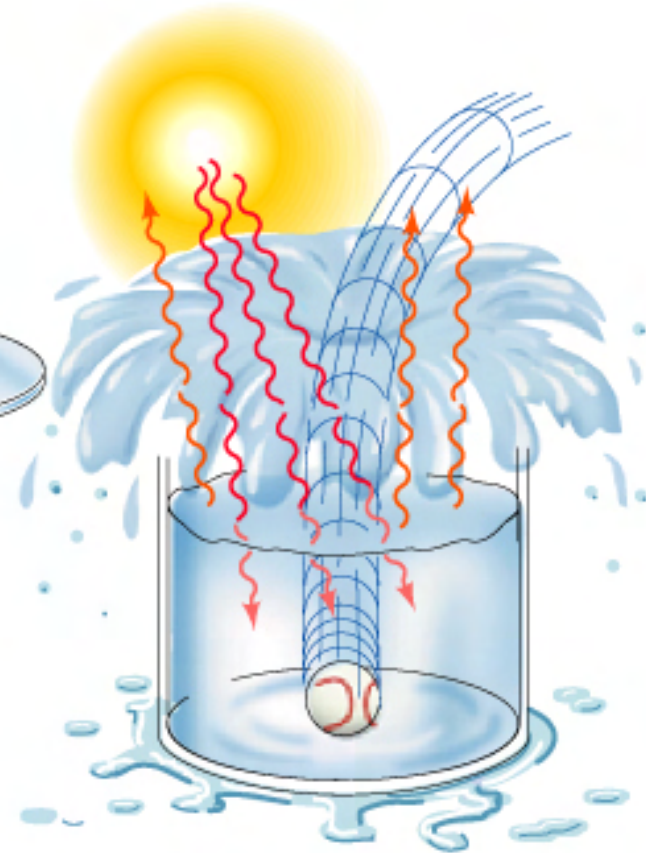
# Three basic types of system



A. Isolated system



B. Closed system

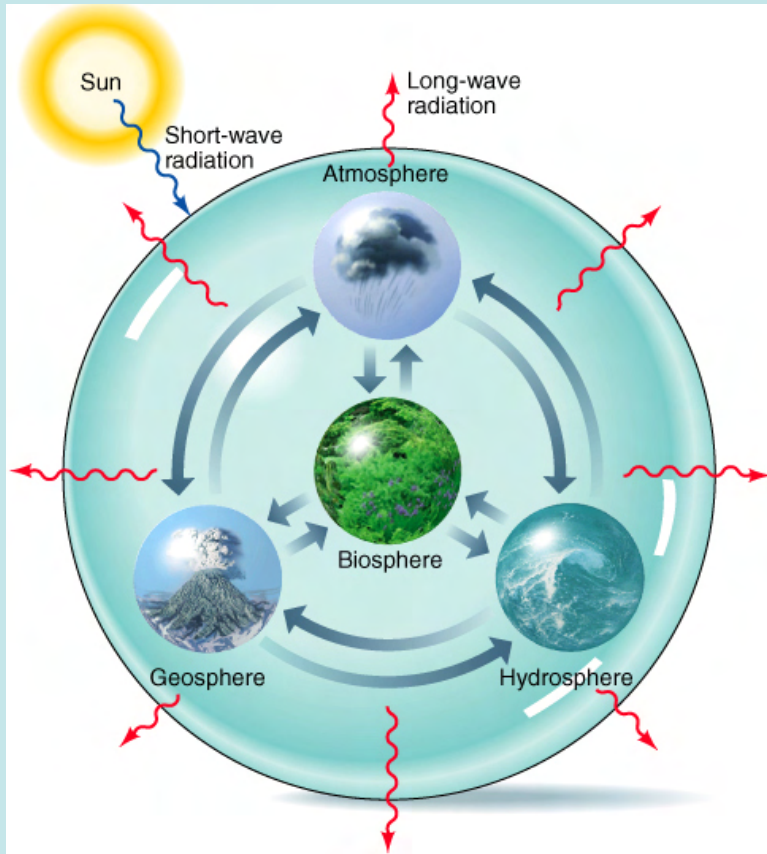


C. Open system

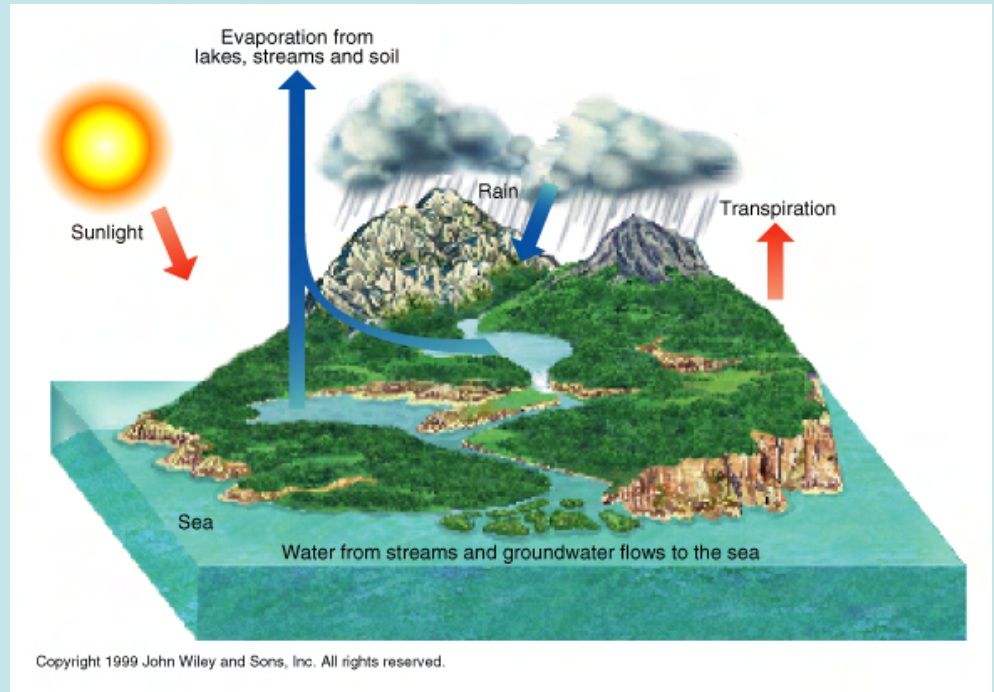
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# A closed system



# An open system

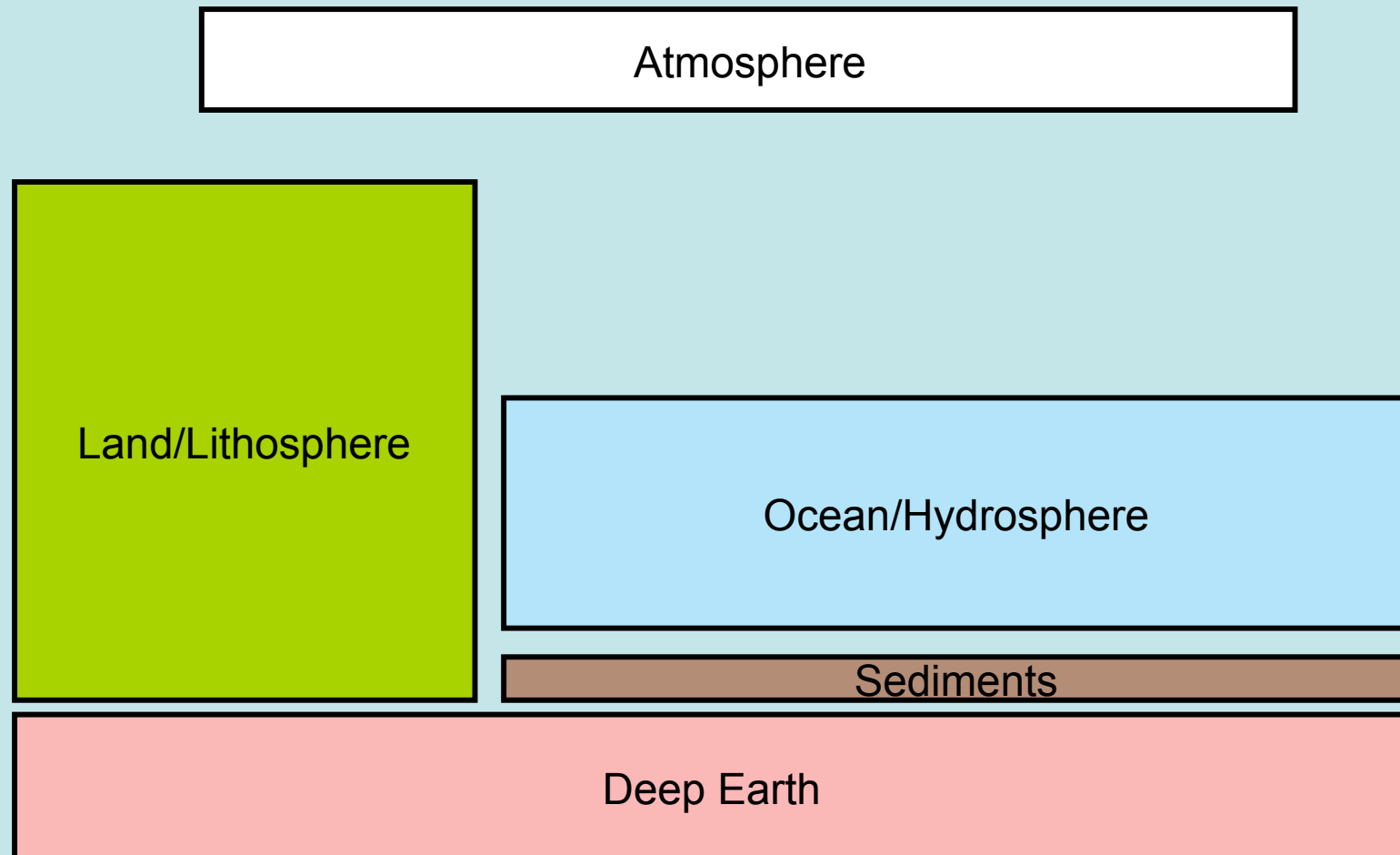


# Reservoirs

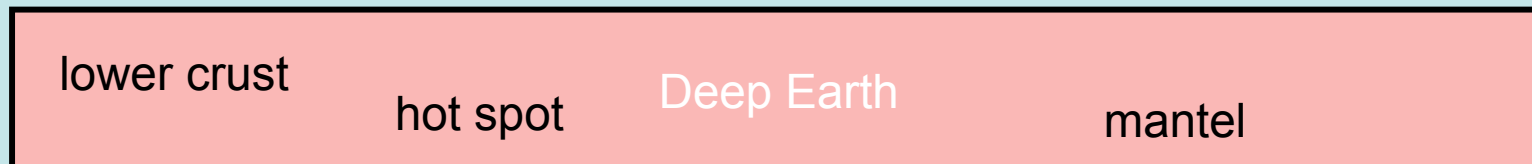
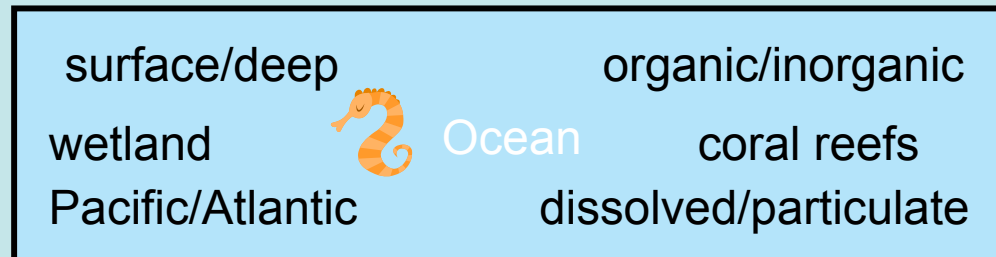
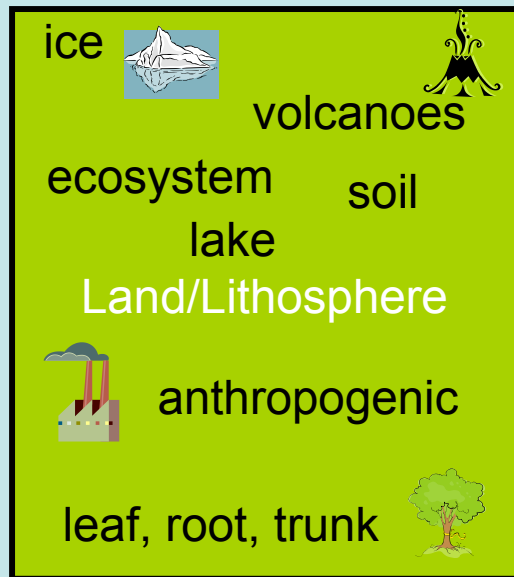
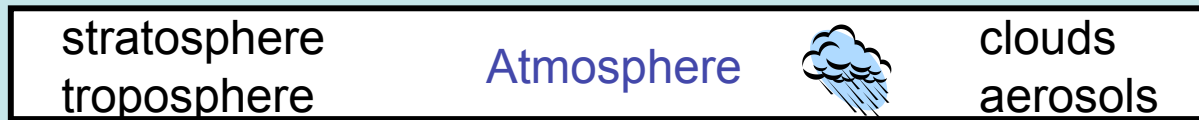
A reservoir is a physically well-defined system. A given setting with defined physical and/or biological boundaries. In each reservoir, the relevant chemical, physical and biological properties are assumed to be (reasonably) uniform. A reservoir will contain a collection of matter.

**EXAMPLES?**

# Major Reservoirs



# Additional Reservoirs

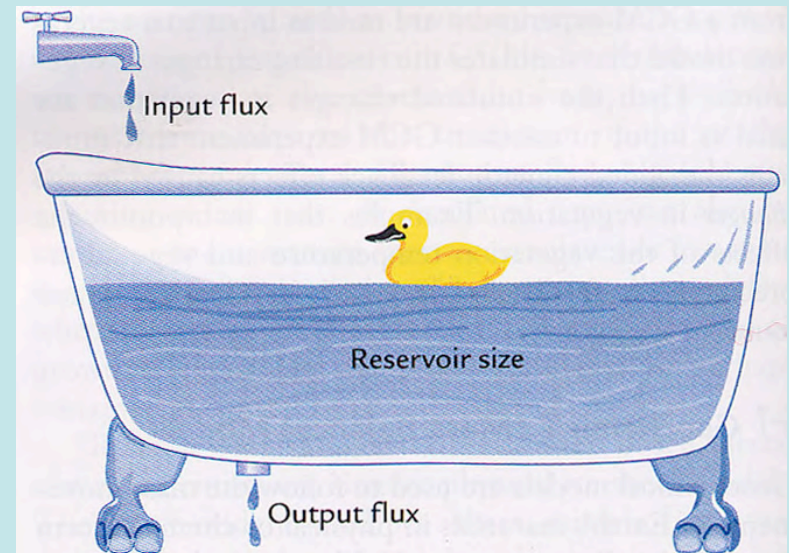


# Fluxes - Material Transport

*Fluxes* transfer of matter from one reservoir to another. A flux into a reservoir is sometimes referred to as a *source*, a flux out of the reservoir as a *sink*.

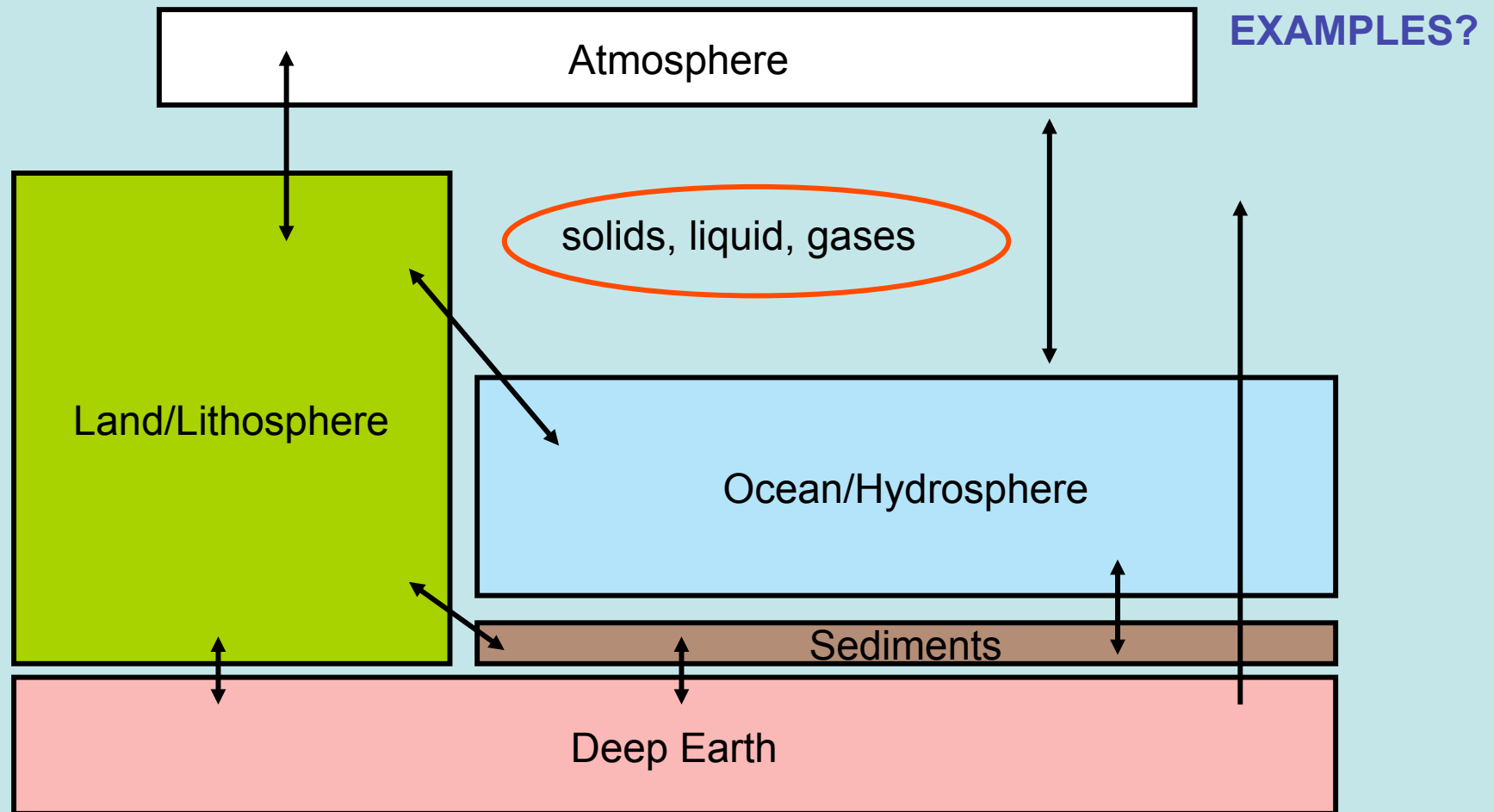
For a perfectly mixed reservoir, the concentration of a component in the outflow is equal to the uniform concentration inside the reservoir.

Biogeochemical Cycles – Matter and energy move all the time at different rates from one earth reservoir to another.



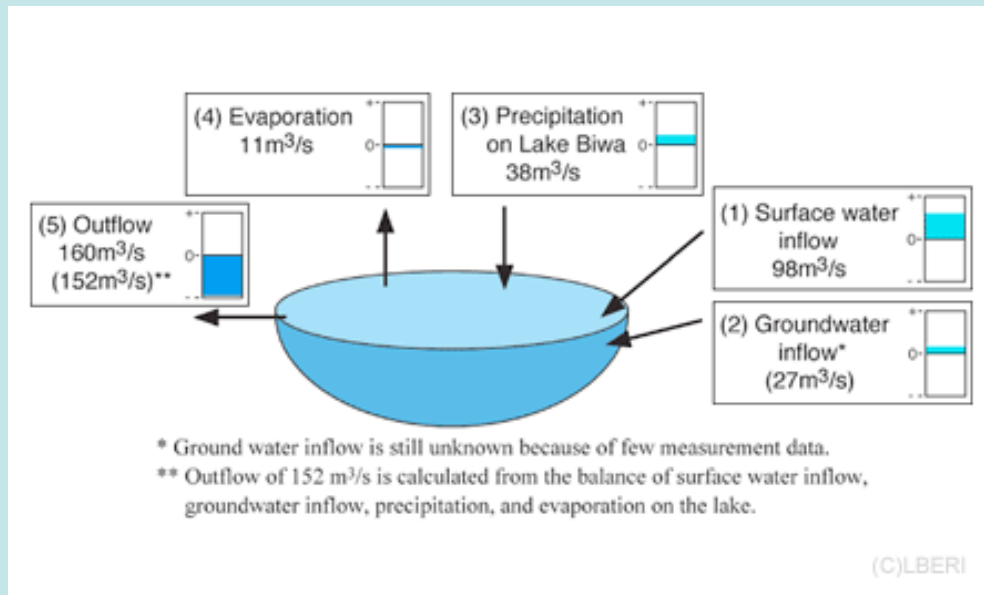
# Material Transfer

Matter and energy flow between and within these reservoirs



# Representing Biogeochemical Cycles

The two main tasks in depicting a biogeochemical cycle is the definition of the reservoirs and the parameterization of the fluxes. There are no magic guidelines, other than to clearly define the goals of the work and system of investigation and to start as simple as possible. Obviously, it is only possible to provide direct information on reservoirs, fluxes and parameters that are explicitly represented.



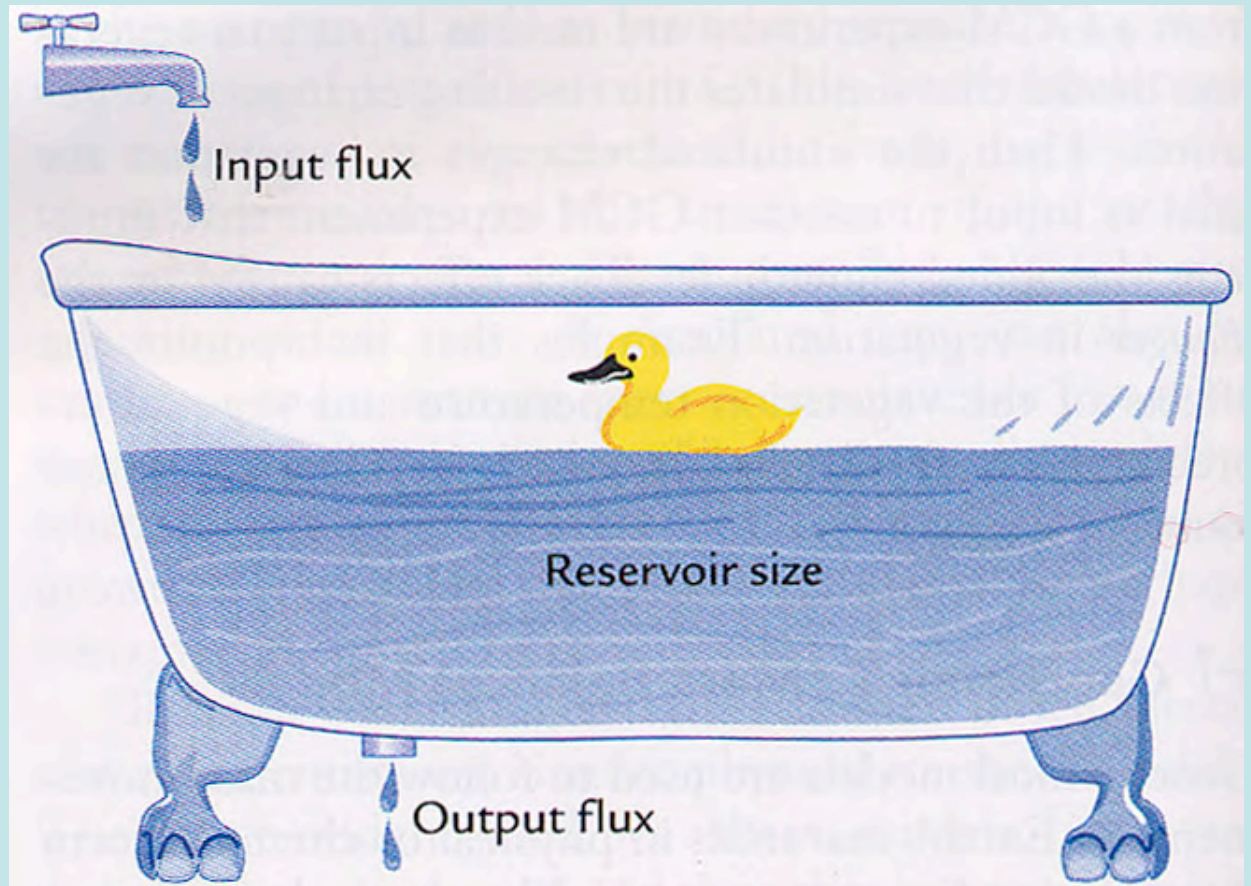
# Steady State

Steady-state is a common assumption made about the changes in the components of a system (lack of)

For steady-state:

$$\text{Flux}_{\text{in}} = \text{Flux}_{\text{out}}$$

An  
equilibrium  
state





# Residence Time

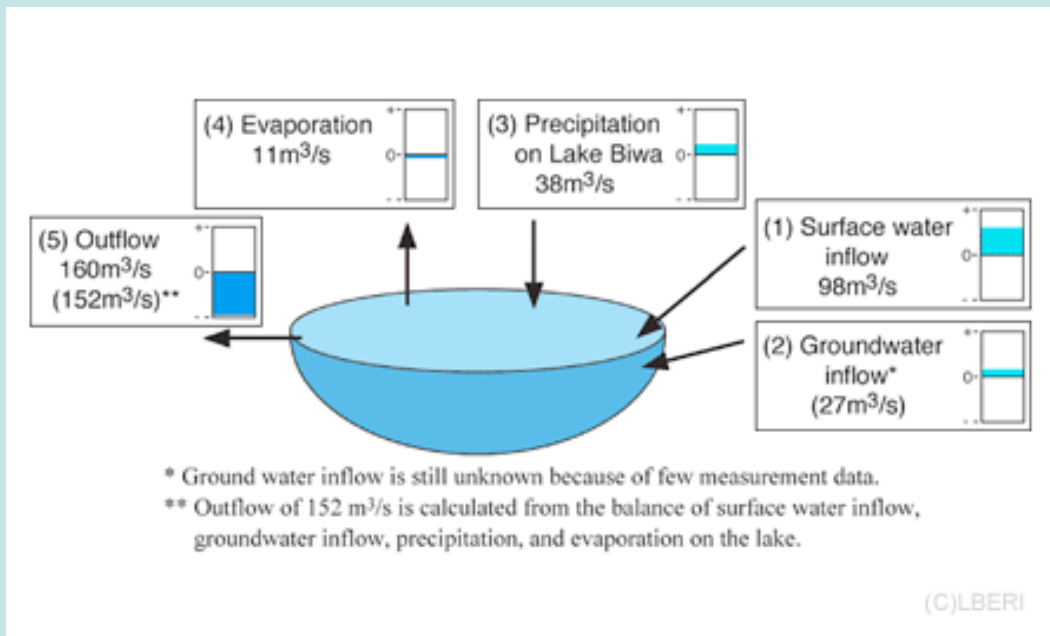
- **Residence Time** – how quickly a substance cycles through a reservoir (exchange rate)
  - **Content** – the total amount of any constituent in a reservoir (standing stock)
  - **Capacity** – maximum concentration of a substance a reservoir can reach before saturation occurs
  - **Rate of In/outflux** – how much of a substance get into/out a reservoir at a given time.
- Residence times for different elements vary widely
  - Humans can alter the rate of influx/outflux by our activity (pumping, diversion, adding pollution)

# Mass Balance

The turnover time is defined as

$$t_R = \frac{M}{F_{out}}$$

where  $M$  is the mass of the reservoir (say, the total number of moles of organic carbon in marine biota) and  $F_{out}$  is the total flux out of the reservoir (i.e., the sink or source).



Content = 1,000,000 m<sup>3</sup>  
Input = 163 m<sup>3</sup>/s

Residence Time  
1,000,000/163 =  
6000 seconds = 1.66 hours

# Non Steady State Conditions

- In many instances the source (Q) and sink (S) rates are not constant with time or they may have been constant and suddenly change (transient events or perturbation).
- To describe how the mass in a reservoir changes with time after an increase in source (or sink) for a reservoir

**Starting with:  $dM/dt = Q_0 - S = Q_0 - kM$**

**We let the input change to a new value  $Q_1$  and we assume that the initial amount at  $t = 0$  is  $M_0$ .**

**The new equation is:  $dM/dt = Q_1 - kM$**

**and the solution is:  $M(t) = M_1 - (M_1 - M_0) \exp(-kt)$**

**This describes how M changes from  $M_0$  to the new equilibrium value  $M_1 (= Q_1 / k)$  with a response time equal to  $k^{-1}$ .**

**For constant exponential change  $Q = Q_0 \exp[m(t - t_0)]$**

**The solution for  $dM/dt$  for these conditions is:**

**$M = M_0 \left\{ \frac{m}{m+k} \exp[-k(t-t_0)] + \frac{k}{m+k} \exp[m(t-t_0)] \right\}$  for  $t_0 < t < t_1$**

# Reactive Transport Models

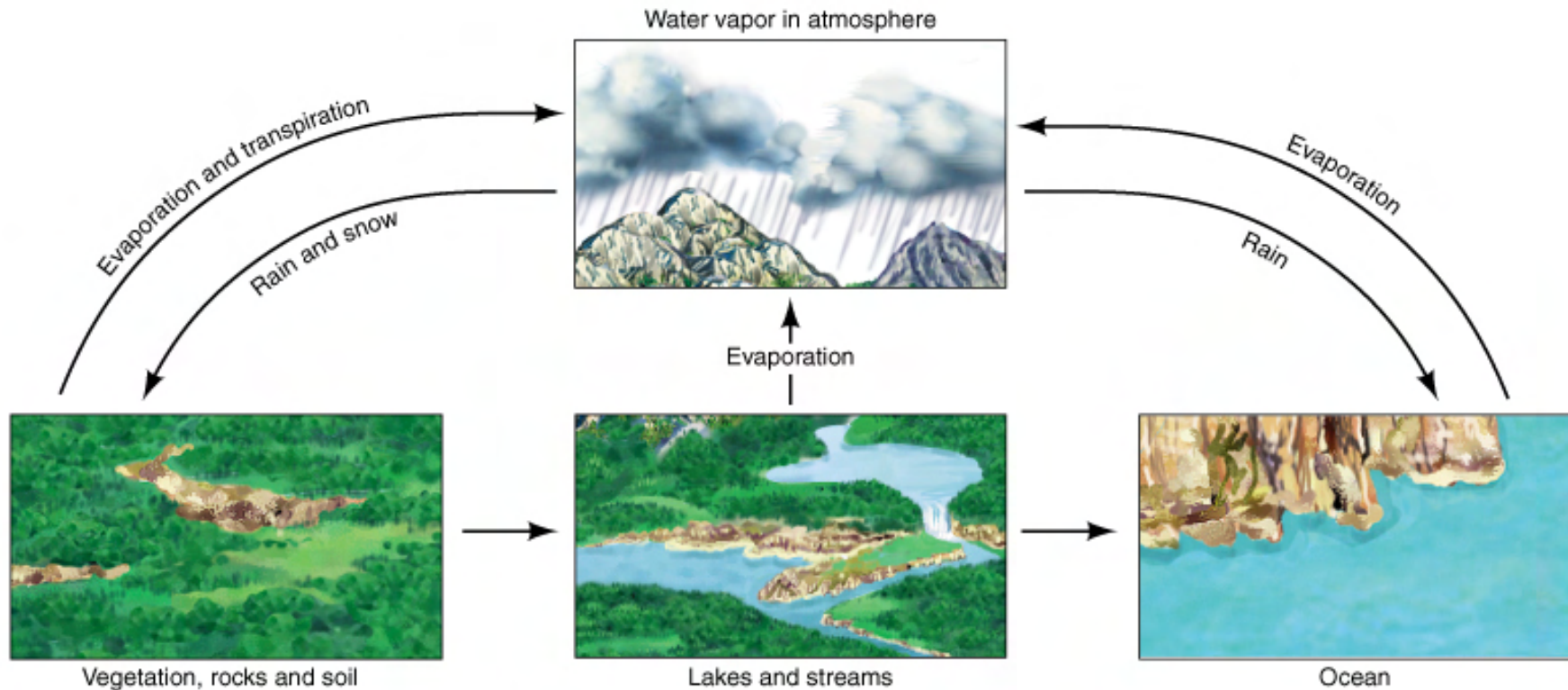
Reactive transport models

$$\frac{dC_{res}}{dt} = \frac{1}{\bar{t}_f} (C_{in} - C_{res}) + R$$

For a system with a single inlet and a single outlet

where  $C_{in}$  is the concentration of the species in the inflow,  $R$  is the rate, per unit volume, at which the species is produced in the system (note: when the species is being consumed  $R$  is negative), and  $t_f$  is the mean residence time (or transit time) of the carrier fluid in the system.

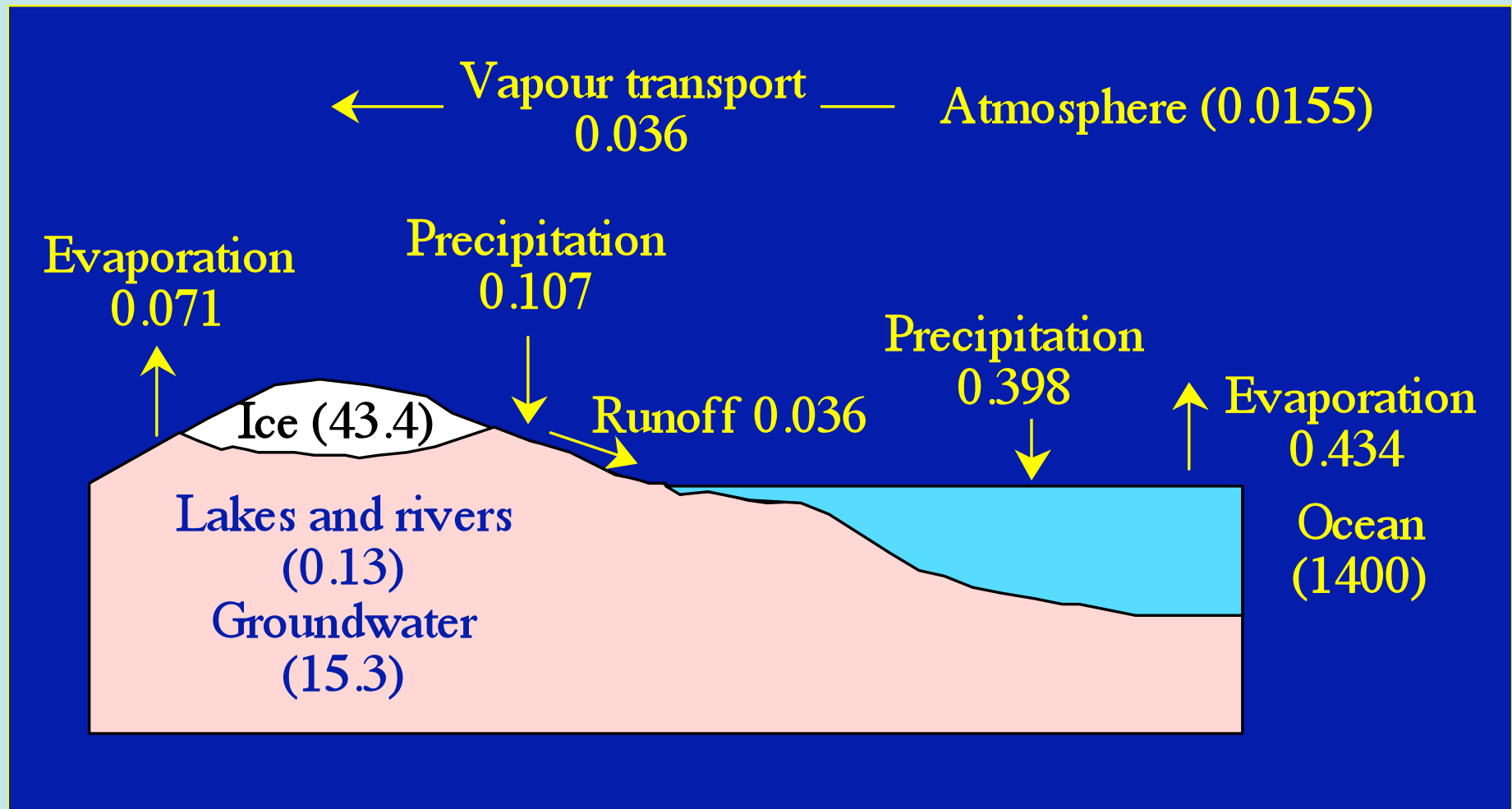
# Box models - Reservoirs and Fluxes



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# Changes in the Water Cycle

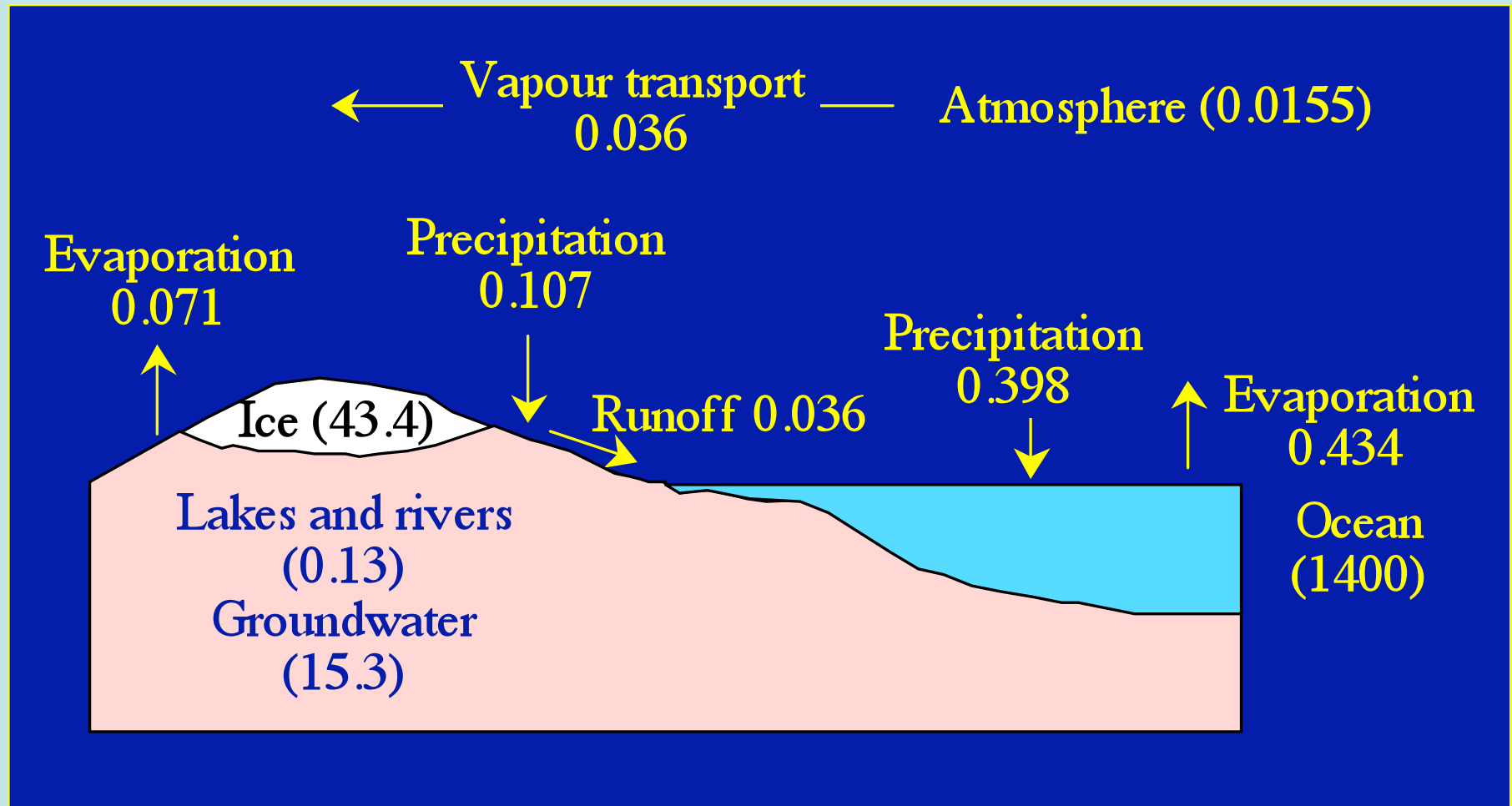
# Box models - Reservoirs and Fluxes



Reservoir total inventories (in brackets) in units of  $10^6 \text{ km}^3$ .

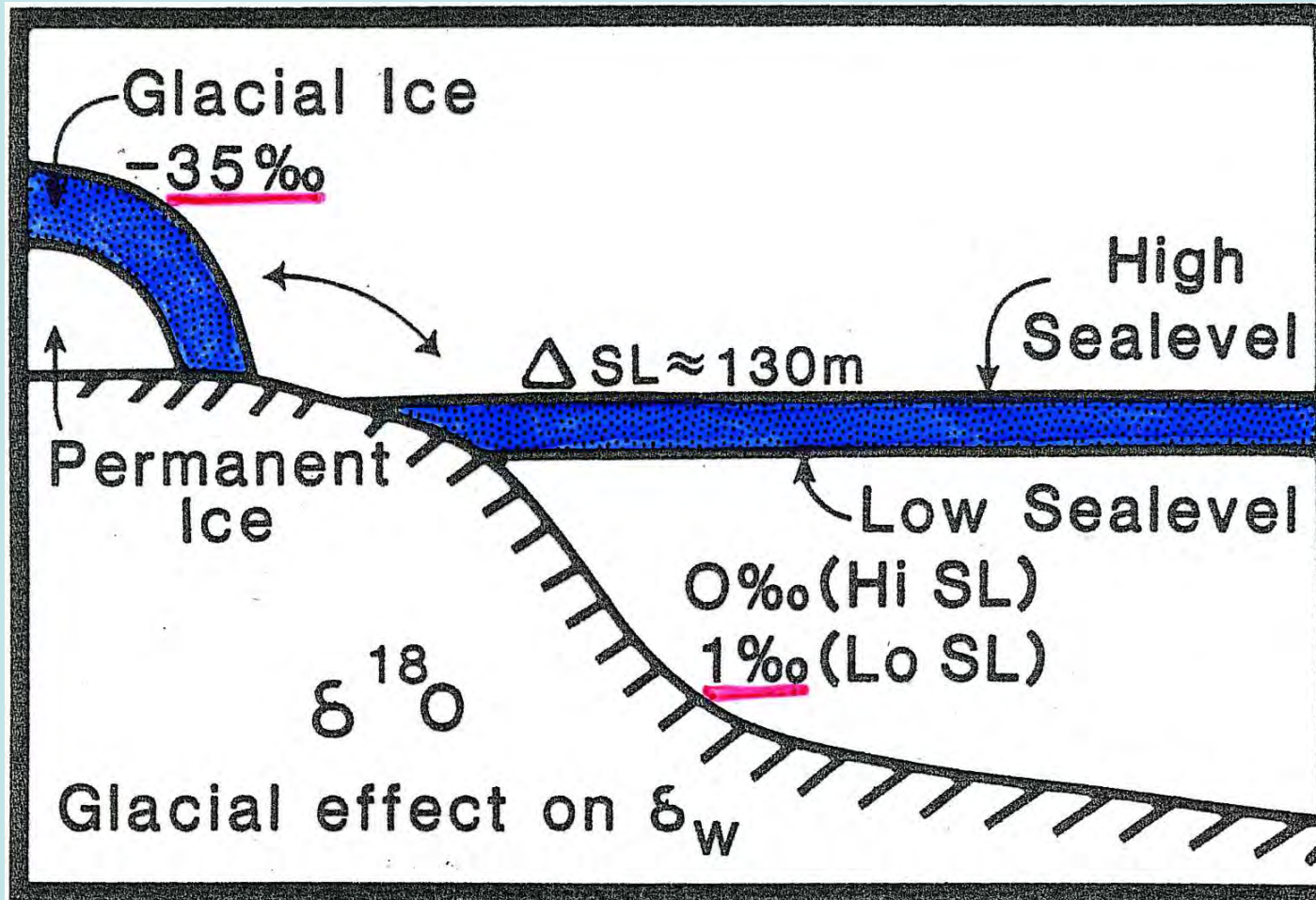
Fluxes in units of  $10^6 \text{ km}^3 \text{ yr}^{-1}$ .

# Box models - Reservoirs and Fluxes



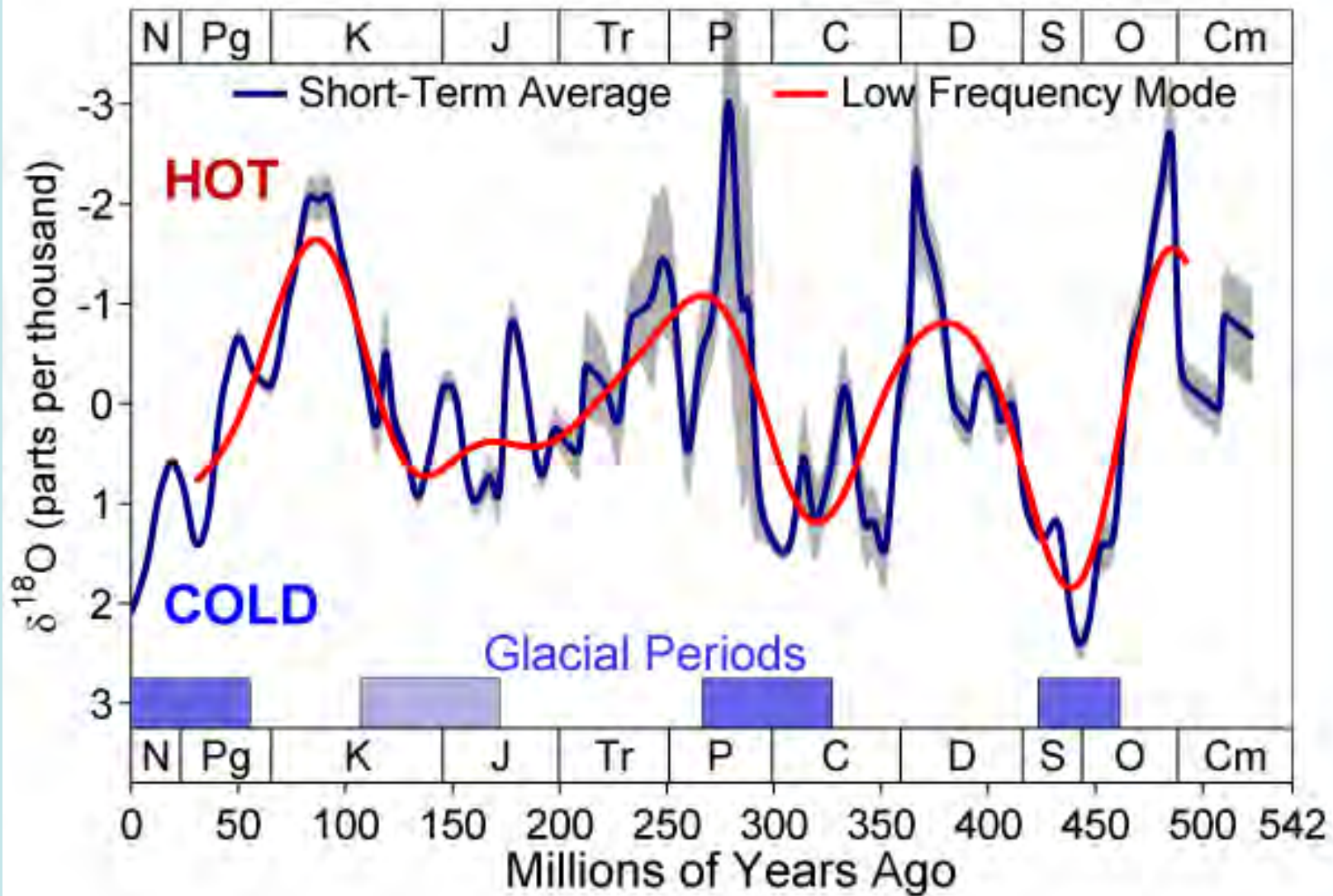
Ocean Flux in =  $0.398$  (precipitation) +  $0.036$  (runoff) =  $0.434$   
 Flux out =  $0.434$  (evaporation)  
 Residence Time  $1400/0.434 = 3200$  years

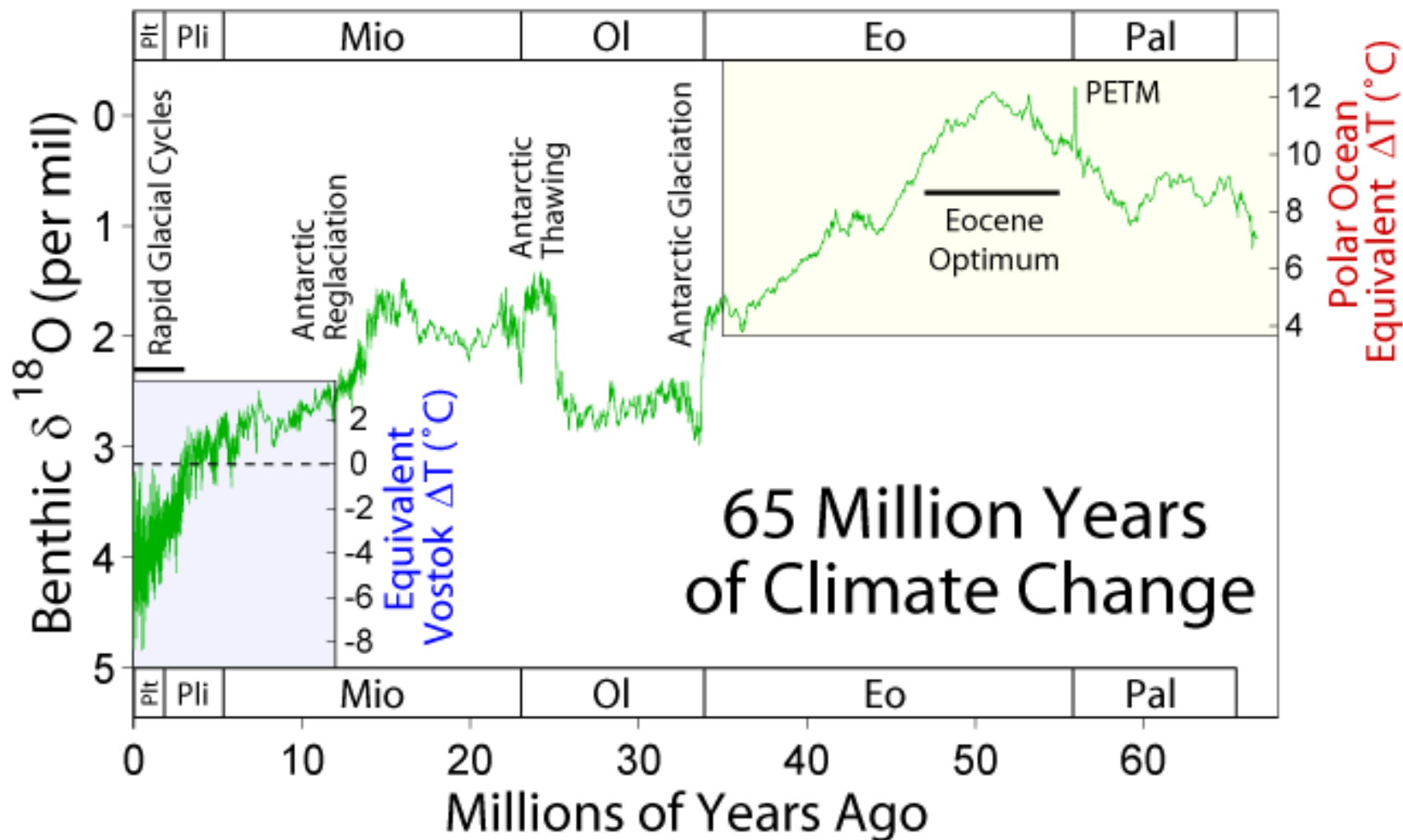


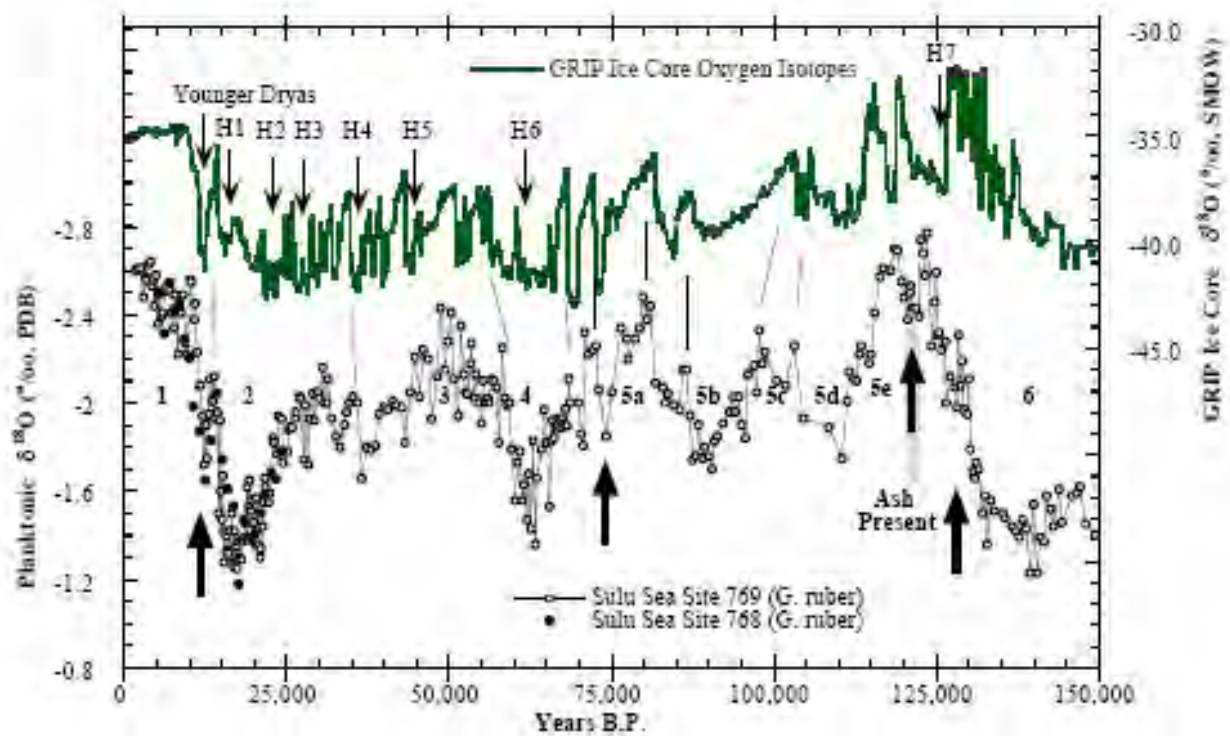
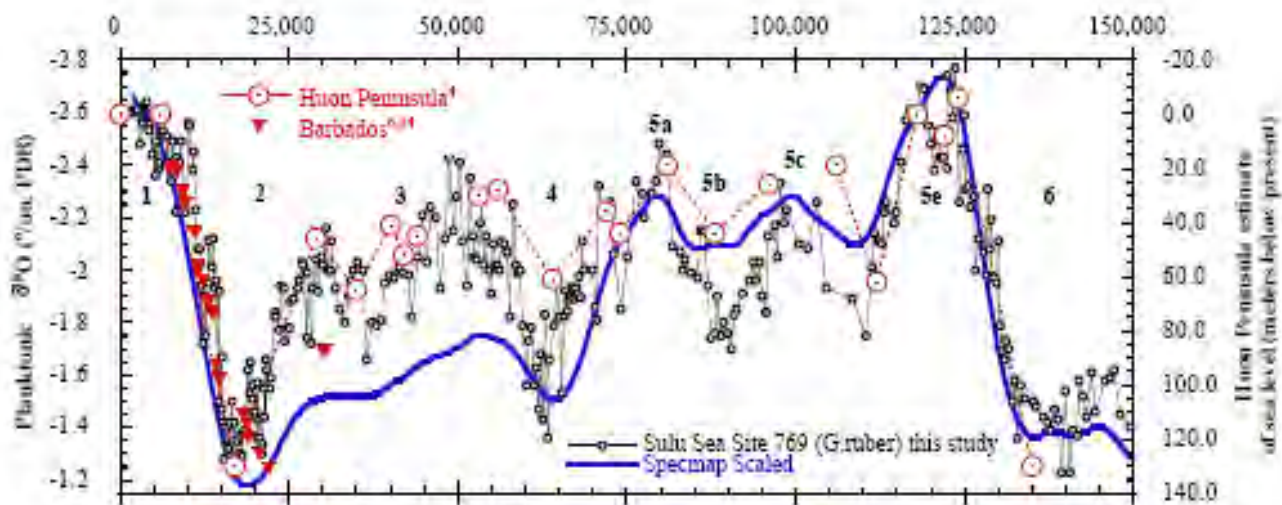


Oxygen isotope fluctuations in seawater as recorded in marine sediments can be indicative of ice volume and thus sea level changes. Temperature effects will be included as well. Indicative of exchange among water reservoirs.

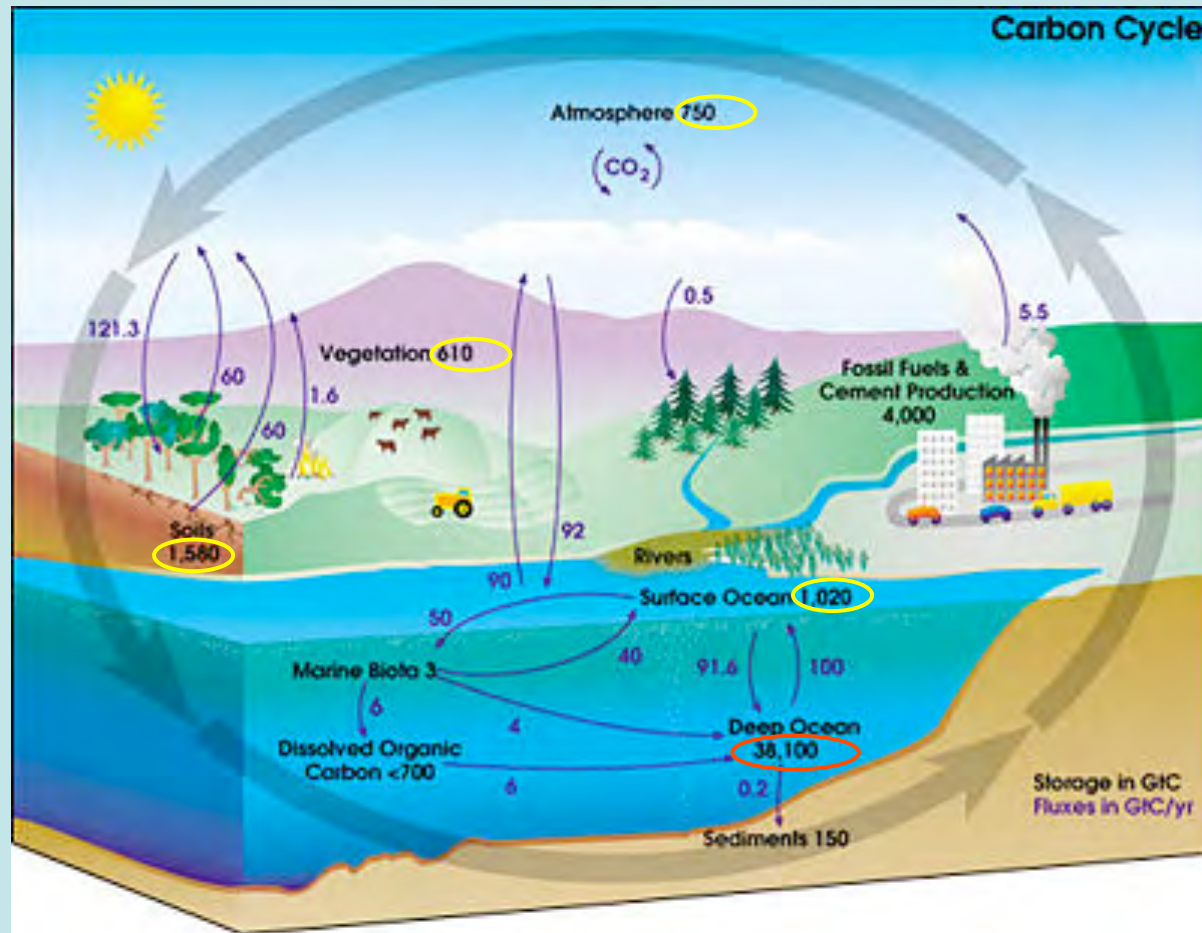
# Phanerozoic Climate Change





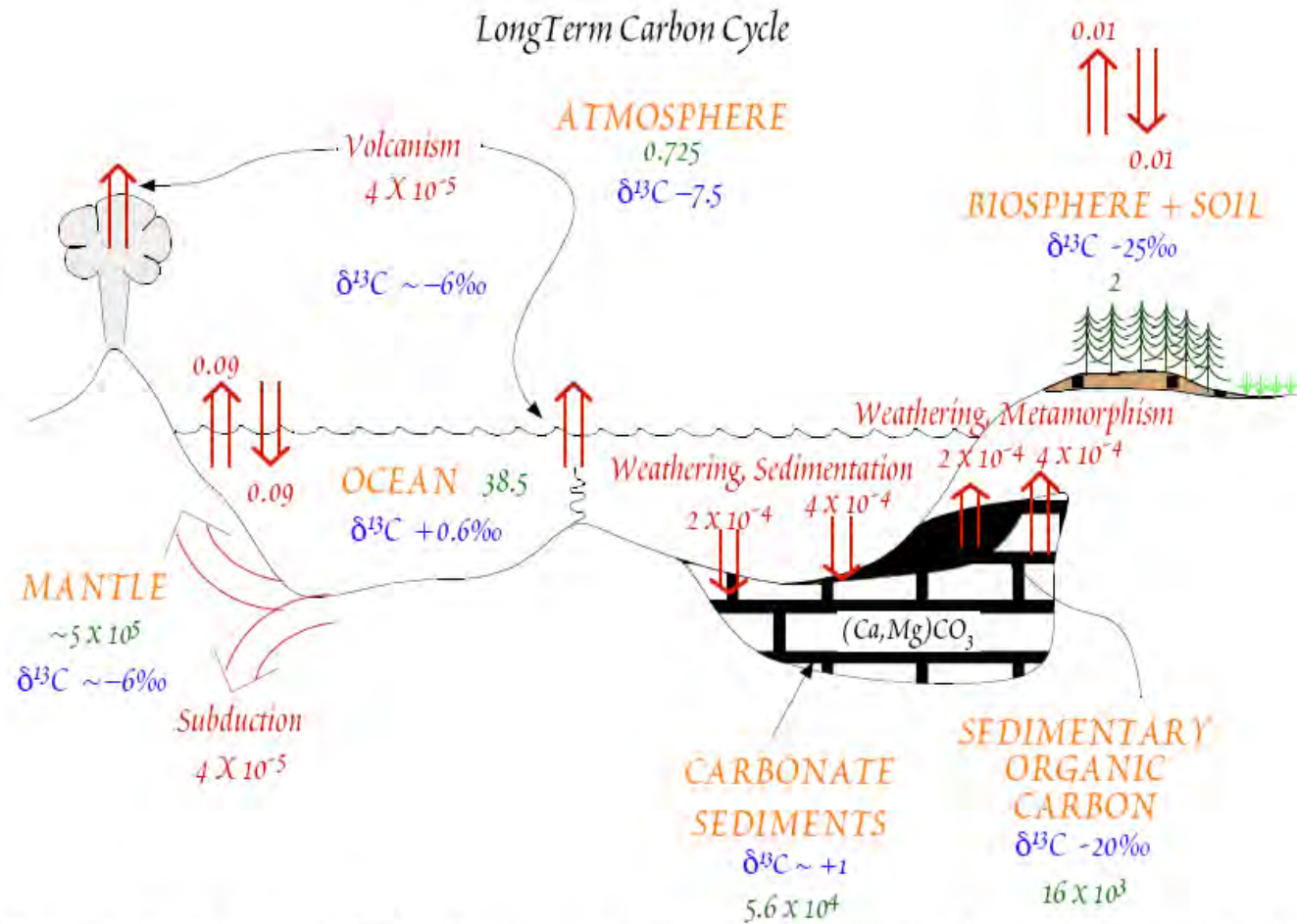


# The Carbon Cycle



The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GigaTons, circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen.

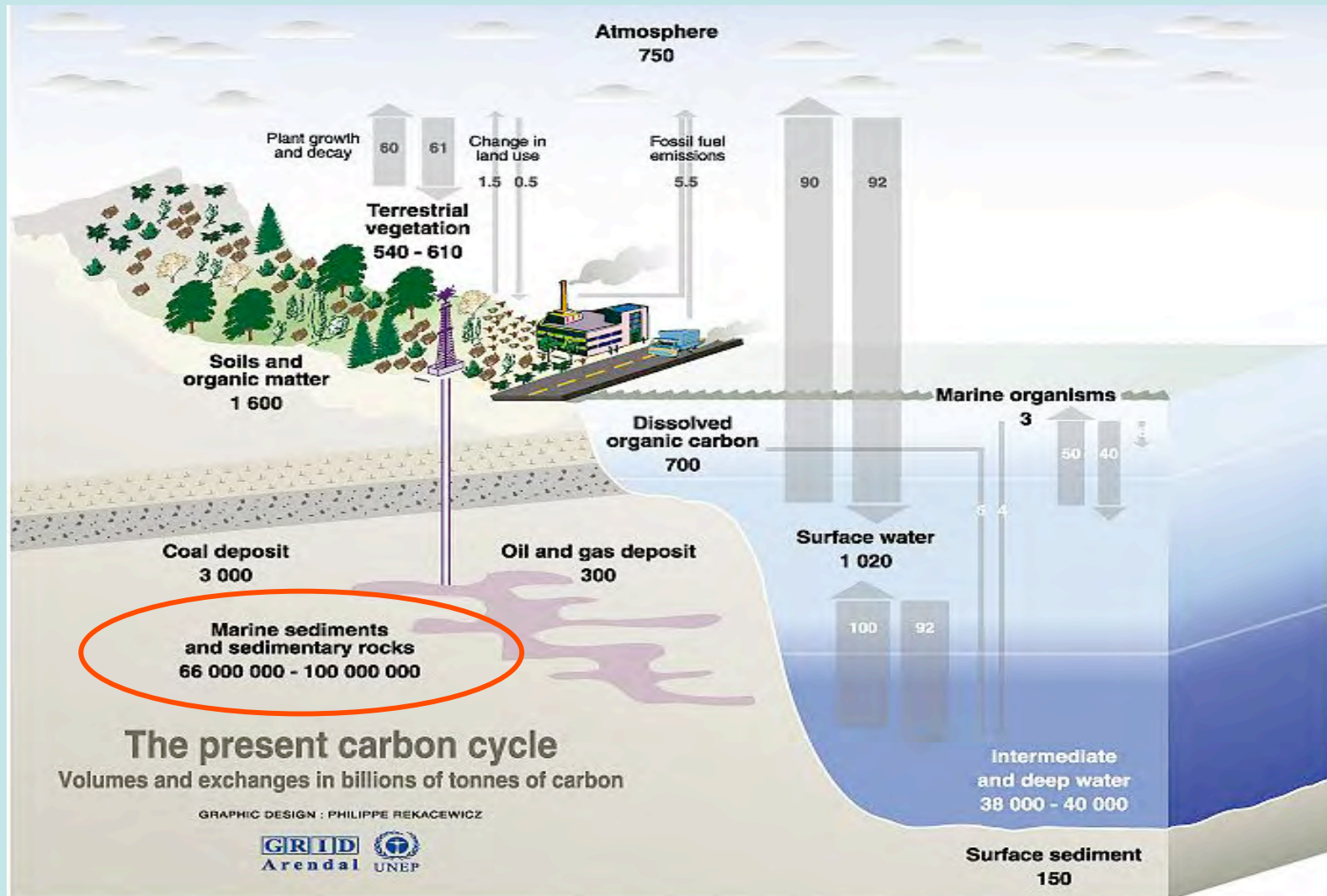
# The Carbon Cycle



On geologic times scales, the carbon cycle model can be augmented by 3 reservoirs, sedimentary carbonate, sedimentary organic carbon, and the mantle, as well as fluxes between these reservoirs and the oceans and atmosphere.

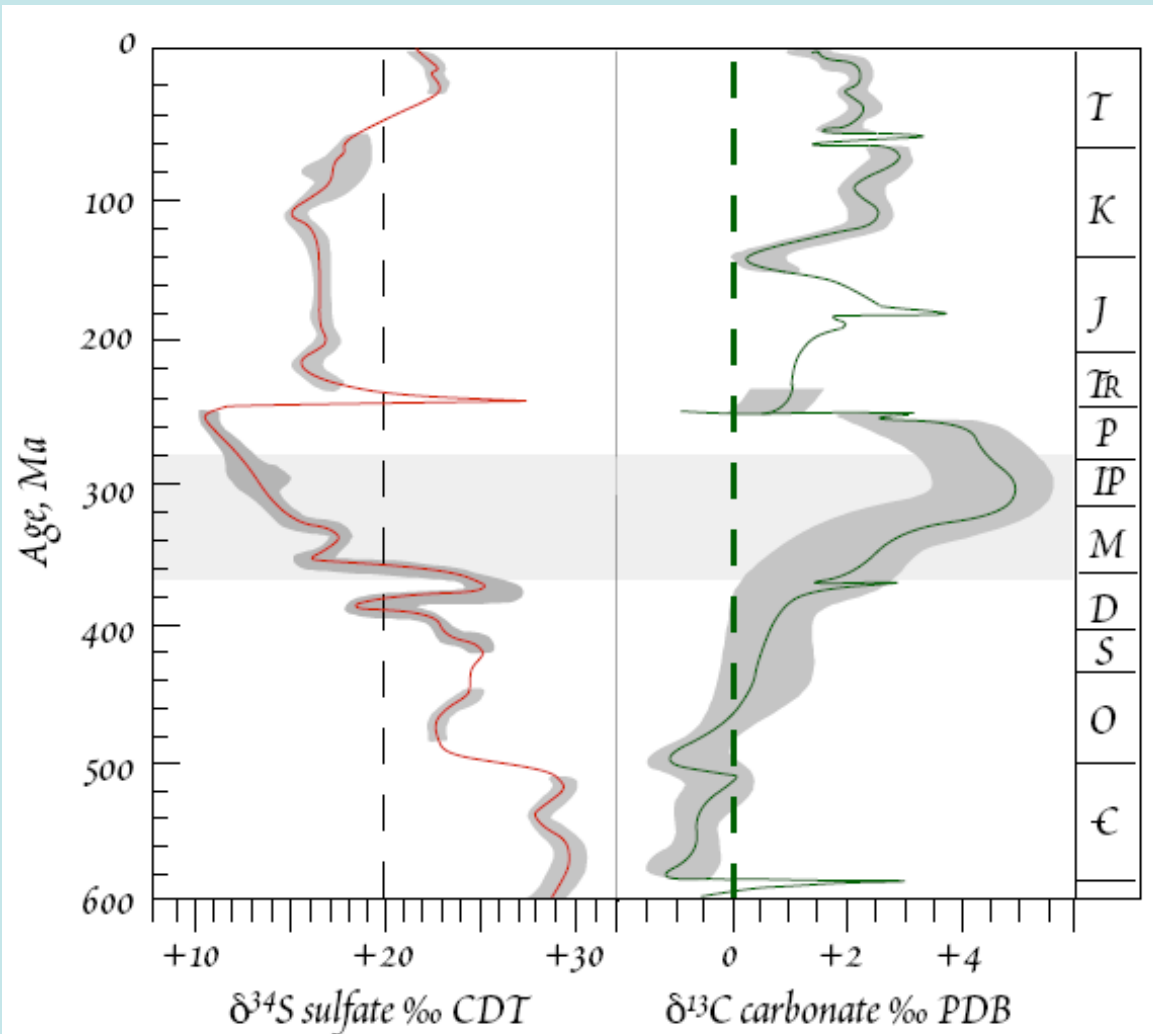
Figure 38.1. The Carbon Cycle. Green numbers show the amount of carbon (in  $10^{18}$  grams) in the reservoirs. Fluxes between these reservoirs (arrows) are shown in italics in units of  $10^{18}$  g/yr (in red). Masses and fluxes refer to the pre-Industrial Revolution state of the system. Uncertainties on many of the masses and fluxes are large. Also shown are estimates of the carbon isotopic composition.

# The Carbon Cycle



Sources: Center for climatic research, Institute for environmental studies, university of Wisconsin at Madison; Okanagan university college in Canada, Department of geography; World Watch, November-December 1998; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

# The Carbon Cycle

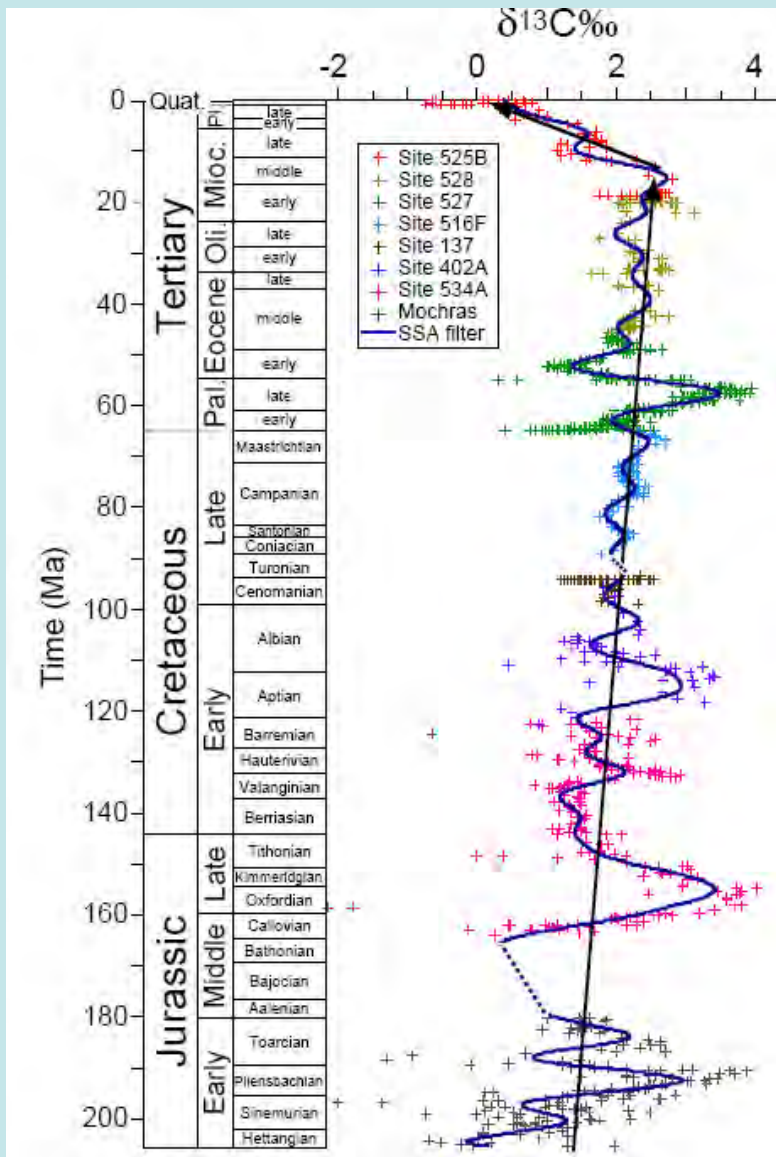


When more C is removed into the reduced organic C reservoir residual C in the ocean and carbonates becomes enriched in  $^{13}\text{C}$  (heavy) and atmospheric  $\text{CO}_2$  is lower and  $\text{O}_2$  is higher (less consumed for oxidation).

Figure 38.3. Isotopic compositions of carbon and sulfur in the oceans through Phanerozoic time. After Holser (1984).



# The Carbon Cycle



The long-term increases in  $\delta^{13}\text{C}_{\text{carb}}$  (e.g. more organic C burial) that began in the Mesozoic were accompanied by major evolutionary changes among the primary producers in the marine biosphere. Three groups of eucaryotic marine phytoplankton (calcareous nanoplankton, dinoflagellates, and diatoms) began their evolutionary trajectories to ecological prominence at  $\sim 200$  Ma. As Pangea fragmented and the Atlantic Ocean basin widened, the total length of coastline increased and sea level rose, flooding continental shelves and low-lying continental interiors. Nutrients that were previously locked up in the large continental interior were transported to newly formed shallow seas and distributed over wider shelf areas and longer continental margins.

Katz et al., 2005

# The Carbon Cycle

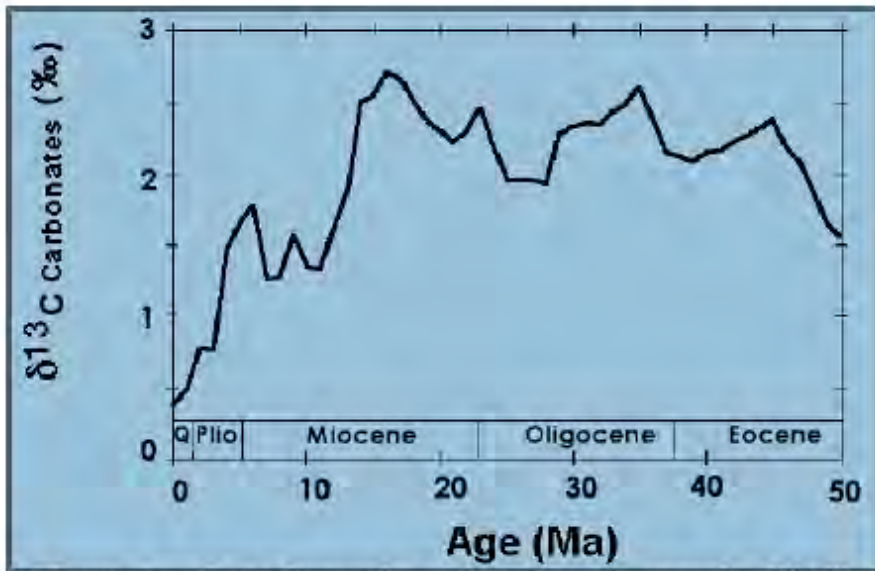


Figure 1. Late Cenozoic carbon isotopic record of bulk marine carbonate averaged in million year increments. Data from *Shackleton and Hall [1984]*

The decline since the late Miocene in addition to changes in ocean circulation could be related to the evolution of C4 plants (less fractionation in organic C burial).

Large perturbations in the global C cycle.  
Gas hydrate ?

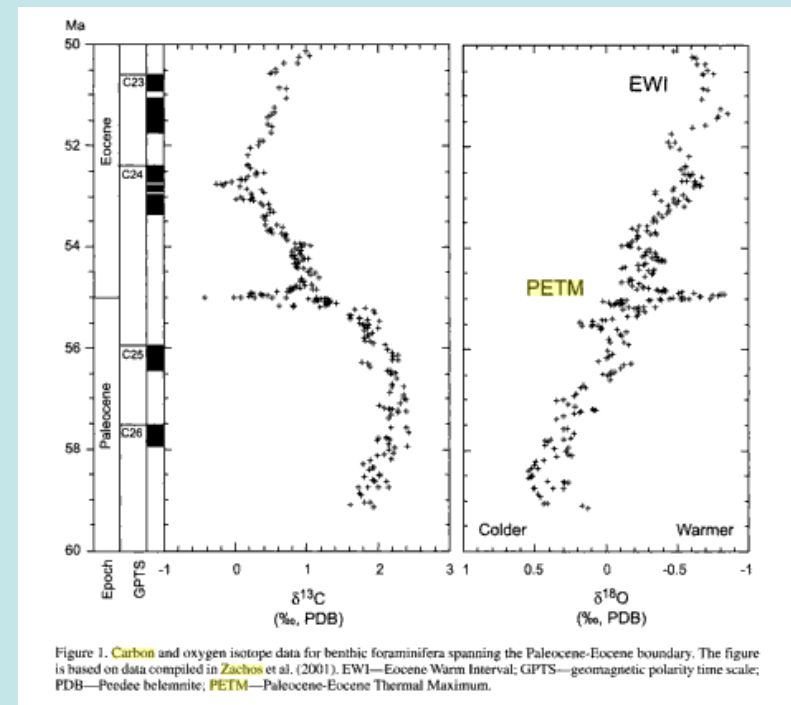


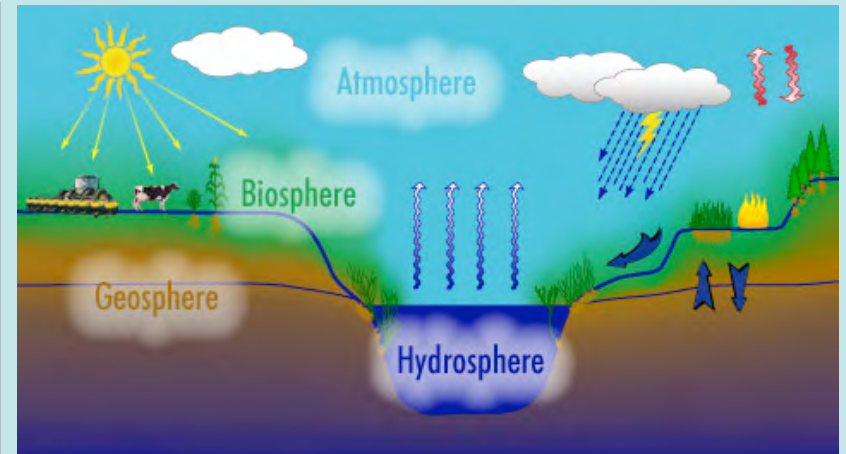
Figure 1. Carbon and oxygen isotope data for benthic foraminifera spanning the Paleocene-Eocene boundary. The figure is based on data compiled in *Zachos et al. (2001)*. EWI—Eocene Warm Interval; GPTS—geomagnetic polarity time scale; PDB—Pee Dee belemnite; PETM—Paleocene-Eocene Thermal Maximum.

# The Nitrogen Cycle

N is present in many chemical forms, both organic and inorganic, in the atmosphere, biosphere, hydrosphere, and geosphere. It occurs in the gas, liquid (dissolved in water), and solid phases. N can be associated with organic species and with inorganic species. Important inorganic species include  $N_2$ , nitric acid ( $HNO_3$ ), nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), nitrous oxide ( $N_2O$ ), nitric oxide ( $NO$ ), N dioxide ( $NO_2$ ), ammonium ( $NH_4^+$ ), and ammonia ( $NH_3$ ). Most organic N species are bio-molecules, such as proteins, peptides, enzymes, and genetic material (RNA and DNA).  $NO_3^-$  and organic-N species exist in solution and as particulates.

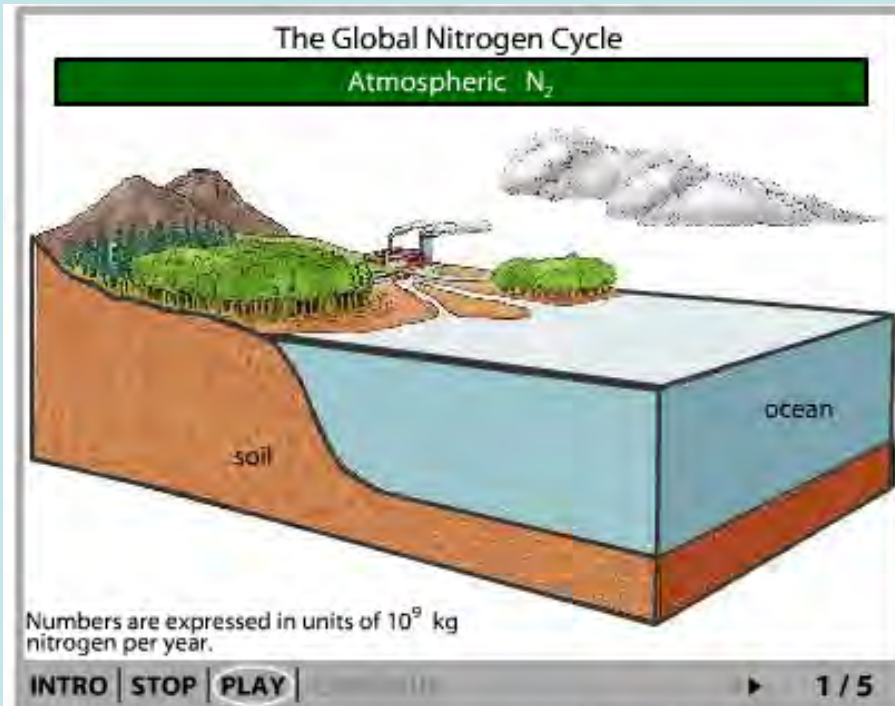
Sizes of Global N Reservoir

Reservoir/Pool Type	Metric Tons	% of Total
Biosphere	$2.8 \times 10^{11}$	0.0002
Hydrosphere	$2.3 \times 10^{13}$	0.014
Atmosphere	$3.86 \times 10^{15}$	2.3
Geosphere	$1.636 \times 10^{17}$	97.7
Crust	$0.13 - 1.4 \times 10^{16}$	0.78-8.4
Soils and Sediments	$0.35 - 4.0 \times 10^{15}$	0.21-2.4
Mantle and Core	$1.6 \times 10^{17}$	95.6

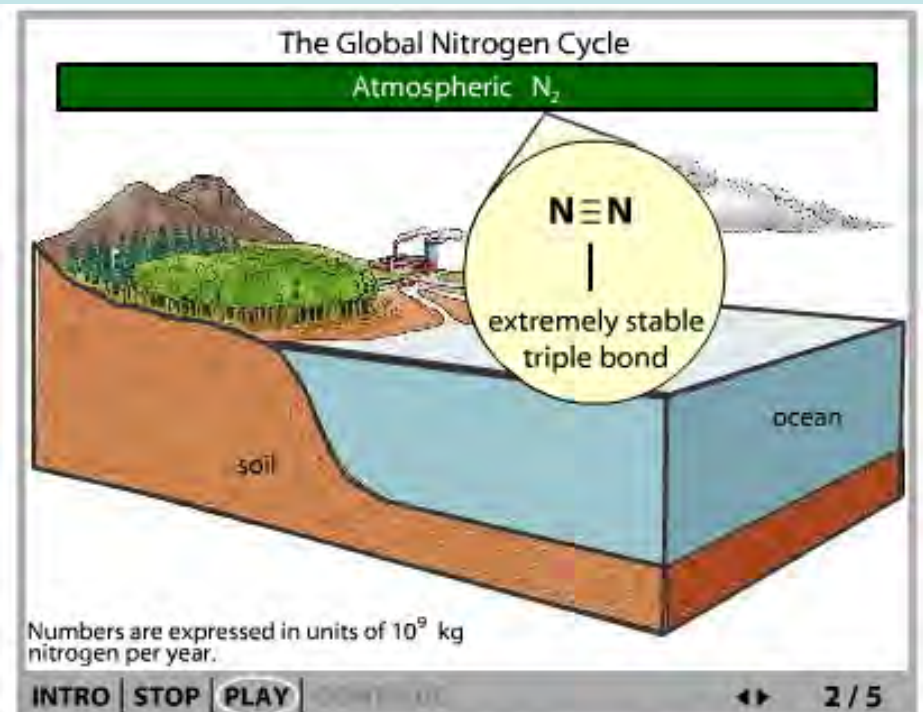


No evidence for change in atmospheric  $N_2$

# The Nitrogen Cycle

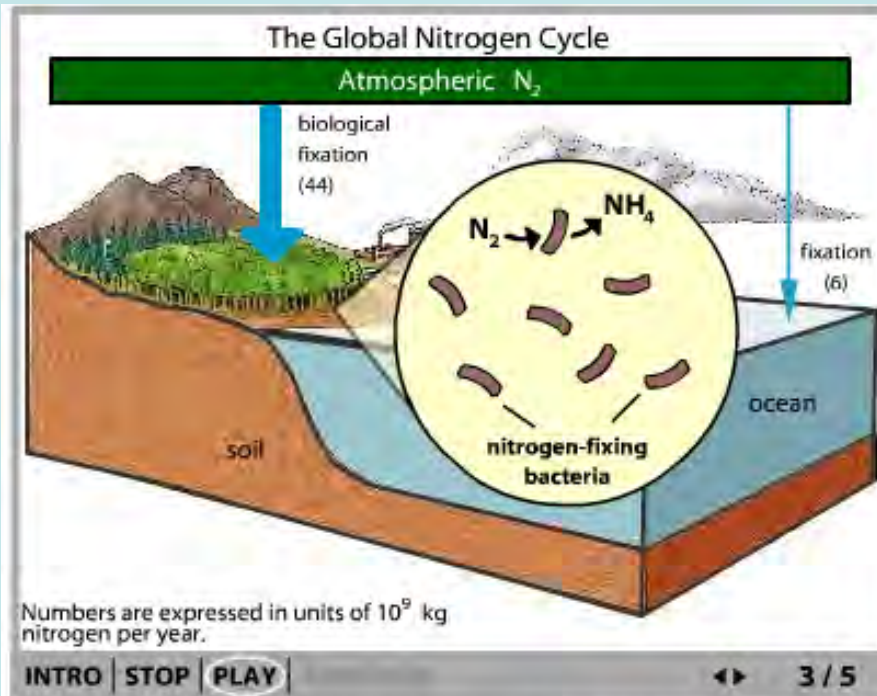


$N_2$  is the most abundant gas in the atmosphere (78%). However, most organisms cannot use this ubiquitous nitrogen source to make their essential, nitrogen-containing molecules (e.g., proteins and DNA). The two nitrogen atoms in  $N_2$  are connected by an extremely stable triple bond, which does not easily break.

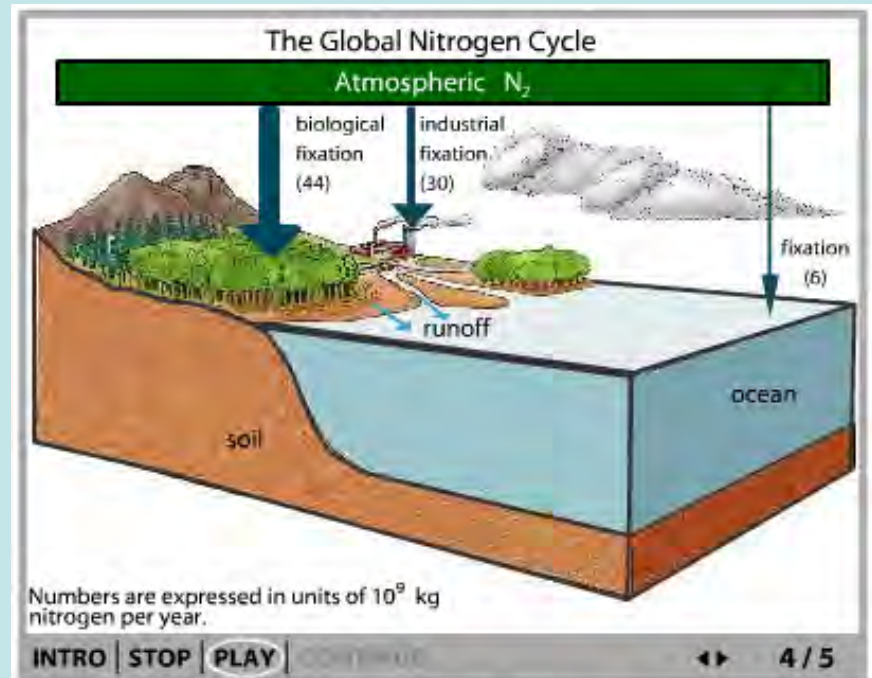


Just a few species of bacteria, called nitrogen fixers, can break the  $N_2$  triple bond. These bacteria convert  $N_2$  into  $NH_4$ , which other bacteria then convert into  $NO_2$  and  $NO_3$ . Plants use  $NO_3$  or  $NH_4$  to produce nitrogen-containing organic molecules. Then, by consuming plants, animals also obtain usable forms of nitrogen.

# The Nitrogen Cycle

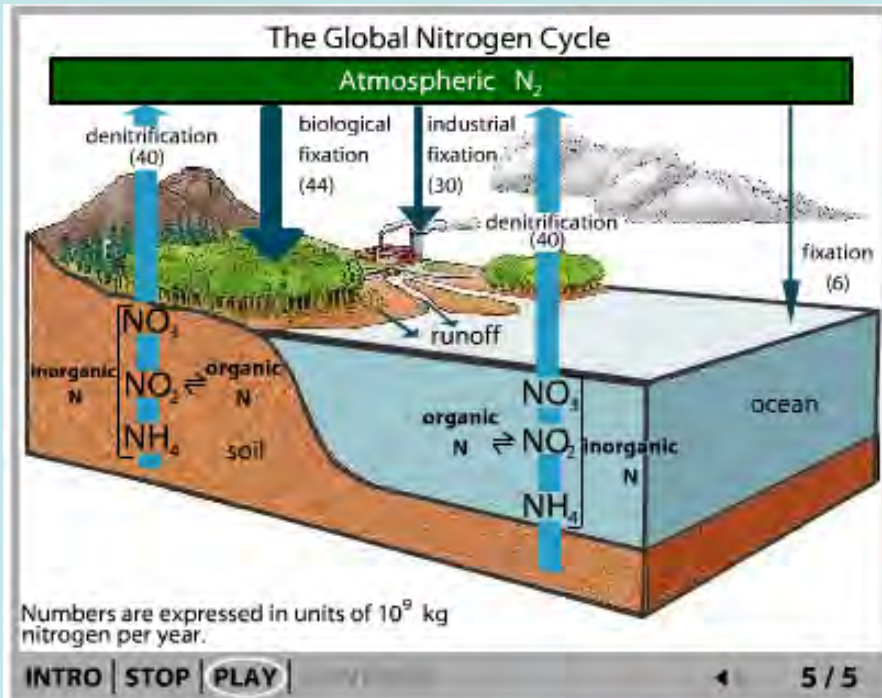


Humans add to the amount of nitrogen fixed on Earth. Through energy-consuming industrial processes, we capture atmospheric  $N_2$  and convert it into  $NH_4$  or  $NO_3$ , key components of most artificially made agricultural fertilizers. Some of this nitrogen enters the ocean through runoff.

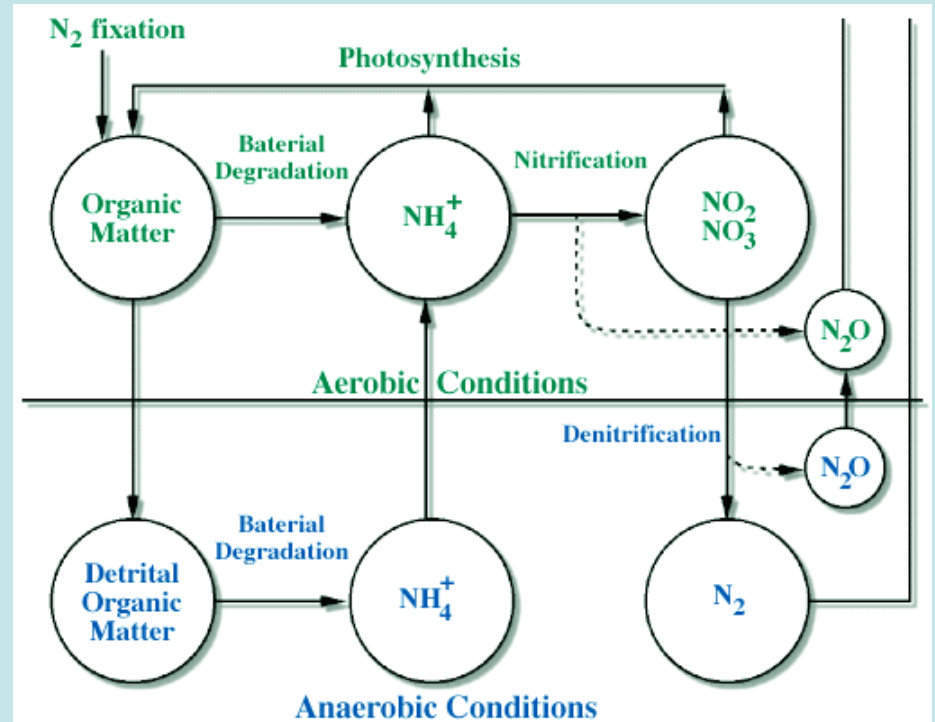


When organisms die, on land and in the oceans, they liberate their organic stores of nitrogen. Some of this nitrogen is converted to inorganic nitrogen compounds, such as  $NH_4$ ,  $NO_2$ , and  $NO_3$ . A number of species of bacteria can then convert these inorganic compounds back into  $N_2$ —a process called denitrification.

# The Nitrogen Cycle

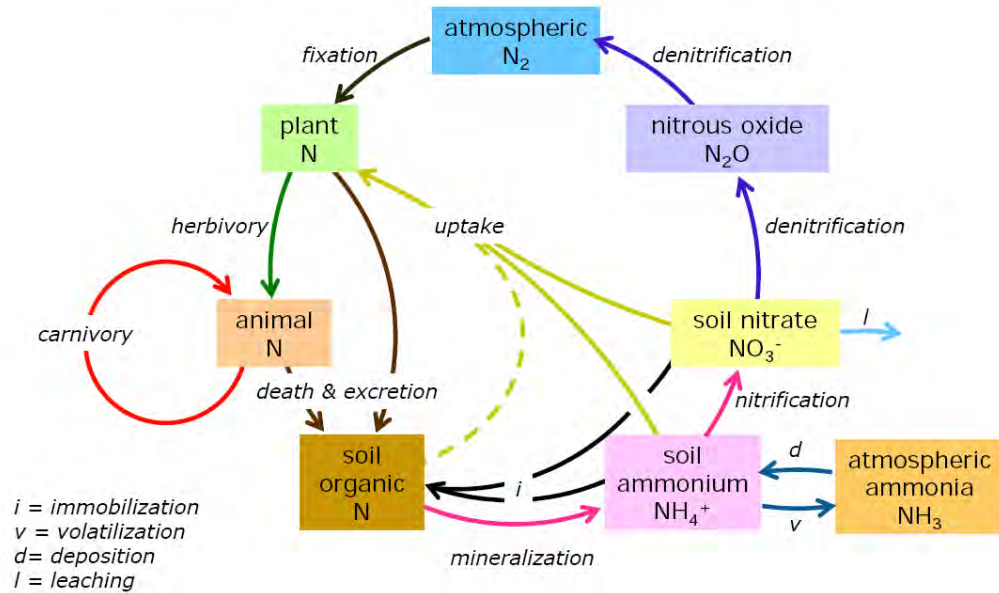


A large quantity of "fixed" nitrogen does not return to the atmosphere. Before becoming converted to  $N_2$  gas, the small, inorganic molecules ( $NH_4$ ,  $NO_2$ , and  $NO_3$ ) are taken up again by organisms and used to create organic compounds. This movement accounts for 95% of the flux in the global nitrogen cycle.

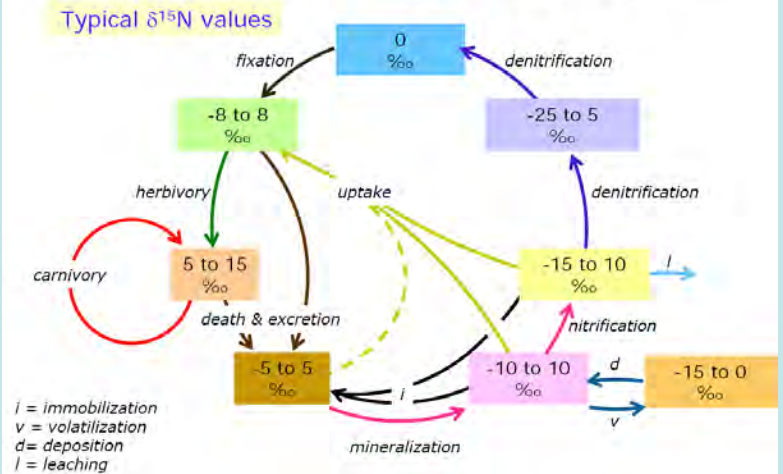


# The Nitrogen Cycle

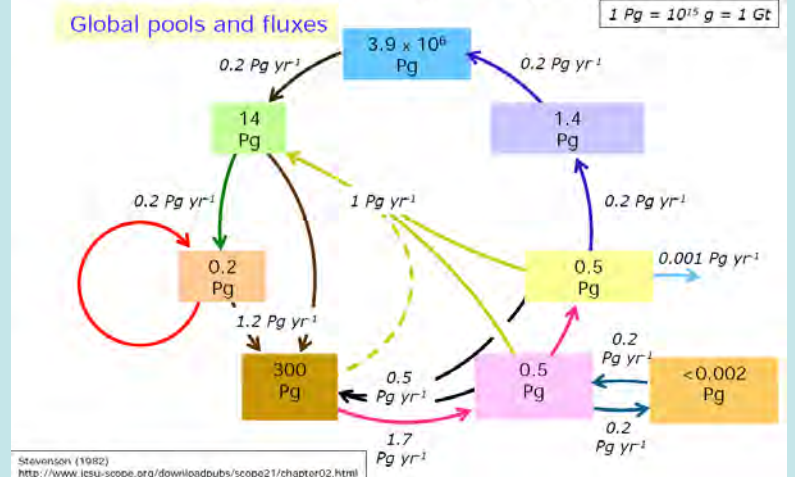
## Terrestrial nitrogen cycle(s)



## Terrestrial nitrogen cycle(s)



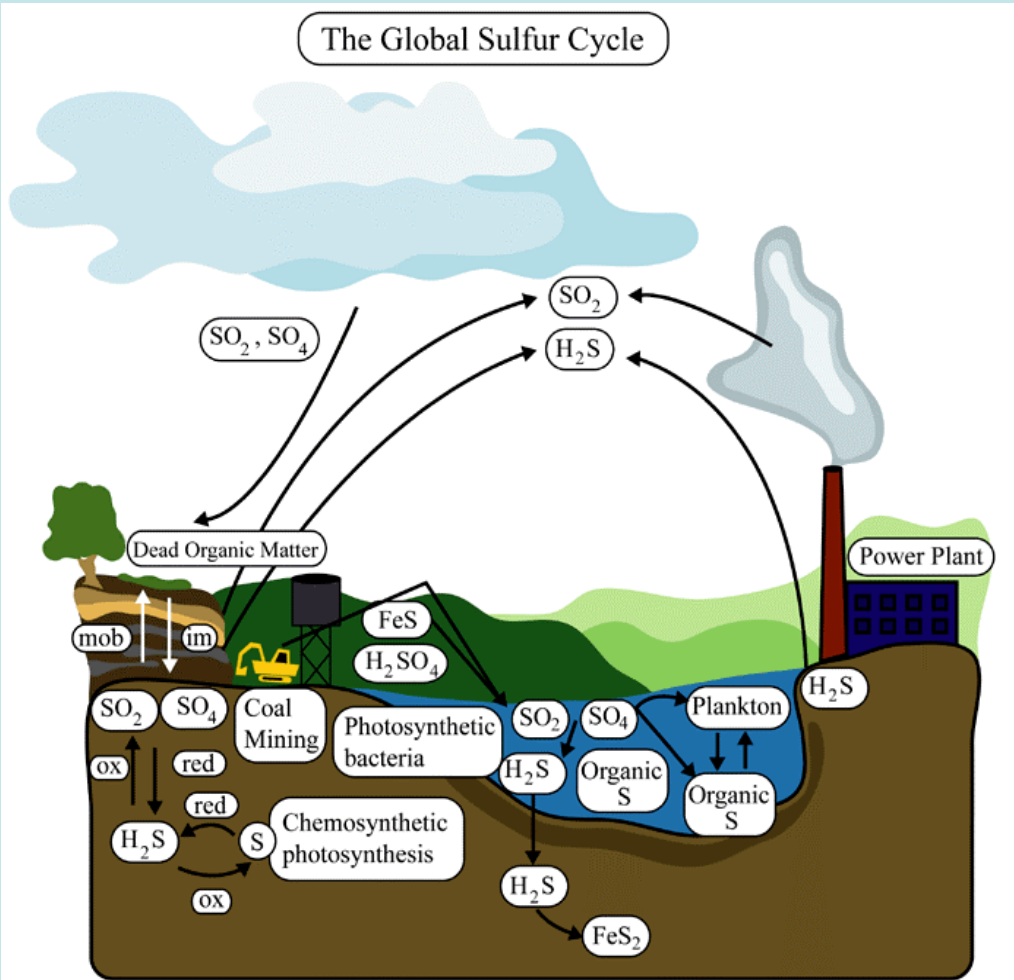
## Terrestrial nitrogen cycle(s)



Transformations and isotopes in the N cycle

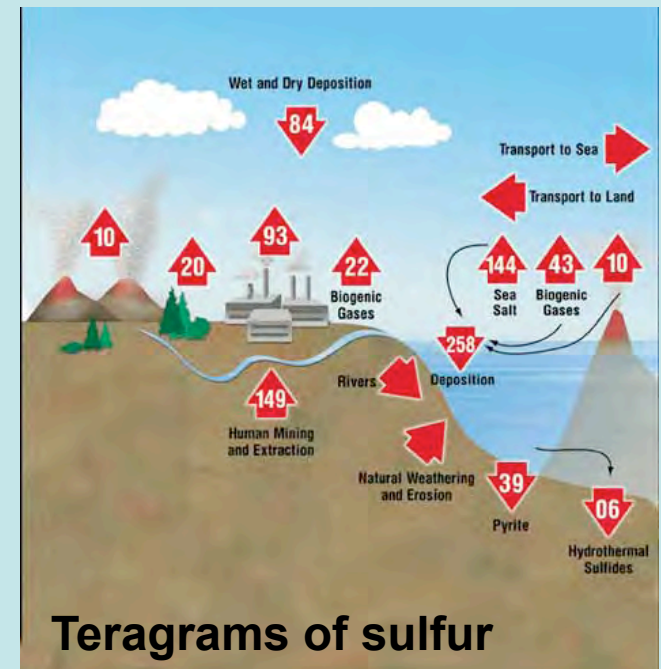
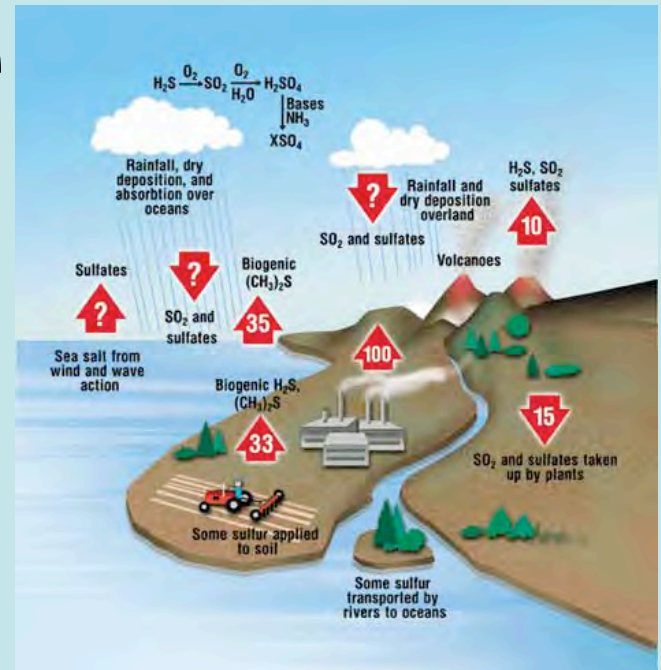
# The Sulfur Cycle

The Global Sulfur Cycle



red: reduction  
 ox: oxidation  
 im: immobilization  
 mob: mobilization

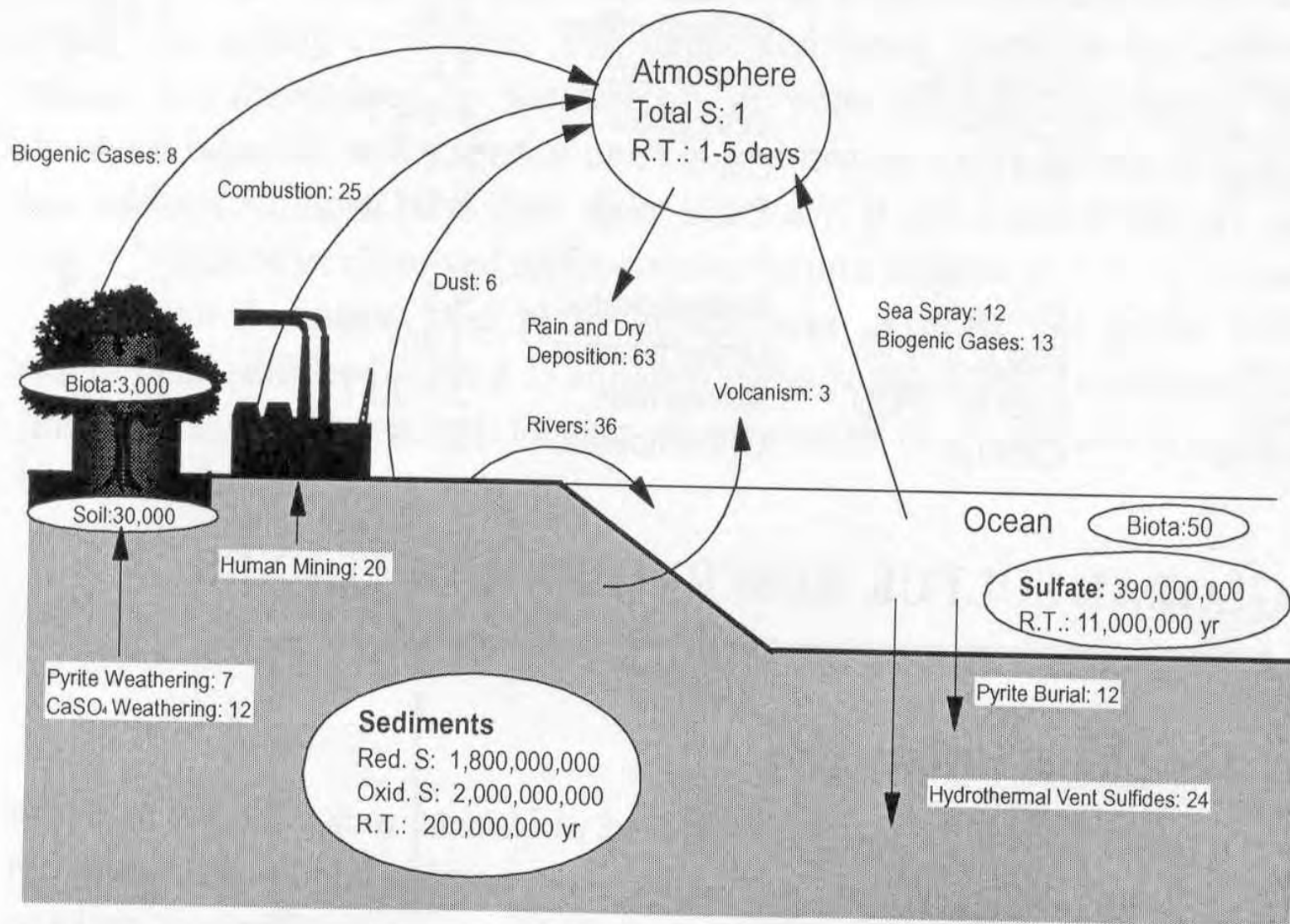
The global sulfur cycle, with two components: gaseous and sedimentary. Human activities which contribute to the cycle include: acid drainage from coal mining and fossil fuel burning.



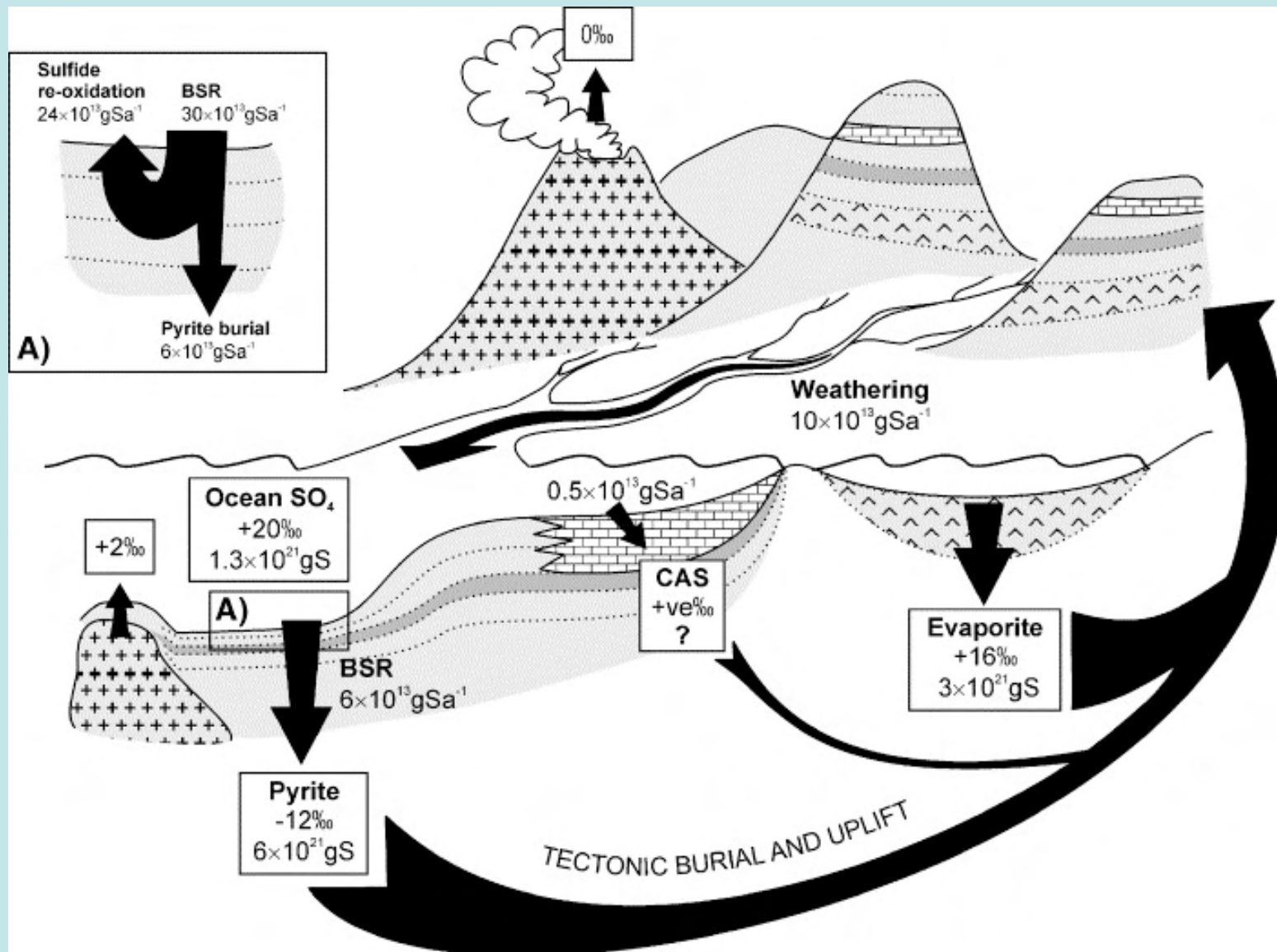
Teragrams of sulfur



# The Sulfur Cycle



# The Sulfur Cycle



# A Representation of the Sulfur Cycle

volcanic 10, 3  
↑

weathering  
72

0 to +10 (5.7)

uplift

seawater  
+21, 128<sup>7</sup>Tg

burial  
gypsum 44, +21  
pyrite 28, -16

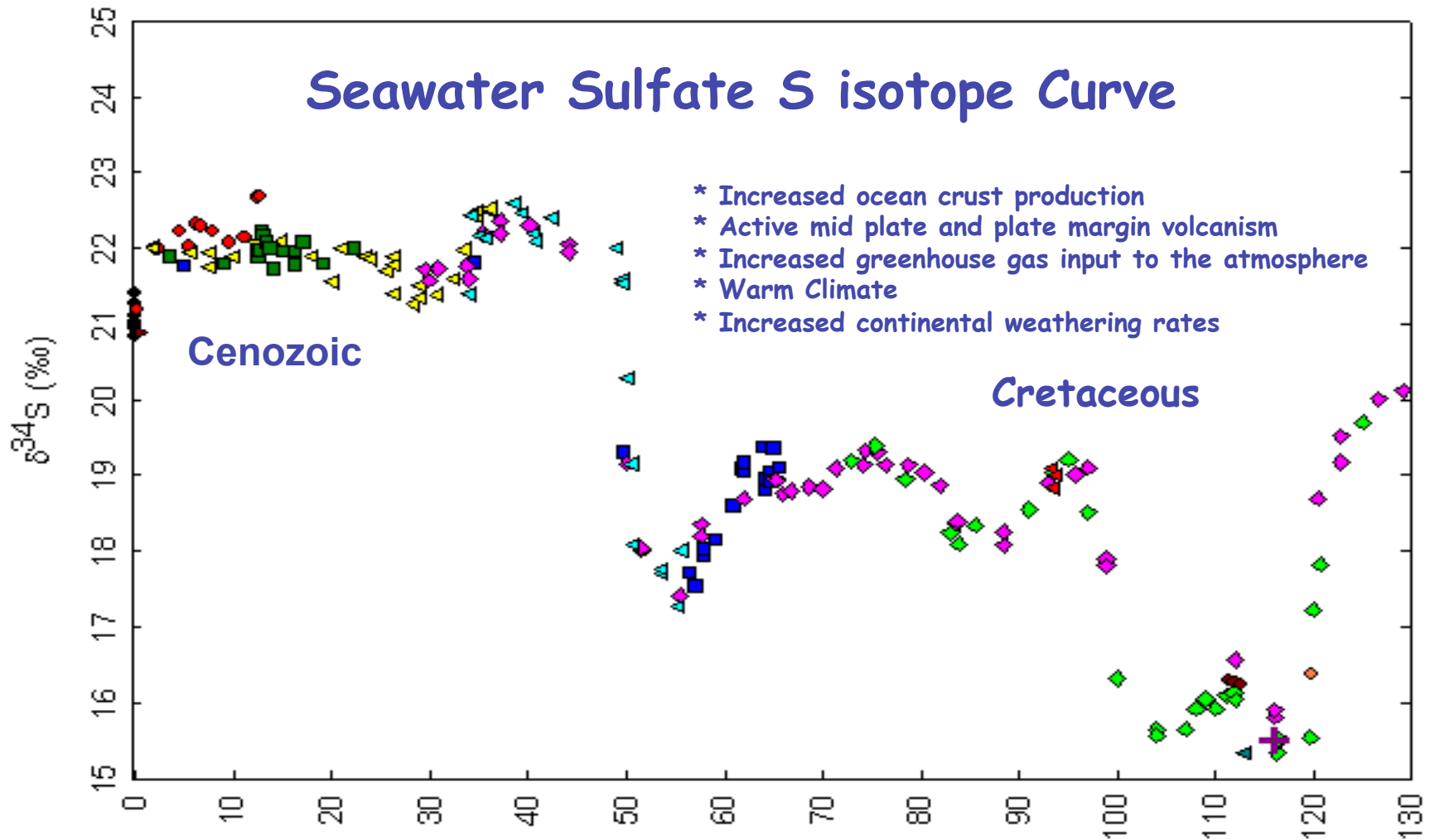
10, 3.5  
hydrothermal

subduction

fluxes in units of Tg (S) yr<sup>-1</sup>, isotope ratios in ‰ CDT

Arthur et al., 1990

# The Sulfur Cycle

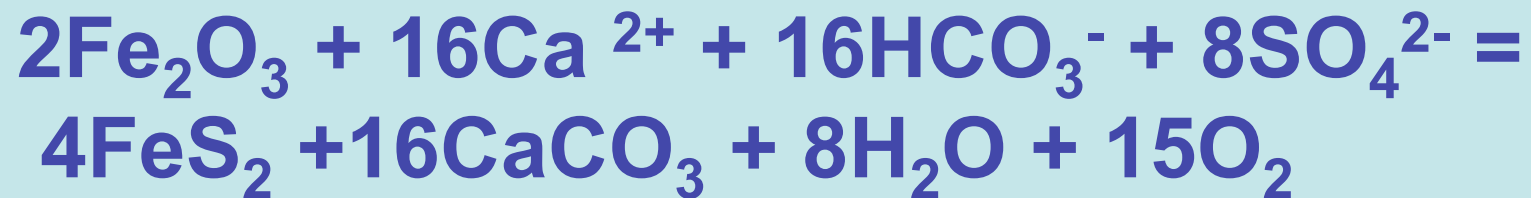


# steady state mass and isotope balance model

$$\begin{array}{c}
 \delta^{34}\text{S of input} \quad \delta^{34}\text{S of seawater} \quad \text{S input flux} \\
 \swarrow \quad \downarrow \quad \swarrow \\
 F_{py} = \frac{(\delta^{34}S_{in} - \delta^{34}S_{SO_4}) * F_{in}}{\Delta^{34}S_{sw - py}} \\
 \uparrow \quad \quad \quad \uparrow \\
 \text{pyrite burial flux} \quad \text{seawater-pyrite isotopic difference}
 \end{array}$$

Evaluate the change in each of the model parameters needed to explain the difference in  $\delta^{34}\text{S}_{SO_4}$ .

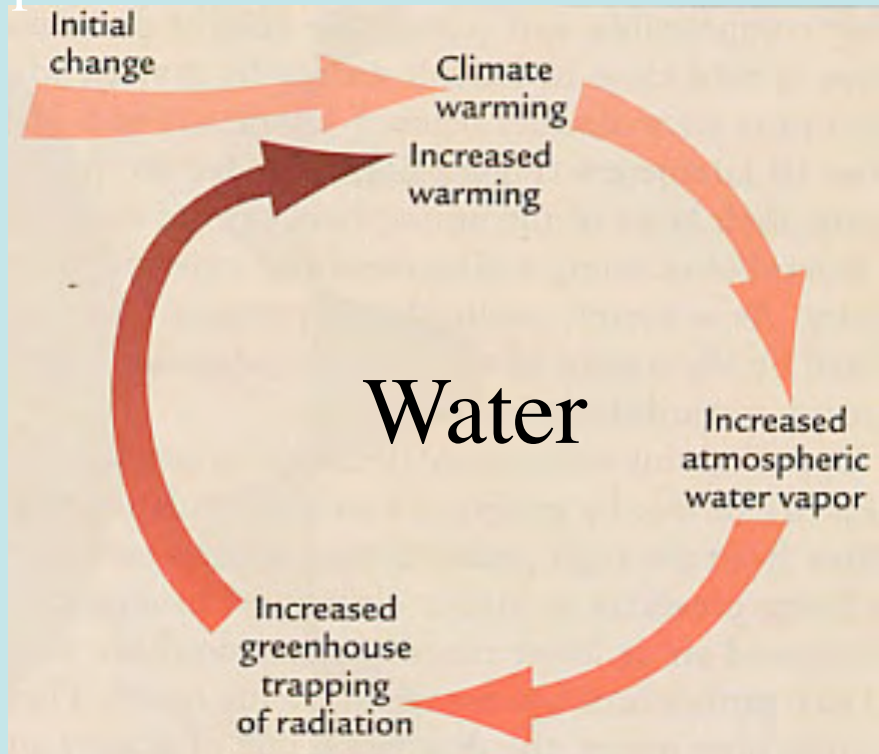
The biogeochemicals cycles of S and C are intimately linked with the principal processes that control the level of atmospheric oxygen.



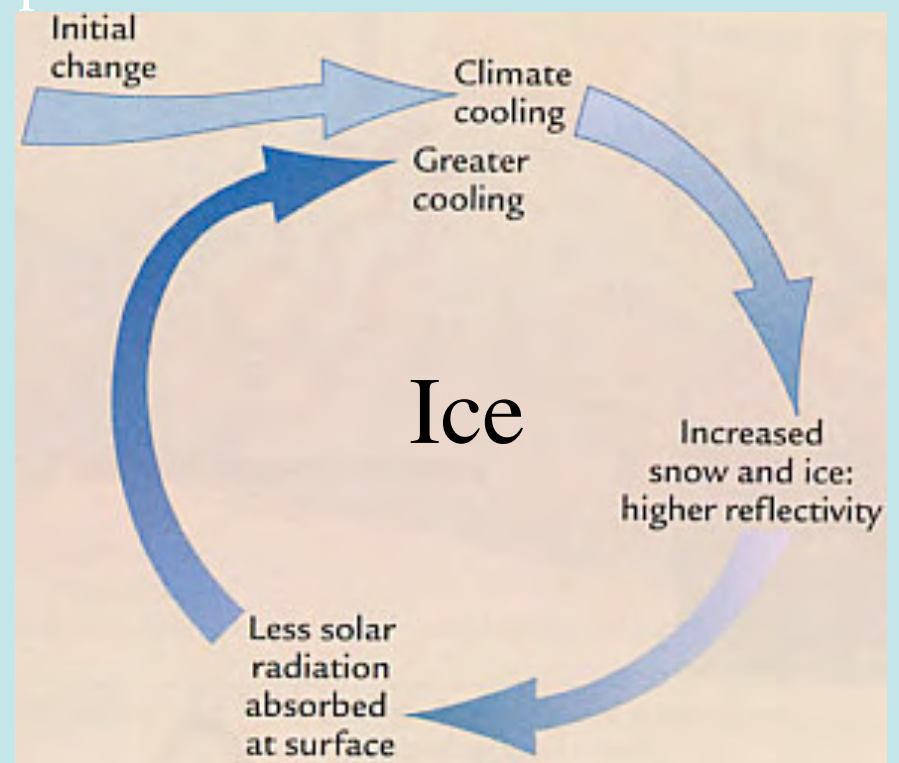
To maintain constant oxygen an periods of organic C burial should be compensated by less pyrite burial resulting in an inverse isotopic relation

# Feedbacks in the Climate System

Forcing/  
perturbation



Forcing/  
perturbation



CO<sub>2</sub> ↑



Temperature



Precipitation



Weathering



River solute load



Biological Productivity



CO<sub>2</sub>





Mountain Uplift ↑

Weathering ↑

CO<sub>2</sub> ↓

Temperature ↓

Weathering ↓



# The Water Cycle

## Global WATER Reservoirs, Fluxes, and Turnover Times

Pools in  $10^6 \text{ km}^3$ , Fluxes in  $\text{km}^3 \text{ y}^{-1}$ ,  
(turnover times)

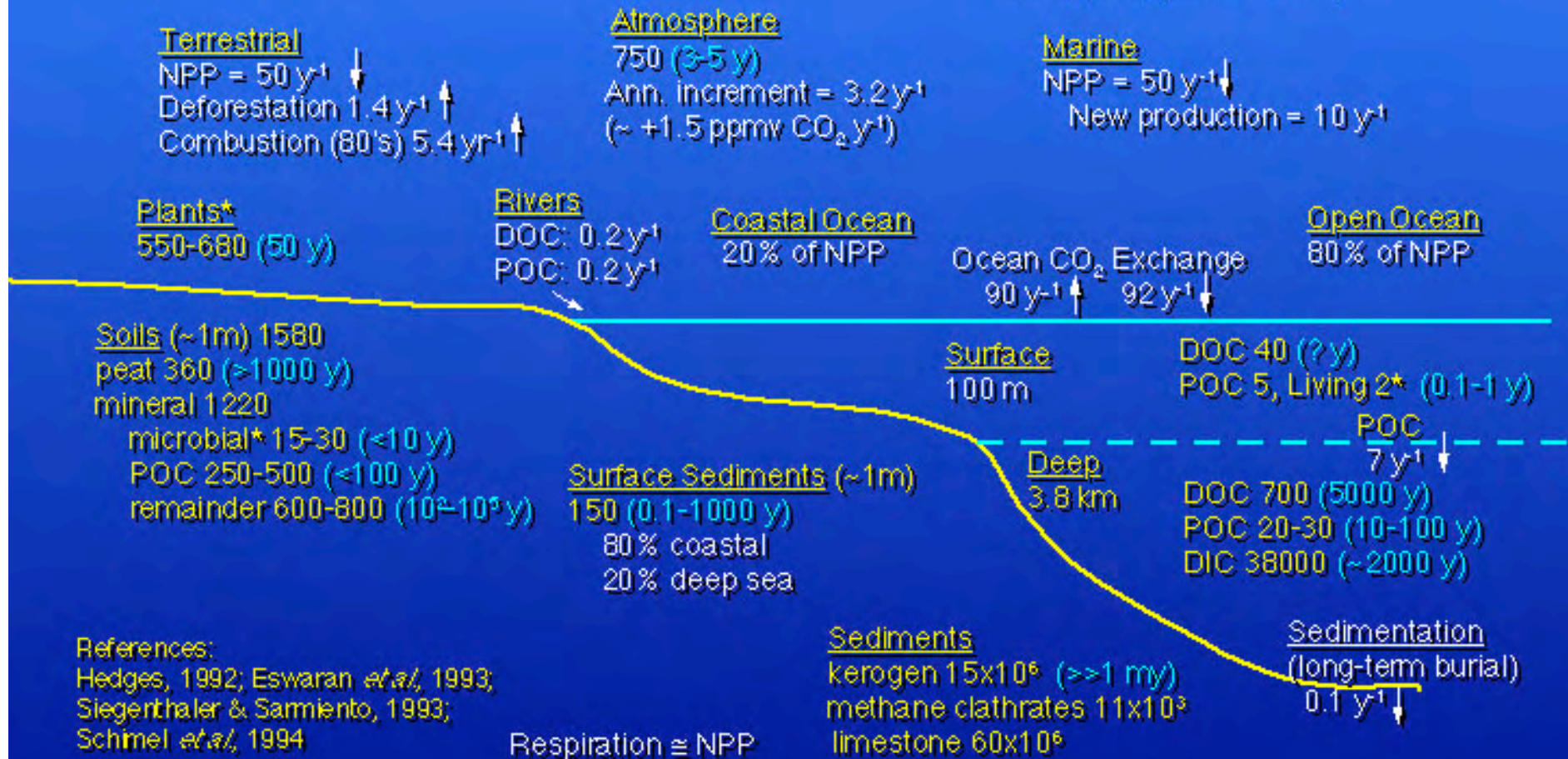


References:  
Schlesinger, 1993; Murray, 1992

# The Carbon Cycle

## Global CARBON Reservoirs, Fluxes, and Turnover Times

Pools in Gt C, Fluxes in Gt C y<sup>-1</sup>, Gt = 10<sup>15</sup> g;  
 \* = living pools; (turnover times)

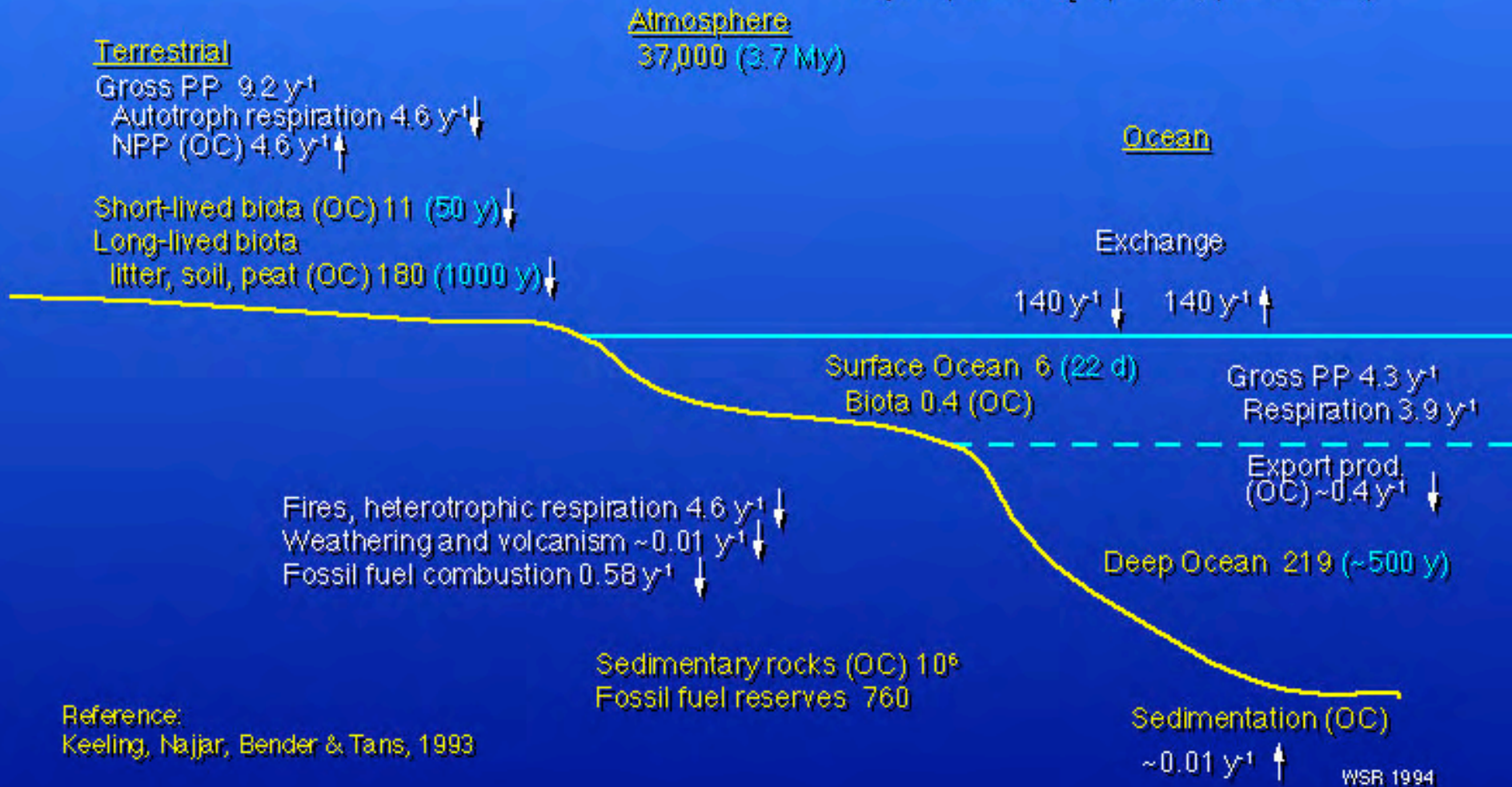


References:  
 Hedges, 1992; Eswaran *et al.*, 1993;  
 Siegenthaler & Sarmiento, 1993;  
 Schimel *et al.*, 1994

# The Oxygen Cycle

## Global OXYGEN Reservoirs, Fluxes, and Turnover Times

Pools in  $10^{15}$  moles  $O_2$ , Fluxes in  $10^{15}$  moles  $O_2$   $y^{-1}$ ,  
Organic pools as  $O_2$  equivalent, (turnover time)



# The Nitrogen Cycle

## Global NITROGEN Reservoirs, Fluxes, and Turnover Times

### Fixation ↓

Natural terrestrial  $190 \text{ y}^{-1}$   
 Natural oceanic  $40 \text{ y}^{-1}$   
 Leguminous crops  $40 \text{ y}^{-1}$   
 Chemical fertilizer  $20 \text{ y}^{-1}$   
 Combustion  $20 \text{ y}^{-1}$

### Terrestrial Biomass

$3.5 \times 10^4$  (50y)

### Soil

$9.5 \times 10^4$  (~2000 y)

### Atmosphere

$\text{N}_2$ :  $3.9\text{-}4.0 \times 10^9$  ( $10^7 \text{ y}$ )  
 Fixed N:  $1.3\text{-}1.4 \times 10^5$  (~5 wk)  
 $\text{N}_2\text{O}$ :  $1.4 \times 10^3$  ( $10^2 \text{ y}$ )

Pools in Tg N, Fluxes in Tg N  $\text{y}^{-1}$ , Tg =  $10^{12}$  g,  
 (turnover times)

### Denitrification ↑

Natural terrestrial  $147 \text{ y}^{-1}$   
 Natural ocean  $30 \text{ y}^{-1}$   
 Industrial combustion  $20 \text{ y}^{-1}$   
 Biomass burning  $12 \text{ y}^{-1}$

### River runoff

$36 \text{ y}^{-1}$

### Marine Biomass

Plants:  $3 \times 10^6$   
 Animals:  $1.7 \times 10^6$

### Ocean

$\text{N}_2$ :  $2.2 \times 10^7$   
 $\text{N}_2\text{O}$ :  $2.0 \times 10^4$   
 Inorganic:  $6 \times 10^5$   
 Organic:  $2 \times 10^5$

### Sediments

$4.0 \times 10^8$  ( $10^7 \text{ y}$ )  
 Weathering  $5 \text{ y}^{-1}$

### Sedimentation

(burial)  $14 \text{ y}^{-1}$  ↓

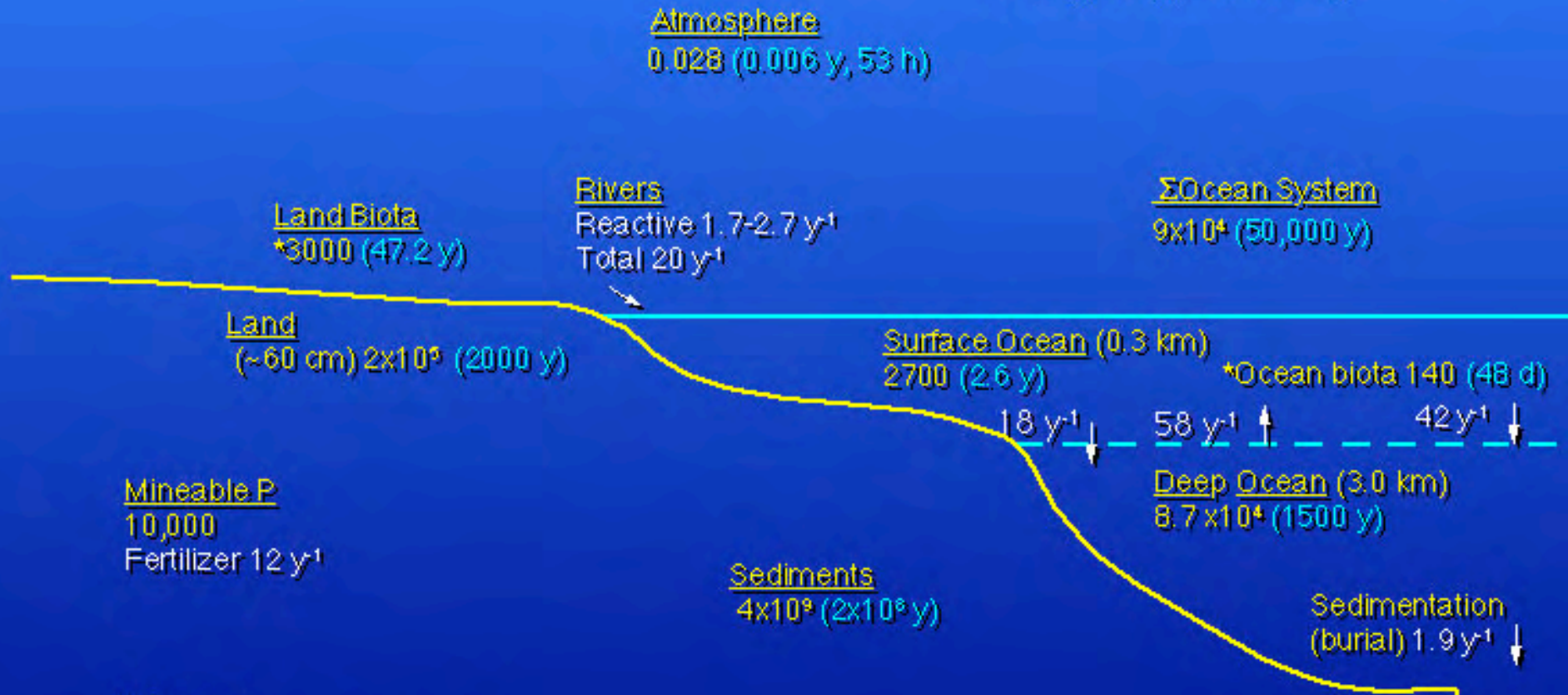
### References:

Burns & Hardy, 1975; Jaffe, 1992; McElroy *et al.*, 1976; Schlesinger & Hartley, 1992; Stedman & Shelter, 1983; Söderlund & Svensson, 1976; Galloway *et al.*, 1995

# The Phosphorus Cycle

## Global PHOSPHORUS Reservoirs, Fluxes, and Turnover Times

Pools in Tg P, Fluxes in Tg P yr<sup>-1</sup>, Tg = 10<sup>12</sup> g,  
 \* = living pools, (turnover times)

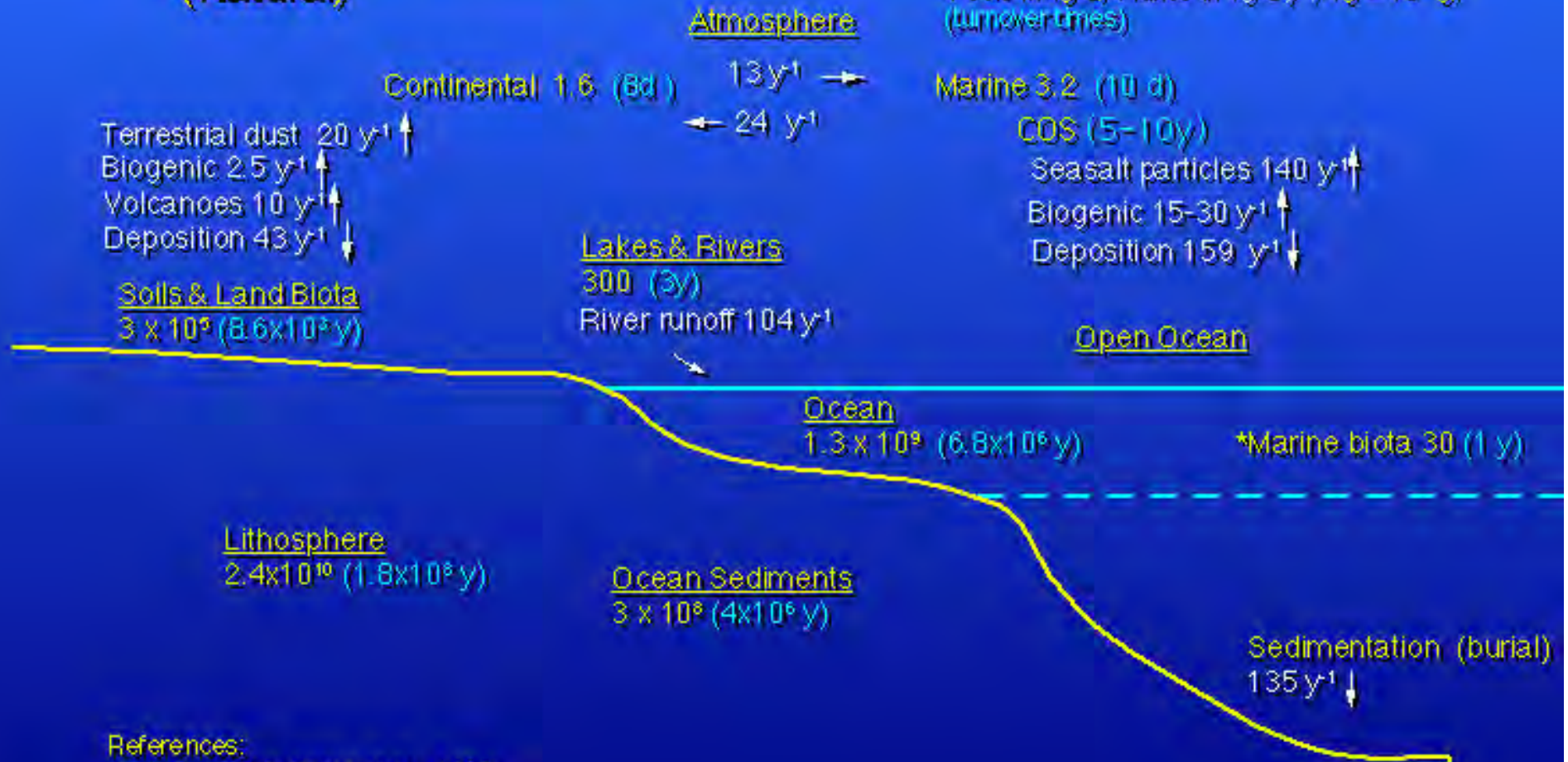


References:  
 Jahnke, 1992; Berner & Rao, 1994

# The Sulfur Cycle Pre-Industrial

## Global **SULFUR** Reservoirs, Fluxes, and Turnover Times (Natural)

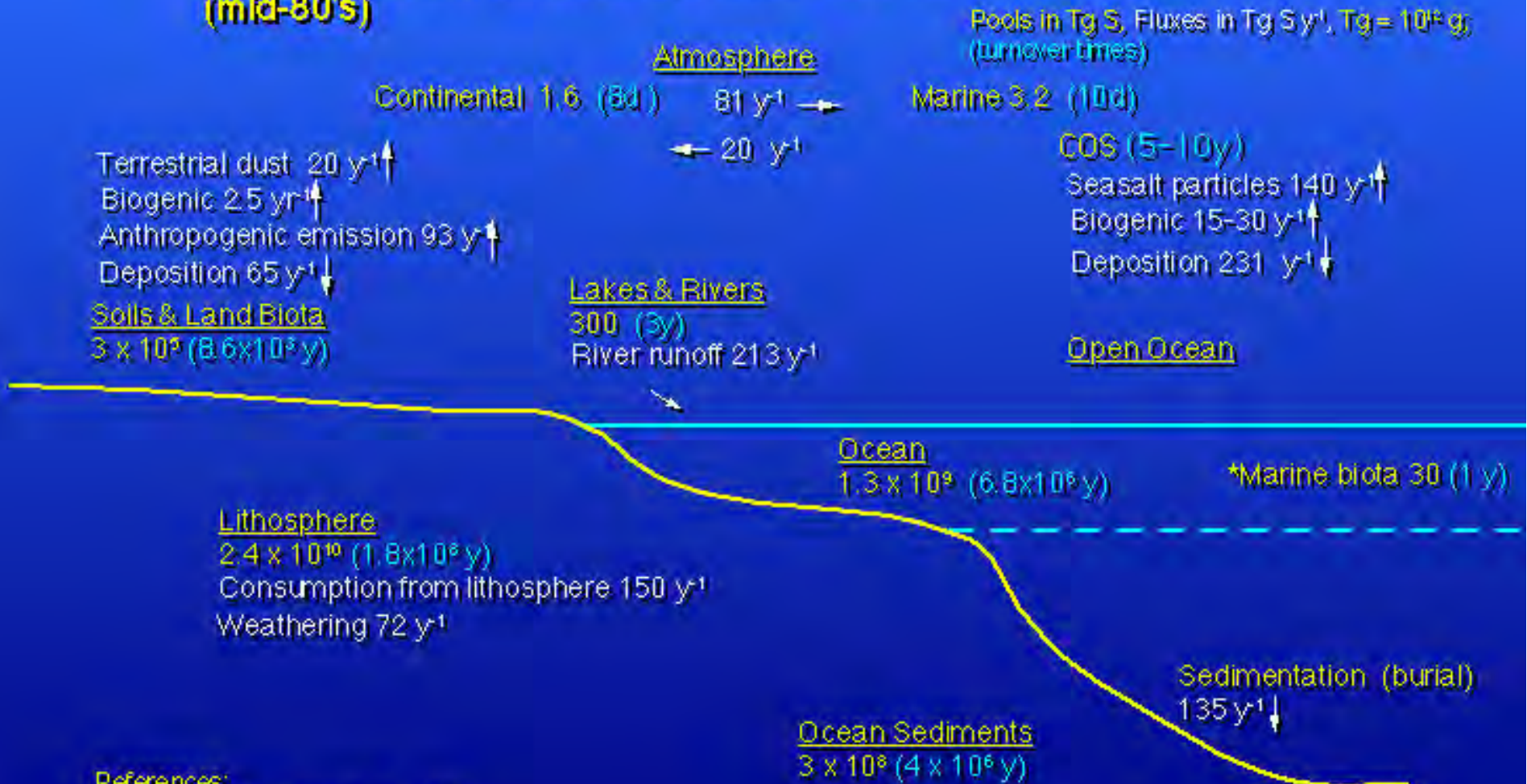
Pools in Tg S, Fluxes in Tg S y<sup>-1</sup>, Tg = 10<sup>12</sup> g;  
(turnover times)



References:  
Andreae, 1990; Bates et al., 1992;  
Charlson, Anderson & McDuff, 1992

# The Sulfur Cycle (mid 1980's)

## Global **SULFUR** Reservoirs, Fluxes, and Turnover Times (mid-80's)



References:

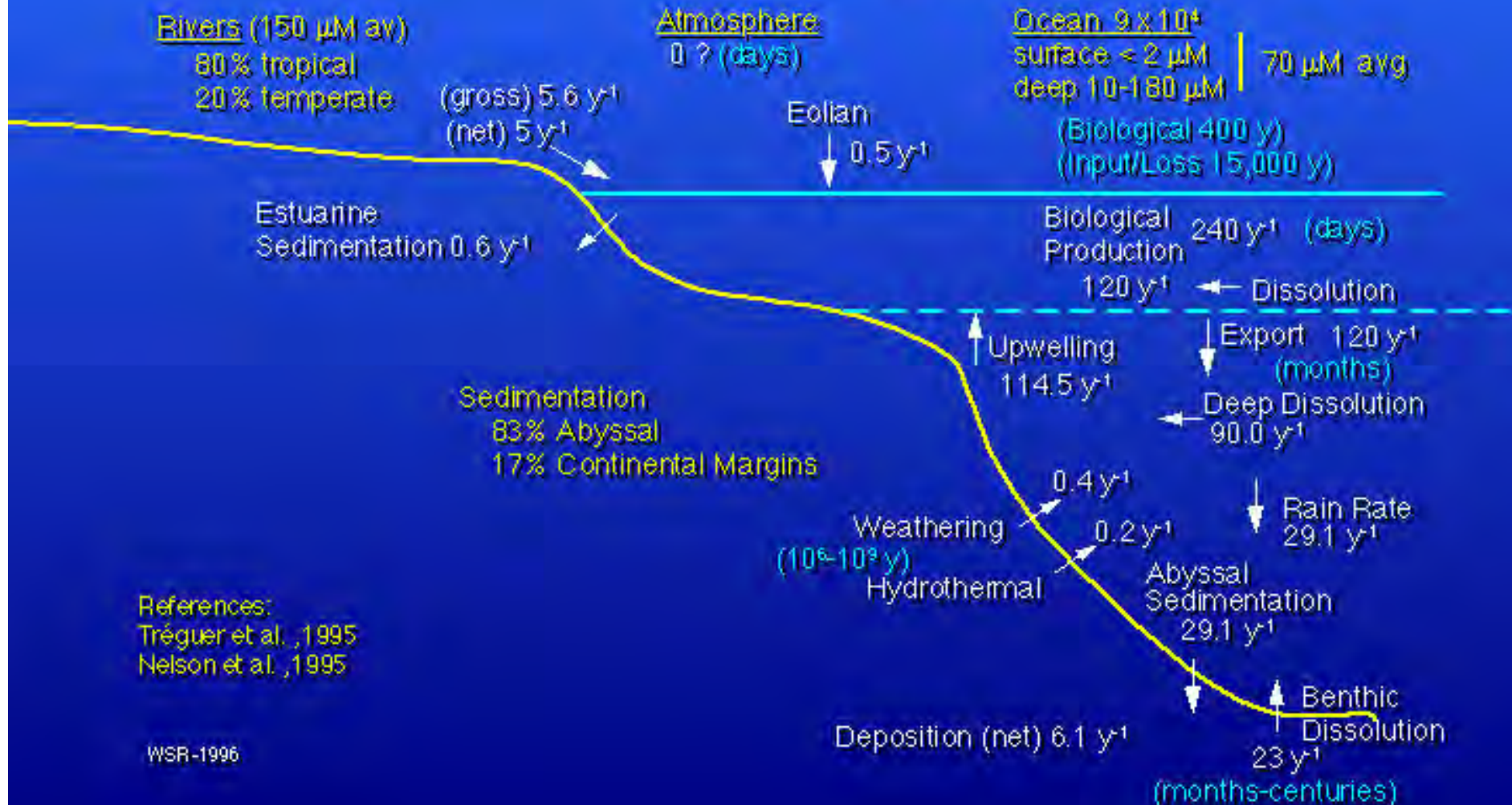
Andreae, 1990; Bates et al., 1992;  
 Charlson, Anderson & McDuff, 1992



# The Silica Cycle

## Global (Ocean) SILICA Reservoirs, Fluxes, and Turnover Times

Pool in Teramoles, fluxes in Teramoles yr<sup>-1</sup>  
(Teramole = 10<sup>12</sup> mole) (turnover times)



References:  
Tréguer et al., 1995  
Nelson et al., 1995

WSR-1996