# Welcome to ATMS 111 Global Warming

***http://www.atmos.washington.edu/2010Q1/111***

**Lisa Benson**

# Chemistry of ocean acidification

When O2 dissolves in water, it remains in its aqueous phase as O2

Not so for CO2, it reacts with H20 to make carbonic acid

# Chemistry of ocean acidification

Coral bleaching risk

When CO2 dissolves in water, carbonic acid is produced via the reaction:

$$CO_2\ (aq) + H_2O <-> H_2CO_3$$

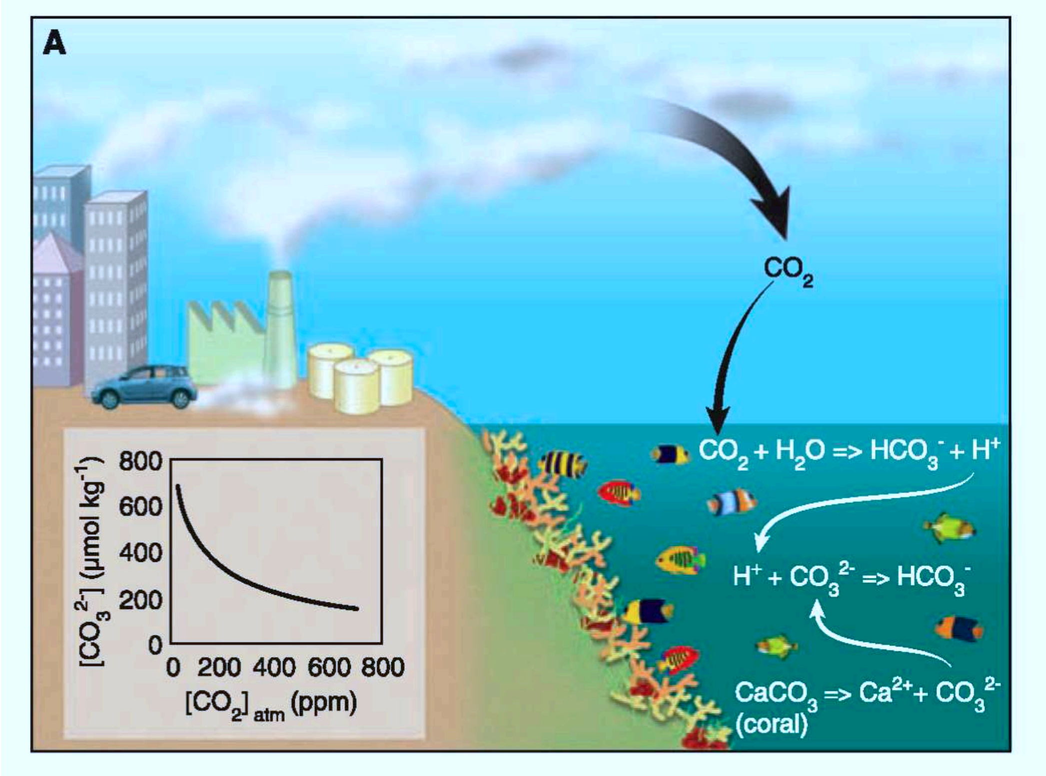
Acid dissociate into ions, including hydrogen ion

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

H+ reacts with carbonate ion as in

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

The double headed arrow means the reaction can go both ways. However, when CO2 concentrations rise the chemistry is out of balance and the response is to make more carbonic acid. This is illustrated in the following slide



Increased ocean $CO_2$ causes hydrogen ions $H^+$ concentration to increase.

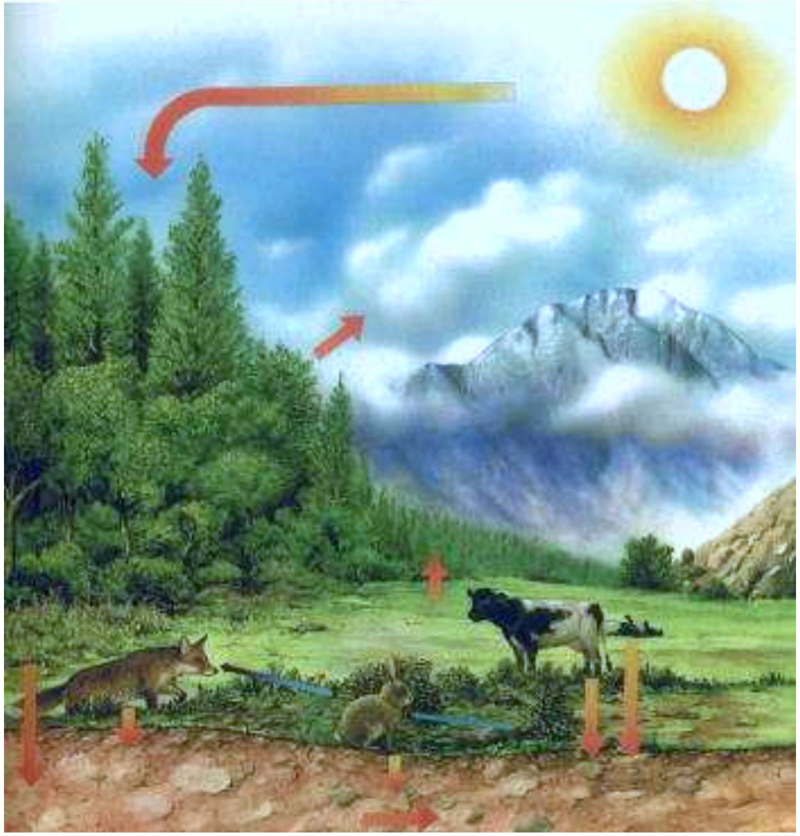
Some $H^+$ combines with carbonate ions to form bicarbonate $HCO^-_3$

The removal of carbonate ions causes further dissociation of $CaCO_3$ , which inhibits shell formation and coral skeletal formation

# The Carbon Cycle

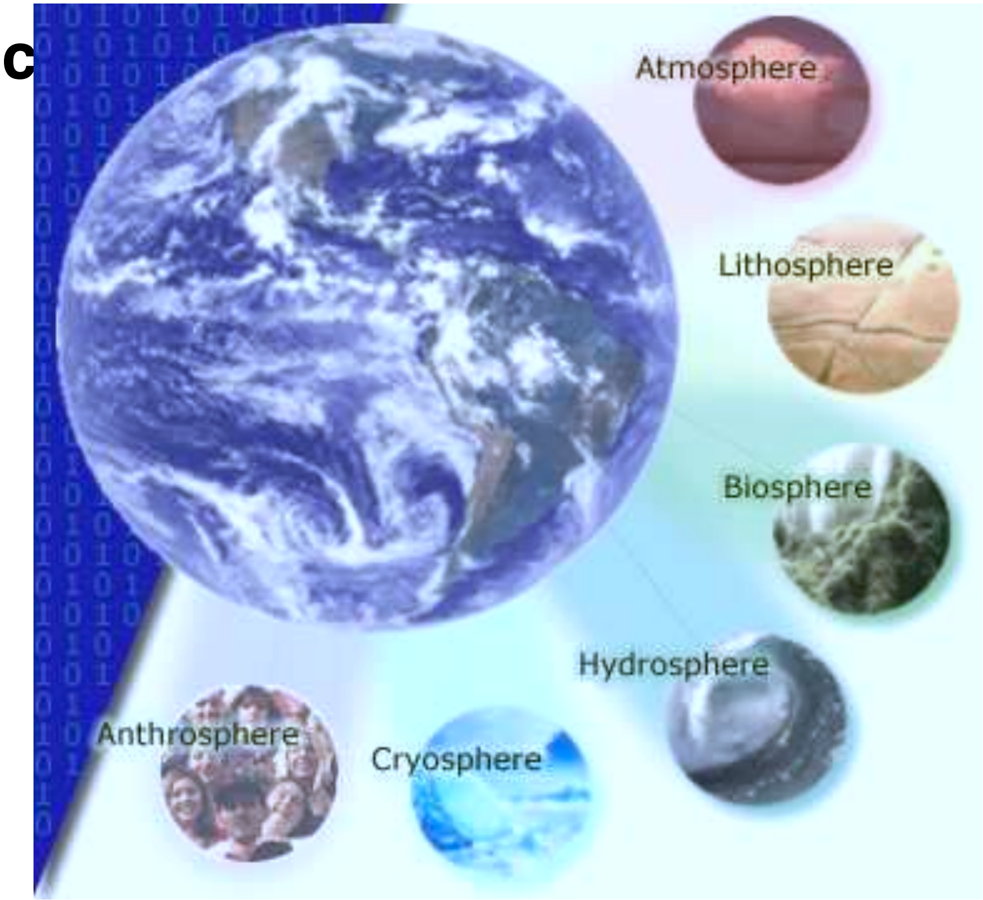
short term organic (plants and animals)
long term organic (fossil fuels)
long term inorganic (limestone)

carbon reservoirs
implications for
global warming

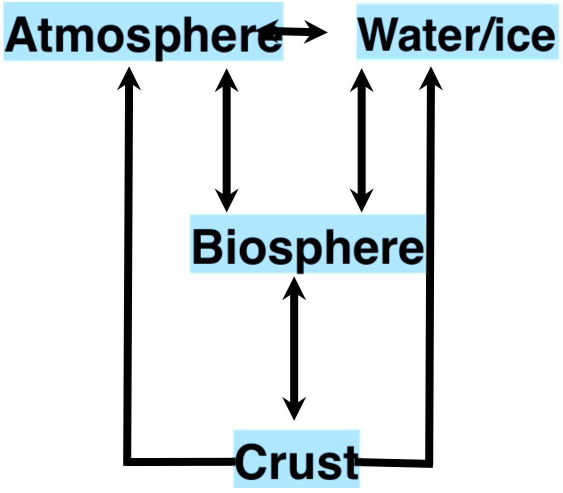


# Components of the “Earth system”

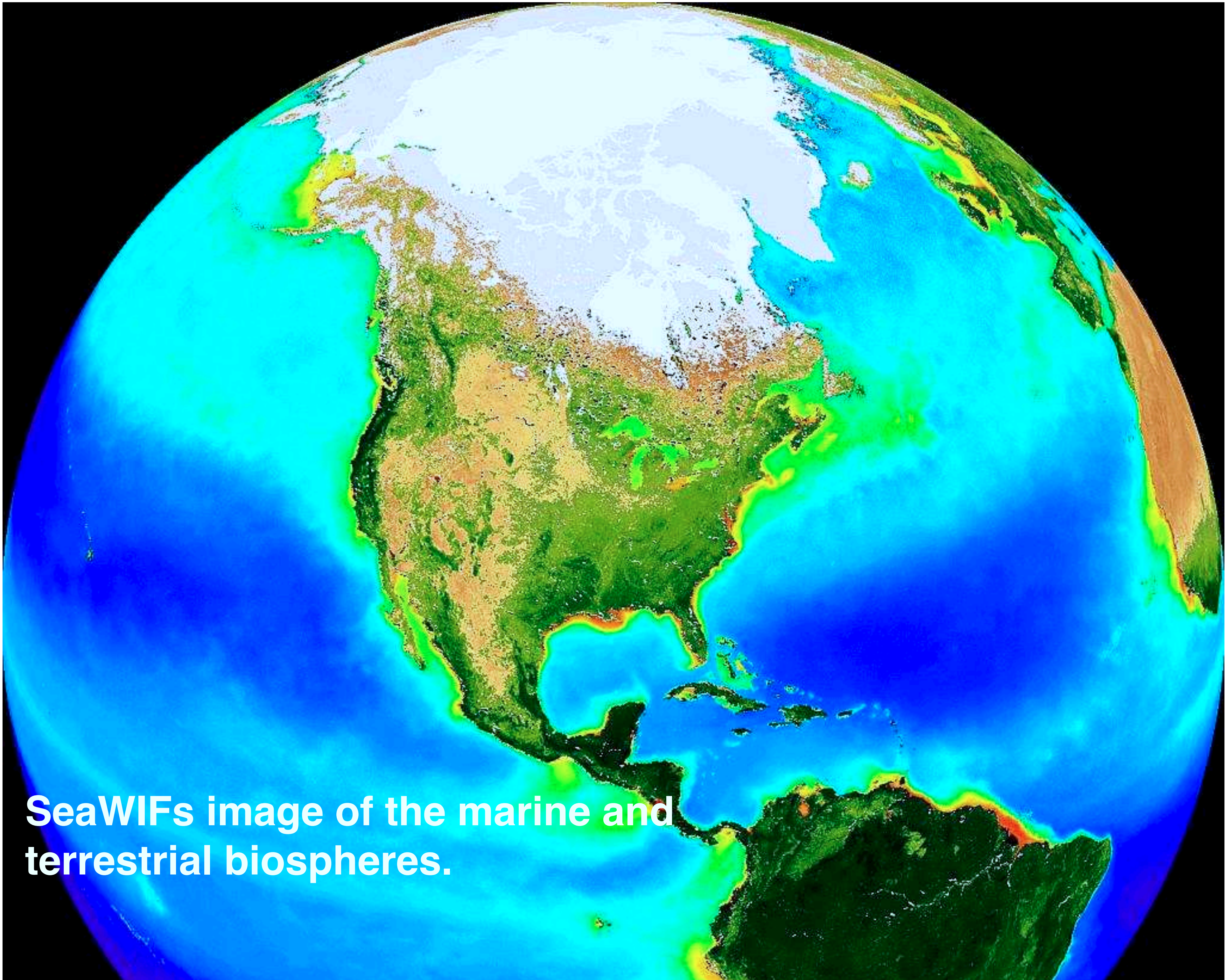
anthrosphere (our influenc
atmosphere (air)
hydrosphere (water)
biosphere (life)
cryosphere (ice)
lithosphere (crust)



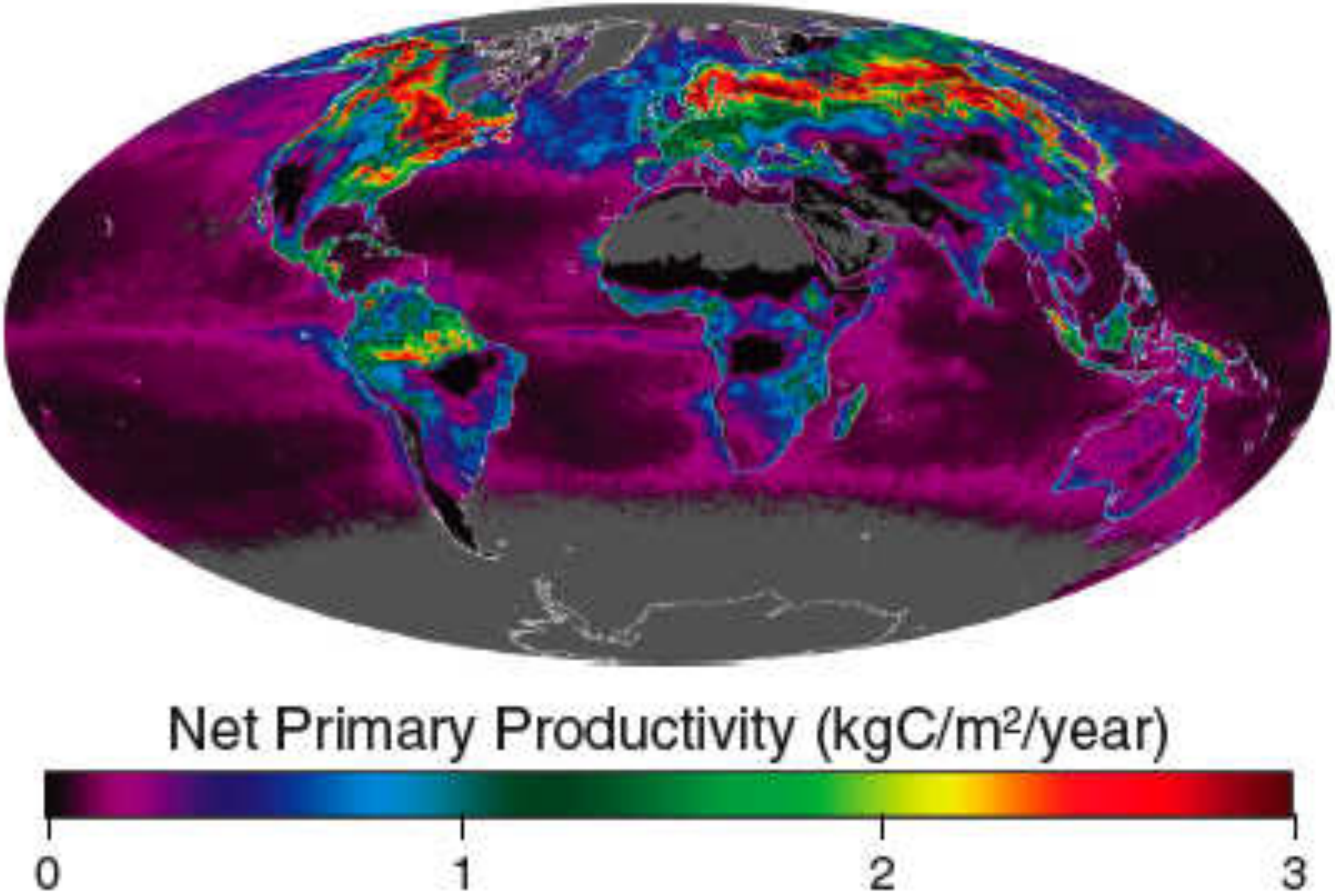
## Natural Carbon Cycle


Atmosphere
Water/ice
Biosphere
Crust

Human’s influence all component of the carbon cycle, except the crust



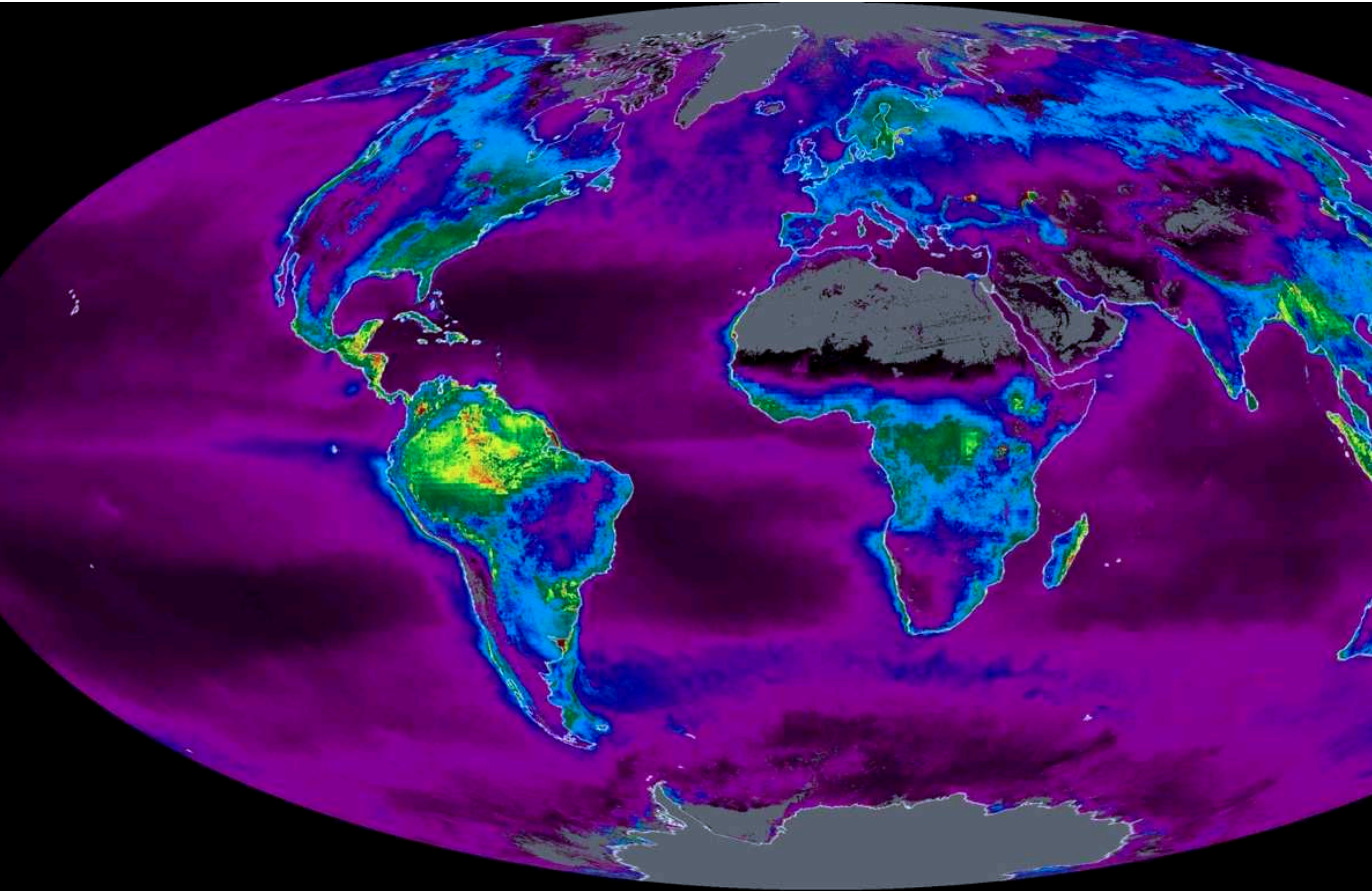
SeaWIFs image of the marine and terrestrial biospheres.



**(photosynthesis)**

**June 2002**

Based on NASA MODIS imagery, which compares the reflected radiation at two wavelengths, one of which is in the red part of the spectrum, where energy is absorbed by plants to produce photosynthesis



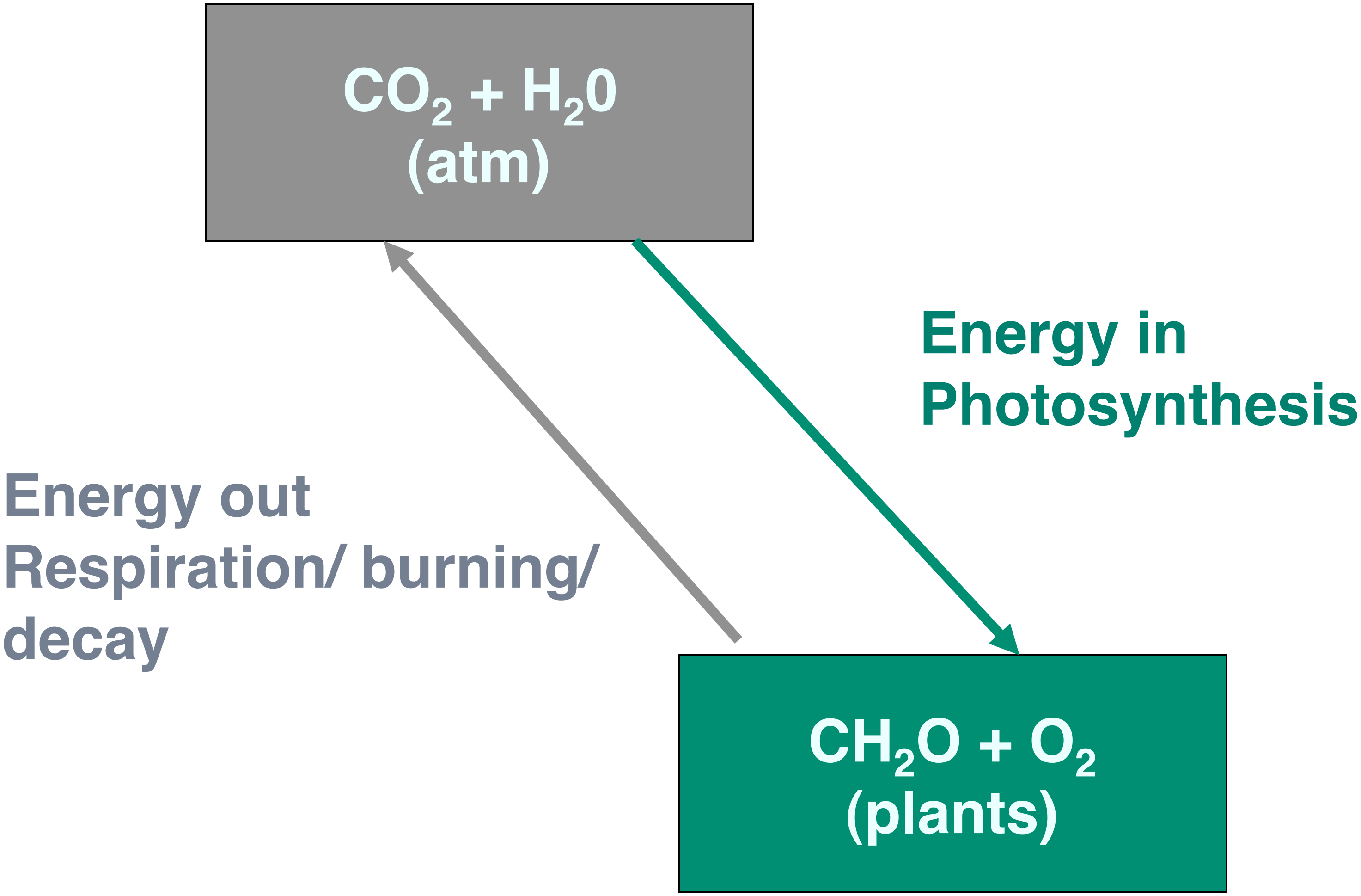
# The chemistry

| | |
|---|---|
| Photosynthesis | $CO_2 + H_2O \rightarrow CH_2O + O_2$ |
| respiration/burning/ decomposition | $CH_2O + O_2 \rightarrow CO_2 + H_2O$ |

$CH_2O$ stands for carbohydrate

# Short term organic carbon cycle

## Part 1 Land



$CO_2 + H_20$
(atm)

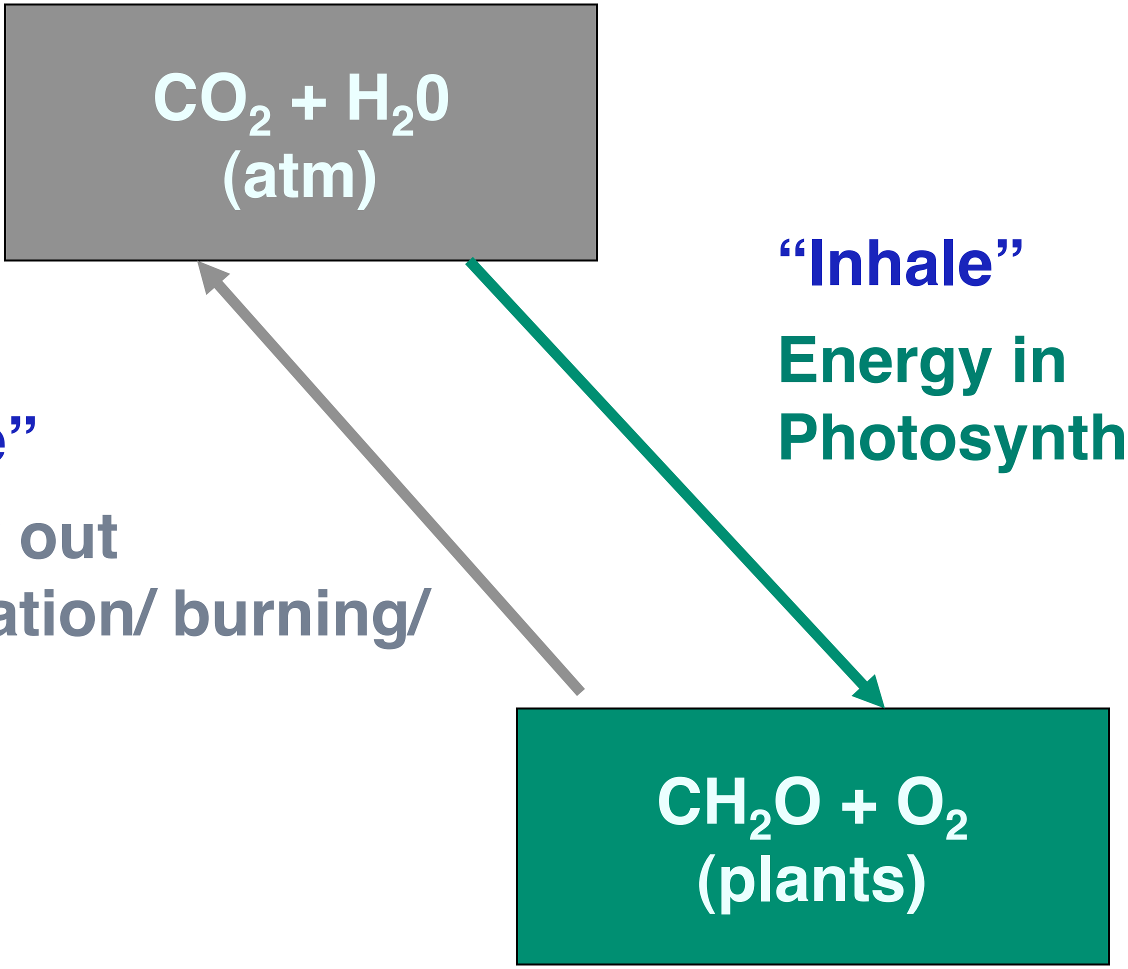
Energy in
Photosynthesis

Energy out
Respiration/ burning/
decay

$CH_2O + O_2$
(plants)

# Short term organic carbon cycle

## “The breathing of the biosphere”



$CO_2 + H_20$
(atm)

**“Inhale”**

Energy in
Photosynthesis

**“Exhale”**

Energy out
Respiration/ burning/
decay

$CH_2O + O_2$
(plants)

The summer “drawdown” of atmospheric CO2 by

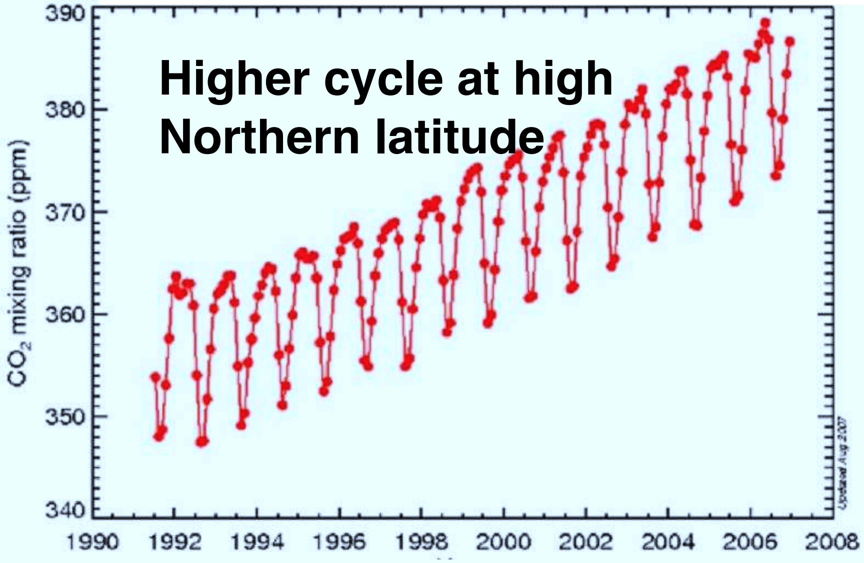
Photosynthesis in spring/summer when sunlight is available...

Decay occurs year-round

Each year ~10% of the atmospheric reservoir of CO2

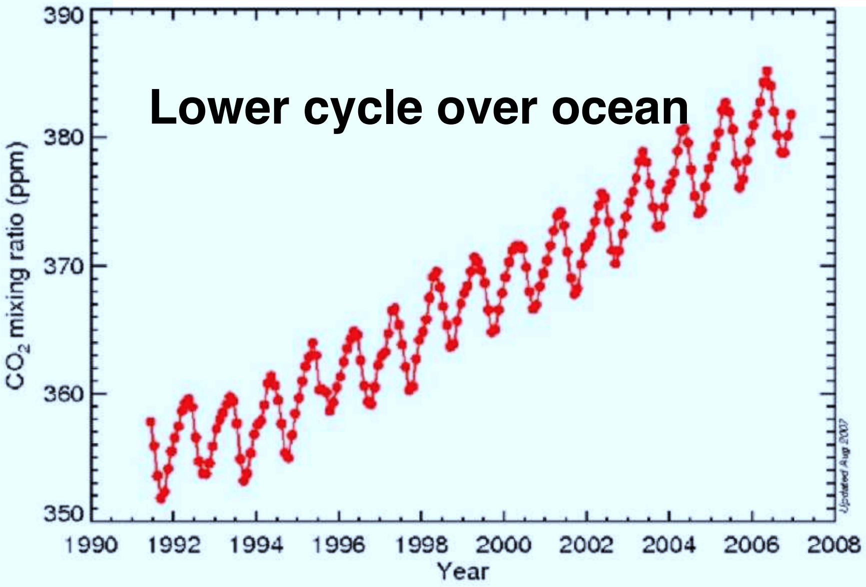
is exchanged with the biosphere

CO2 measured at Alert, CA



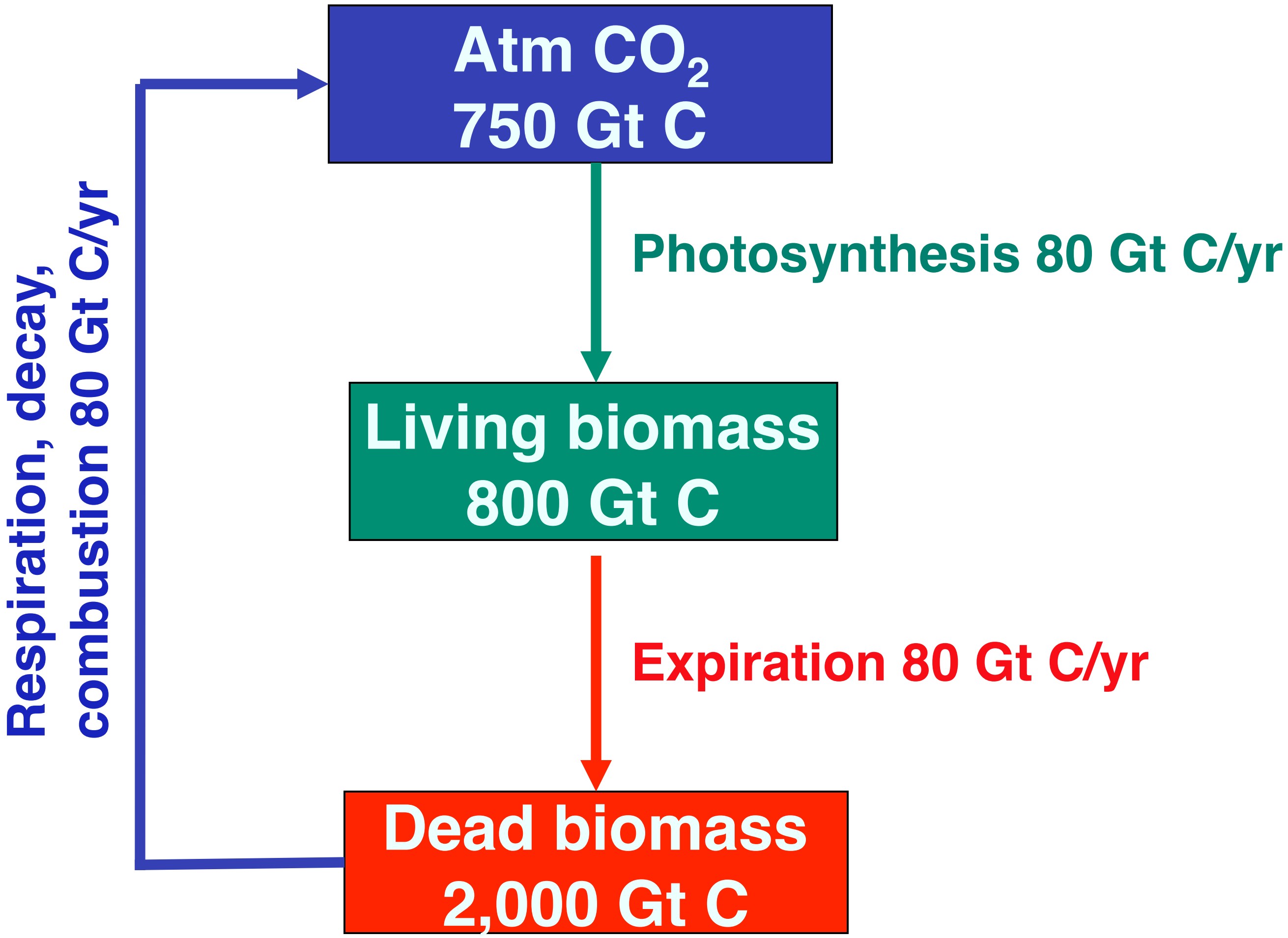
Higher cycle at high Northern latitude

Mauna Loa, Hawaii, USA



Lower cycle over ocean

# Atmosphere – Land Carbon Cycle



Atm $CO_2$
750 Gt C

Photosynthesis 80 Gt C/yr

Living biomass
800 Gt C

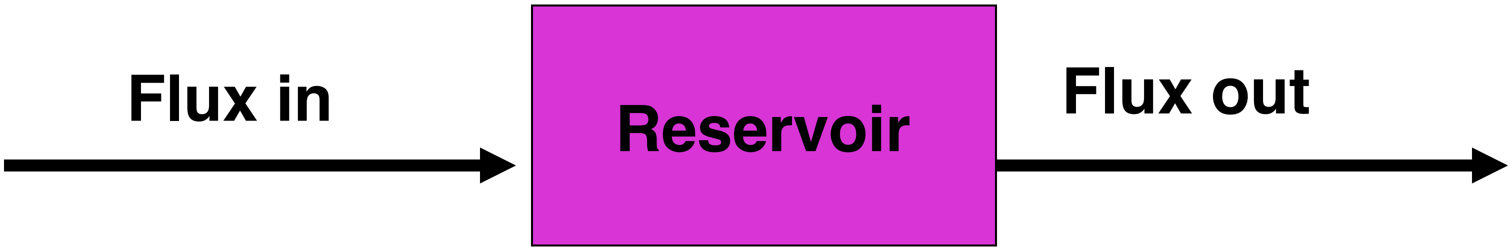
Expiration 80 Gt C/yr

Dead biomass
2,000 Gt C

Respiration, decay, combustion 80 Gt C/yr

# Residence Time

We use box diagrams to describe reservoir and flow or matter

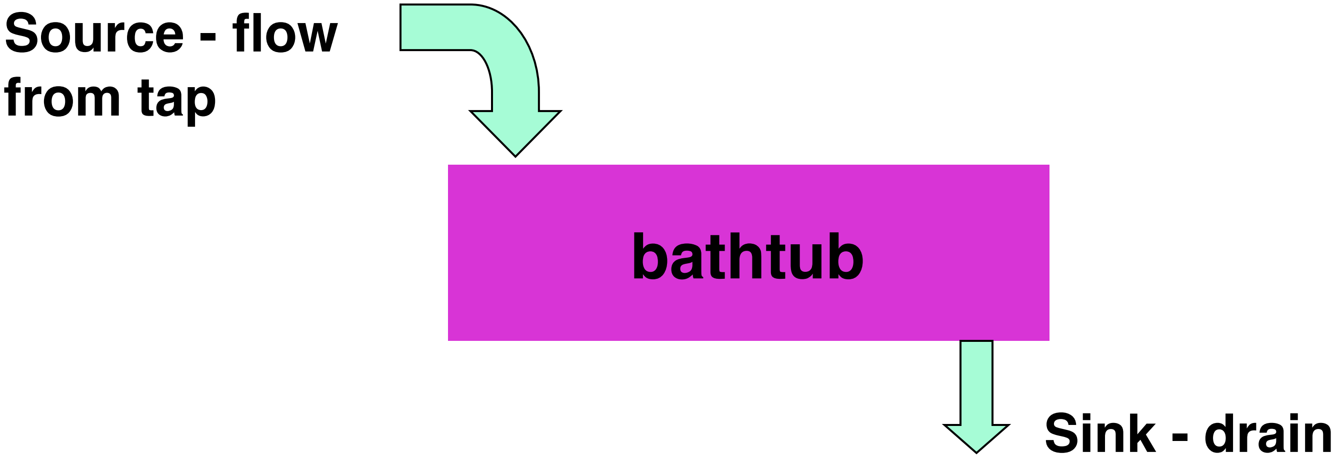


Flux in

Reservoir

Flux out

# An example



Source - flow from tap

bathtub

Sink - drain

**When the flow in equals the flow out, the water level (reservoir) does not change**

**Input Source = Output Sink**

# Residence Time

The average length of time matter spends in a reservoir

$$\text{Residence Time (RT)} = \frac{\text{Reservoir Size}}{\text{Outflow Rate}}$$

5 liters/minute

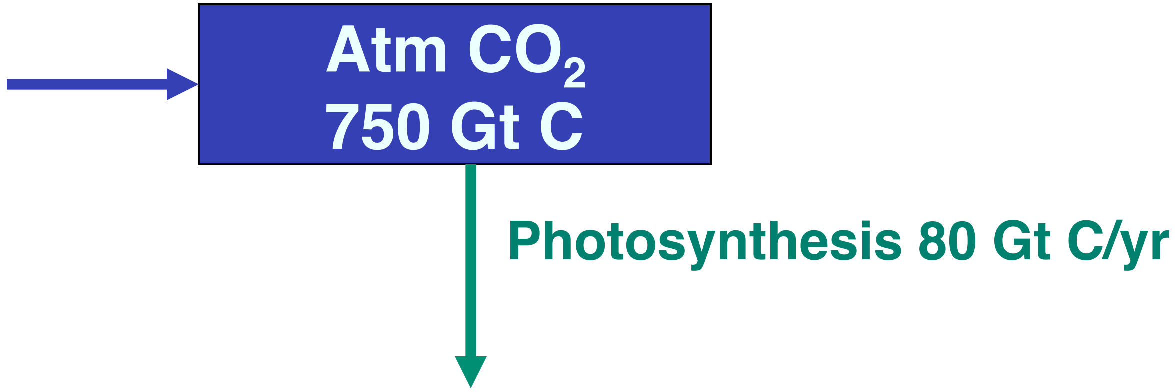
100 liters

5 liters/minute

RT = 100/5 = 20 minutes

# Atmospheric Carbon Residence Time

For carbon exchange with land biomass



Atm $CO_2$
750 Gt C

Photosynthesis 80 Gt C/yr

$$\text{Residence Time (RT)} = \frac{\text{Reservoir Size}}{\text{Outflow Rate}}$$

$$= 750\ \text{Gt} / (80\ \text{Gt/yr}) \sim 9\ \text{yr}$$

# Leaf/Forest Carbon Residence Time

**Leaf biomass**
**160 Gt C**

RT = 160 Gt / (65 Gt/yr)
~ 2 yr

**Tree biomass**
**640 Gt C**

RT = 640 Gt / (15 Gt/yr)
~ 42 yr

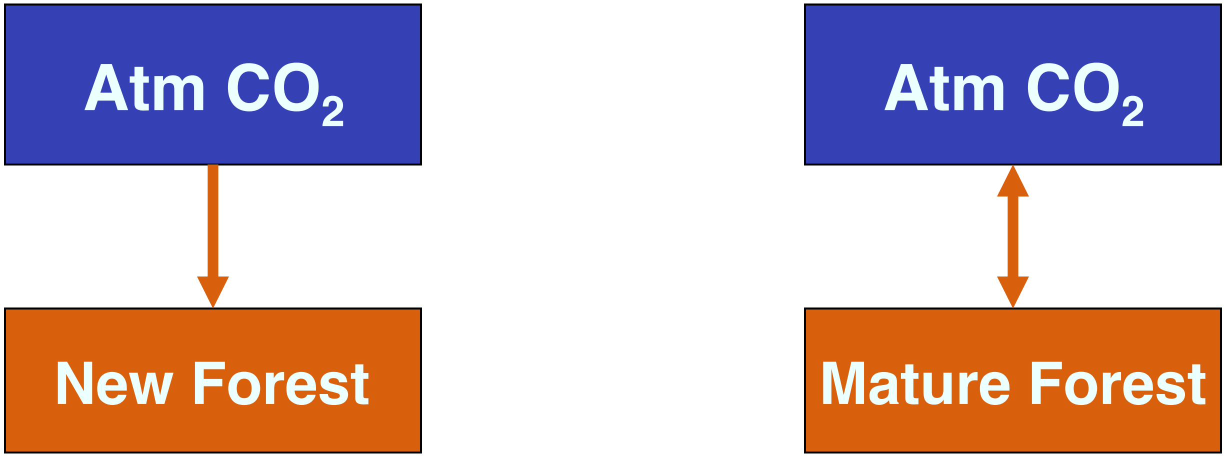
$$\text{Residence Time (RT)} = \frac{\text{Reservoir Size}}{\text{Outflow Rate}}$$

*Warning: Prof Bitz made up these outflow rates

# A Brief Segue on Forests

**Largest component of terrestrial biomass**

**Store CO2 in tree trunks, roots, litter and soil**



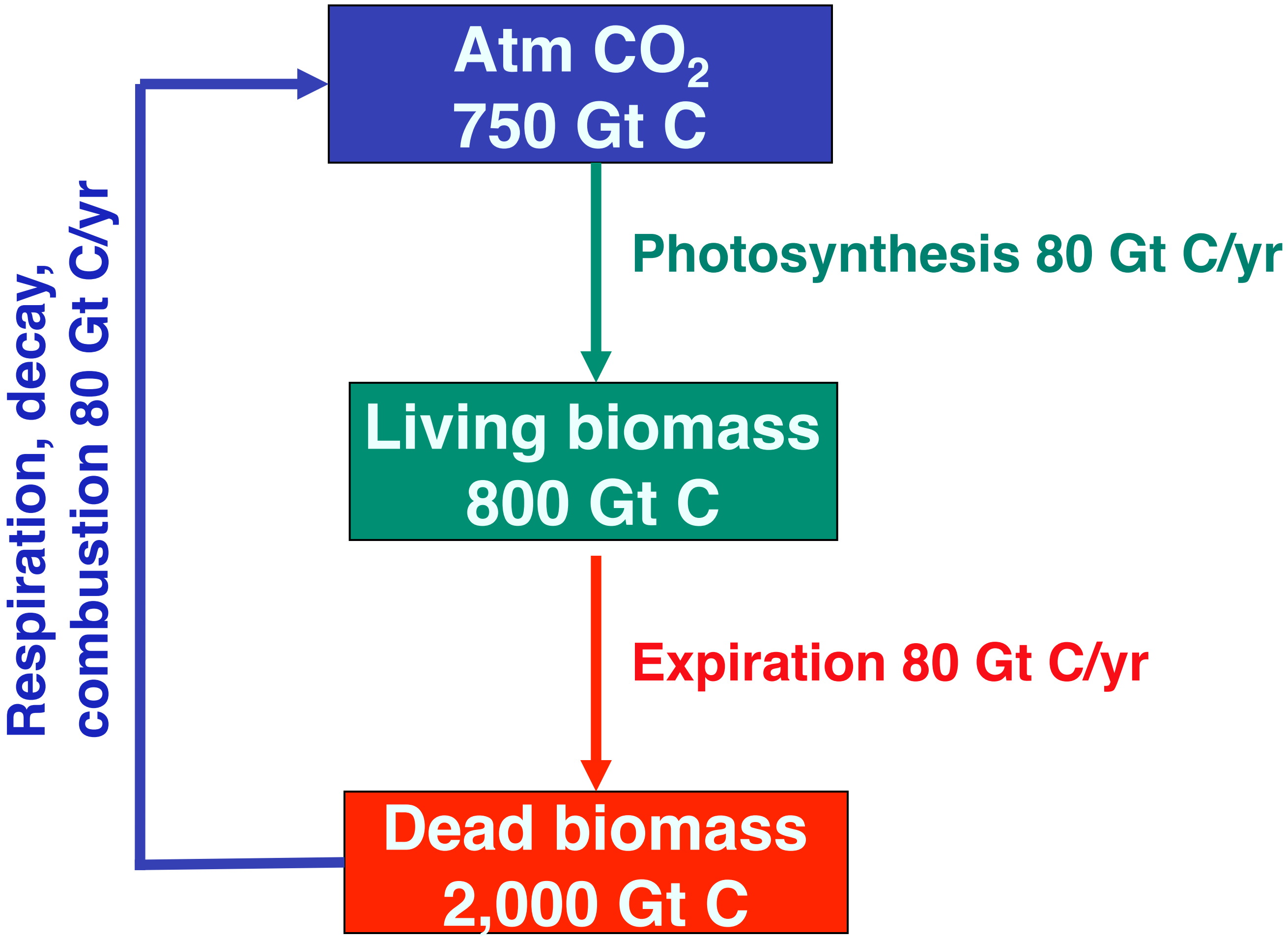
**Mature forests are a carbon reservoir**
**IN CO2 BALANCE with the atmosphere**

*Deforestation* **puts carbon back in the atmosphere;**

***afforestation*** **takes it out.**

**Either one can knock the atmosphere CO2 level out of balance for decades to centuries**

# Atmosphere – Land Carbon Cycle



Atm $CO_2$
750 Gt C

Photosynthesis 80 Gt C/yr

Living biomass
800 Gt C

Expiration 80 Gt C/yr

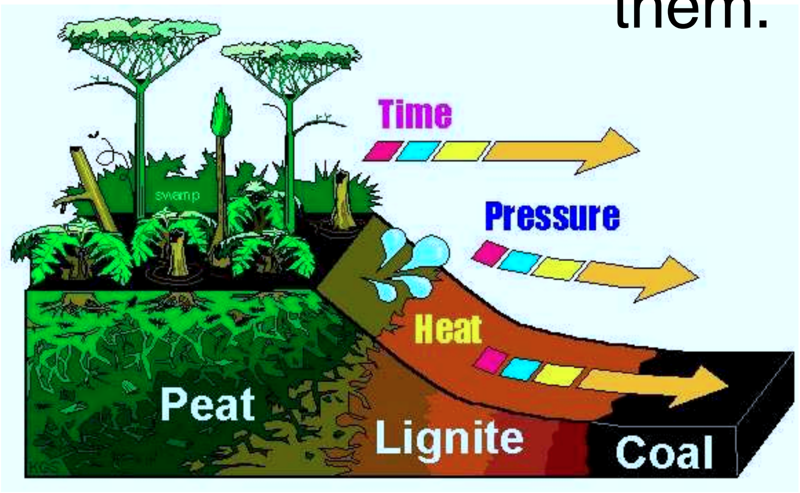
Dead biomass
2,000 Gt C

Respiration, decay,
combustion 80 Gt C/yr

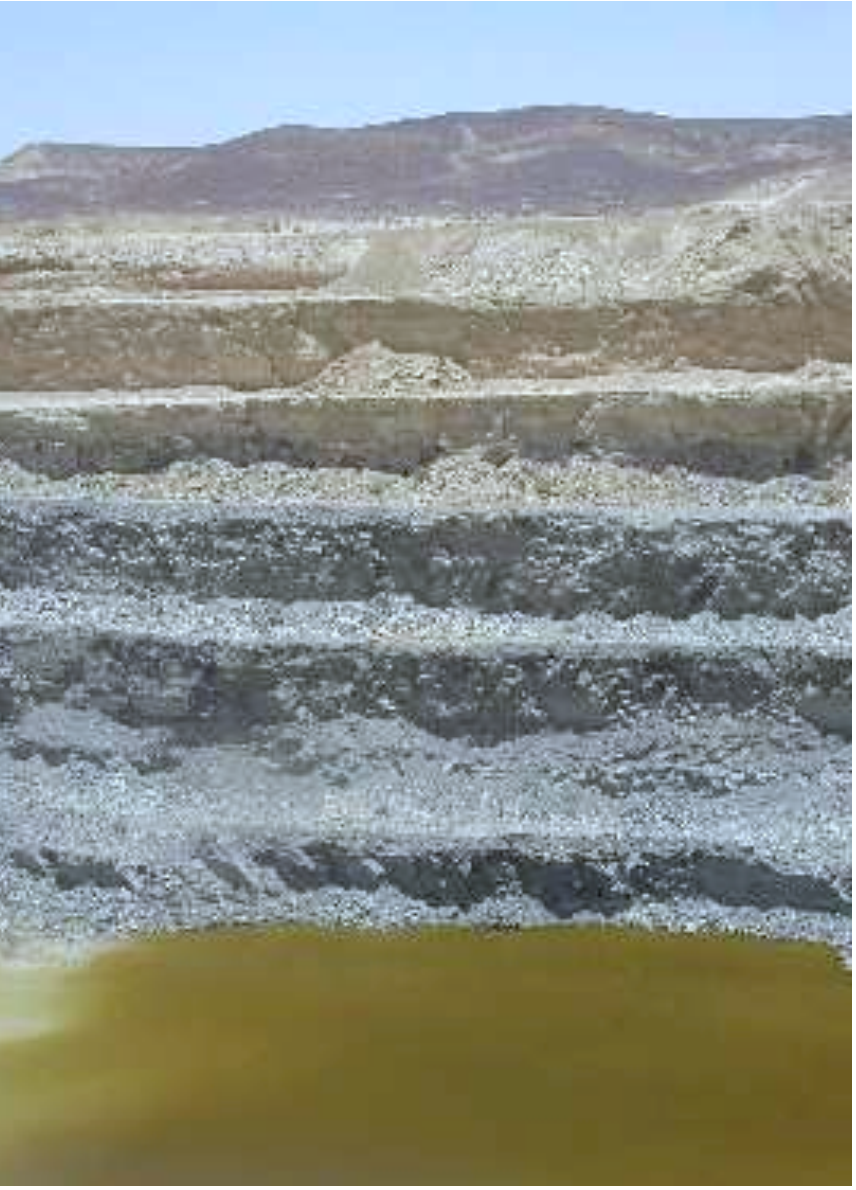
**Dead biomass**
**2,000+ Gt C**

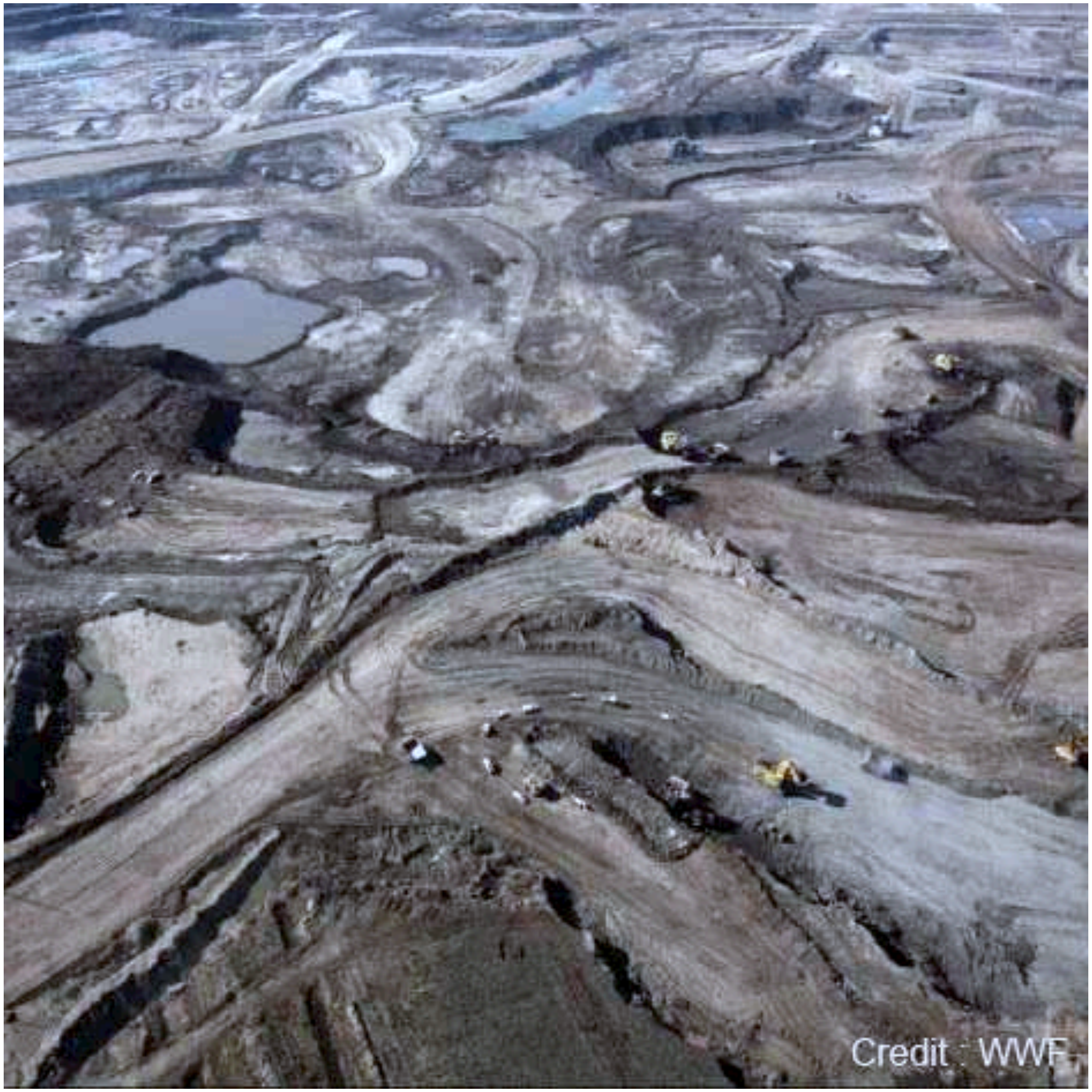
This box includes fossil fuels, such as coal and oil.

Normally their carbon returns to the atmosphere by “weathering”, which is chemical erosion, at a rate 100s of times slower from humans burning them.



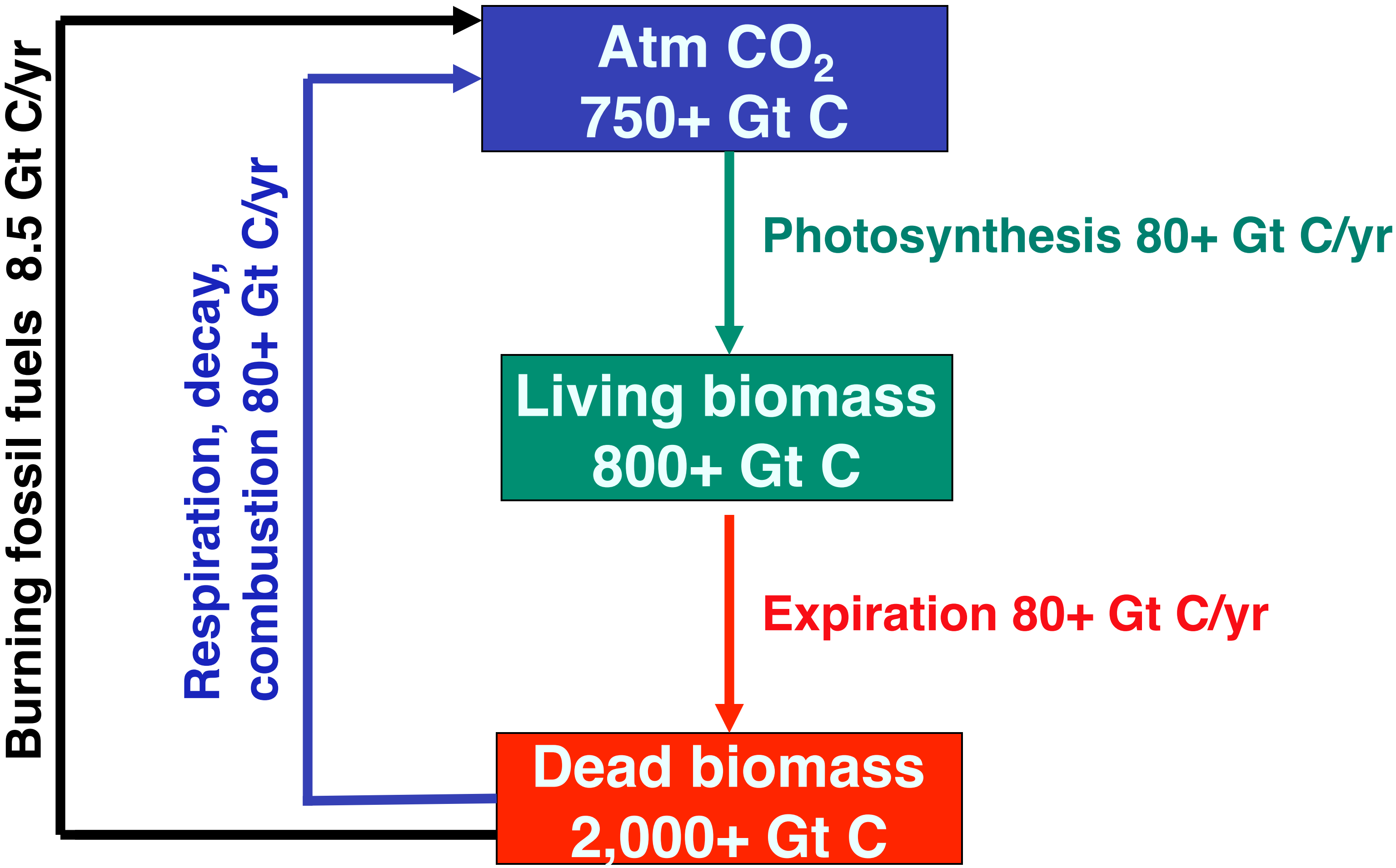
# Oil shale / Tar sands





Credit : WWF

# Atmosphere – Land Carbon Cycle
# With Human SHORT CIRCUIT



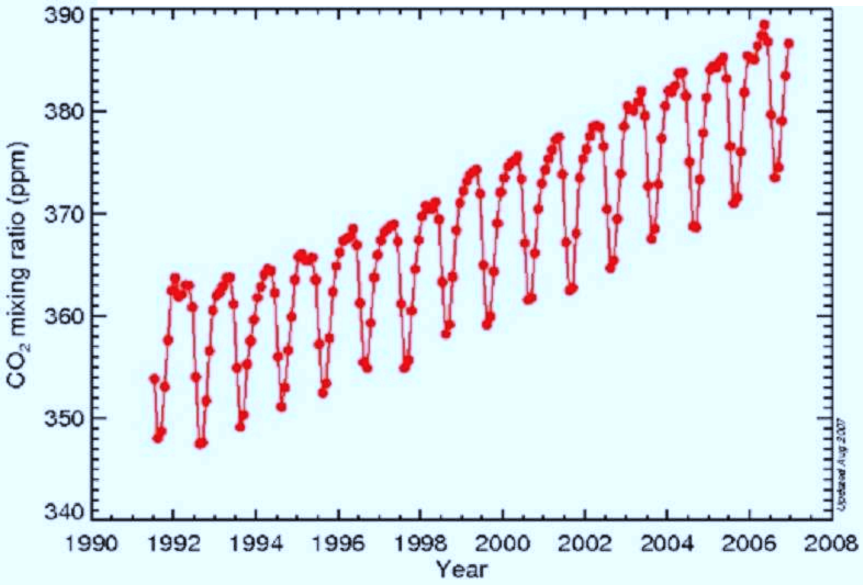
\+ indicates the numbers are rising due to burning fossil fuels

The atmosphere reservoir is gaining 45% of the Carbon added by humans

**The land biosphere sink takes up about 30% for now**

Plants are not expected to keep this rate up as their growth is limited by nitrogen in soils, climate, etc

**CO2 measured at Alert, CA**

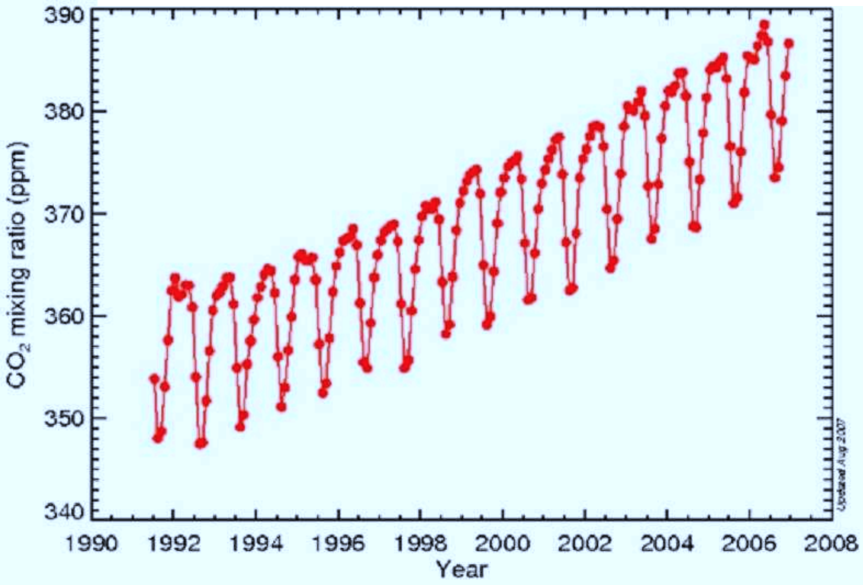


Thus even though the Reservoir Time in the atmosphere, which is the time it takes for a molecule to cycle from atmosphere to the land biosphere, is ~10 yrs

The additional CO2 we are adding lasts longer because it is removed by INCREASING the land (or ocean) uptake, which is happening, but the timescale is not equal to the residence time

This timescale is instead set by the sensitivity of these systems to an **increase** in the atmospheric CO2 concentration. These timescales are not well known, but we think it takes ~100 yr or more.

**CO2 measured at Alert, CA**



# Marine Carbon Cycle – Surface Ocean

When CO2 dissolves in water, carbonic acid is produced via the reaction:

$$CO_2\ (aq) + H_2O <-> H_2CO_3$$

Acid dissociate into ions, including bicarbonate ion

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

Rising CO2 in the atmosphere produces more dissolved CO2 in the ocean surface waters, plus more carbonic acid and bicarbonate ion. **These sinks take up the other 25% for now**.

These reactions acidify the ocean

# Carbon cycle, surface – deep exchange

The surface ocean exchanges water with the deep through deep water formation (part of the meridional overturning circulation), upwelling, and mixing.

Can this remove the extra carbon from the ocean surface?
And keep the sink drawing down atmospheric CO2?

Let's see…

# Biological Pump (downward) rain of dead biomass

Decomposing organic goo
Makes ocean $HCO_3^-$ rich

Soft organic material decays quickly

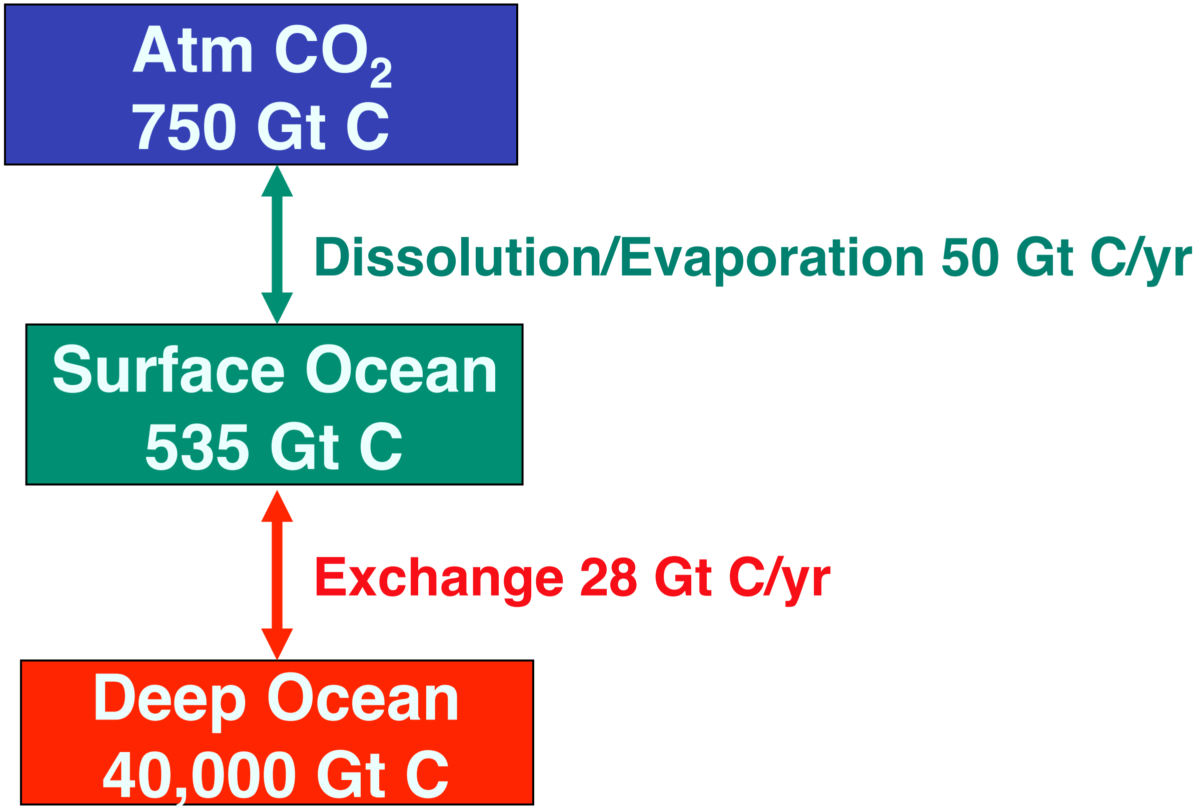
Decomposition uses $O_2$ gives off $CO_2$

Repeat chemistry at surface makes carbonic acid and bicarbonate ion

**Thus the deep ocean has 40,000 Gt of $HCO_3^-$**

**Wow!**

# Atmosphere – Ocean Carbon Cycle
# Organic and Inorganic



Atm $CO_2$
750 Gt C

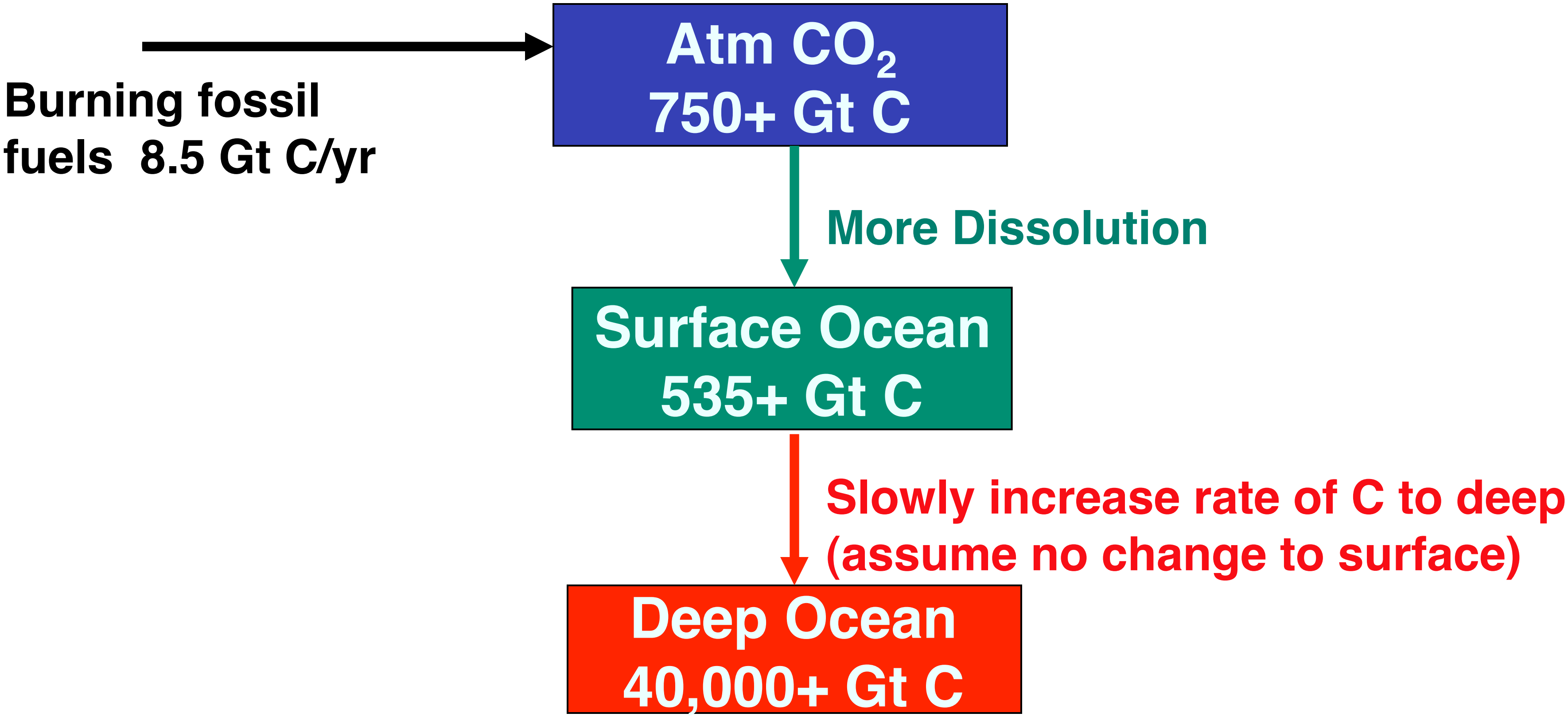
Dissolution/Evaporation 50 Gt C/yr

Surface Ocean
535 Gt C

Exchange 28 Gt C/yr

Deep Ocean
40,000 Gt C

# Atmosphere – Ocean Carbon Cycle
# Organic and Inorganic



**Burning fossil fuels 8.5 Gt C/yr**

**Atm $CO_2$**
**750+ Gt C**

**More Dissolution**

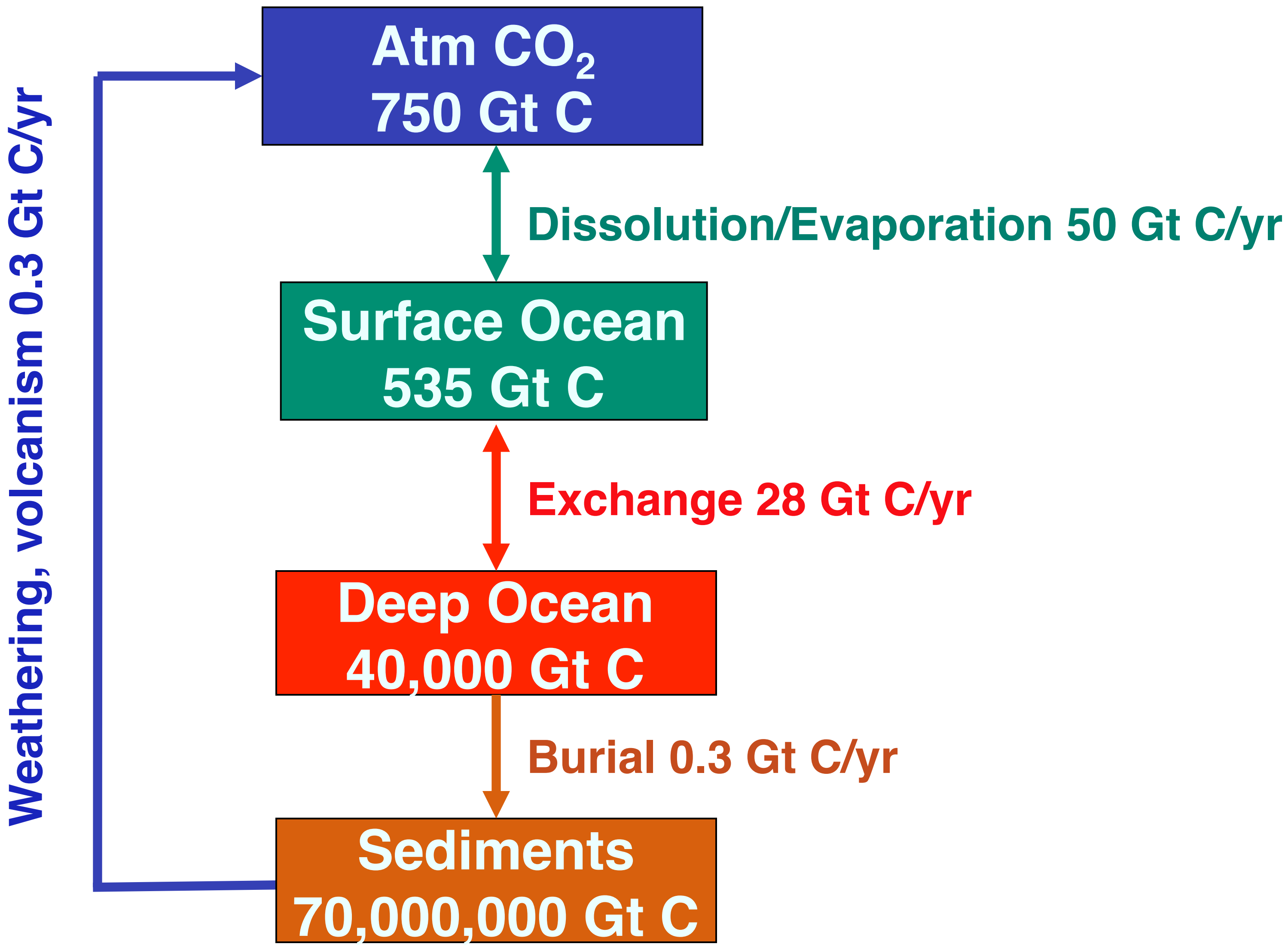
**Surface Ocean**
**535+ Gt C**

**Slowly increase rate of C to deep (assume no change to surface)**

**Deep Ocean**
**40,000+ Gt C**

We can “dump/hide” carbon in the deep ocean.
The natural way is slow, ~1,000 yrs. In short term, expect surface ocean to saturate, reducing anthropogenic CO2 uptake.

# One more reservoir to consider



Atm $CO_2$
750 Gt C

Dissolution/Evaporation 50 Gt C/yr

Surface Ocean
535 Gt C

Exchange 28 Gt C/yr

Deep Ocean
40,000 Gt C

Burial 0.3 Gt C/yr

Sediments
70,000,000 Gt C

Weathering, volcanism 0.3 Gt C/yr

# Sediments in the marine carbon cycle

The very long term inorganic carbon cycle

Sediments are rich in shells from creatures such as phytoplankton

# Calcium carbonate shell formation

$Ca^{2+}$ enters the ocean from weathering (chemical erosion) of rocks. It reacts with some of the 40,000 Gt of $HCO_3^-$

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

# Calcium carbonate formation

**Calcium carbonate $CaCO_3$ is limestone (chalk). It’s also the main ingredient in TUMS and phytoplankton shells.**

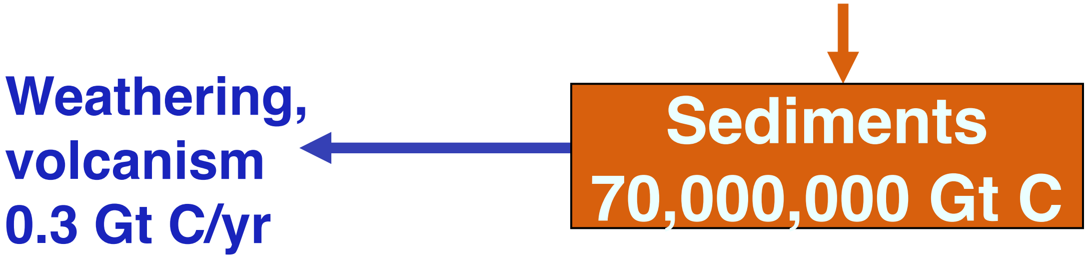
**Carbonate formation removes carbon from the atmosphere-ocean reservoir and puts it in long term storage. This is the process that will eventually remove the carbon we are adding.**

**Limestone weathering must increase to bring extra calcium ion into the deep ocean... Rising atmospheric CO2 makes rainwater more efficient at weathering. But it still takes time to break down rocks.**

**This is so a <u>slow process</u>.**

# Residence Time of Carbon in Sediments

Time to move C from sediments back to atmosphere



**Weathering, volcanism 0.3 Gt C/yr**

**Sediments 70,000,000 Gt C**

$$\text{Residence Time (RT)} = \frac{\text{Reservoir Size}}{\text{Outflow Rate}}$$

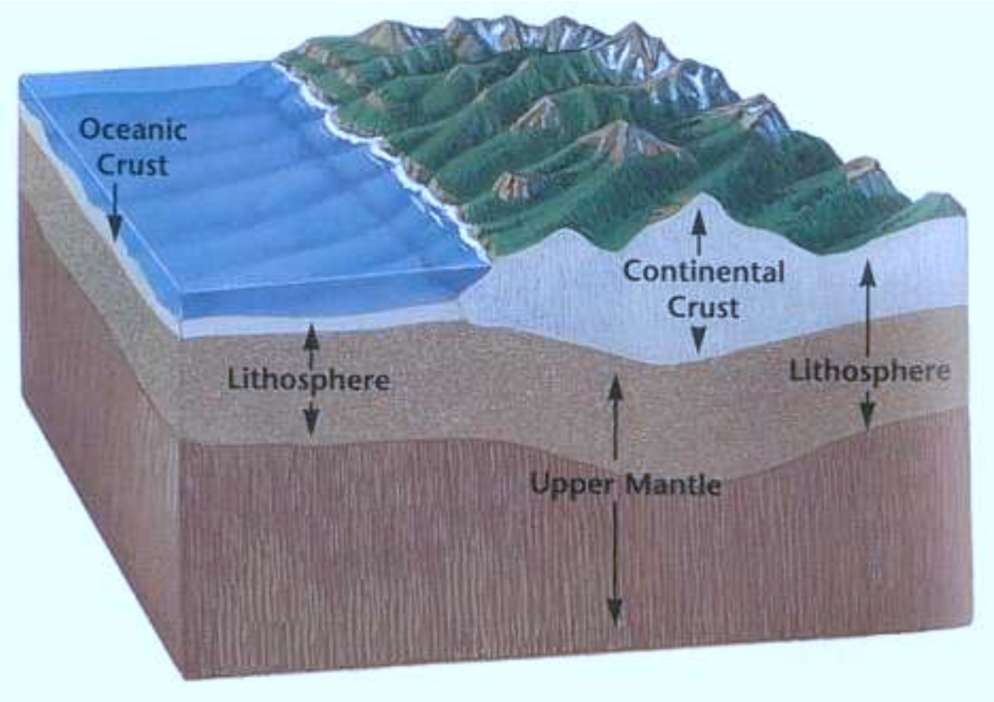
$$= 70{,}000{,}000 \text{ Gt} / (0.3 \text{ Gt/yr})$$

**~ 200 million years!**

# The Rock Cycle

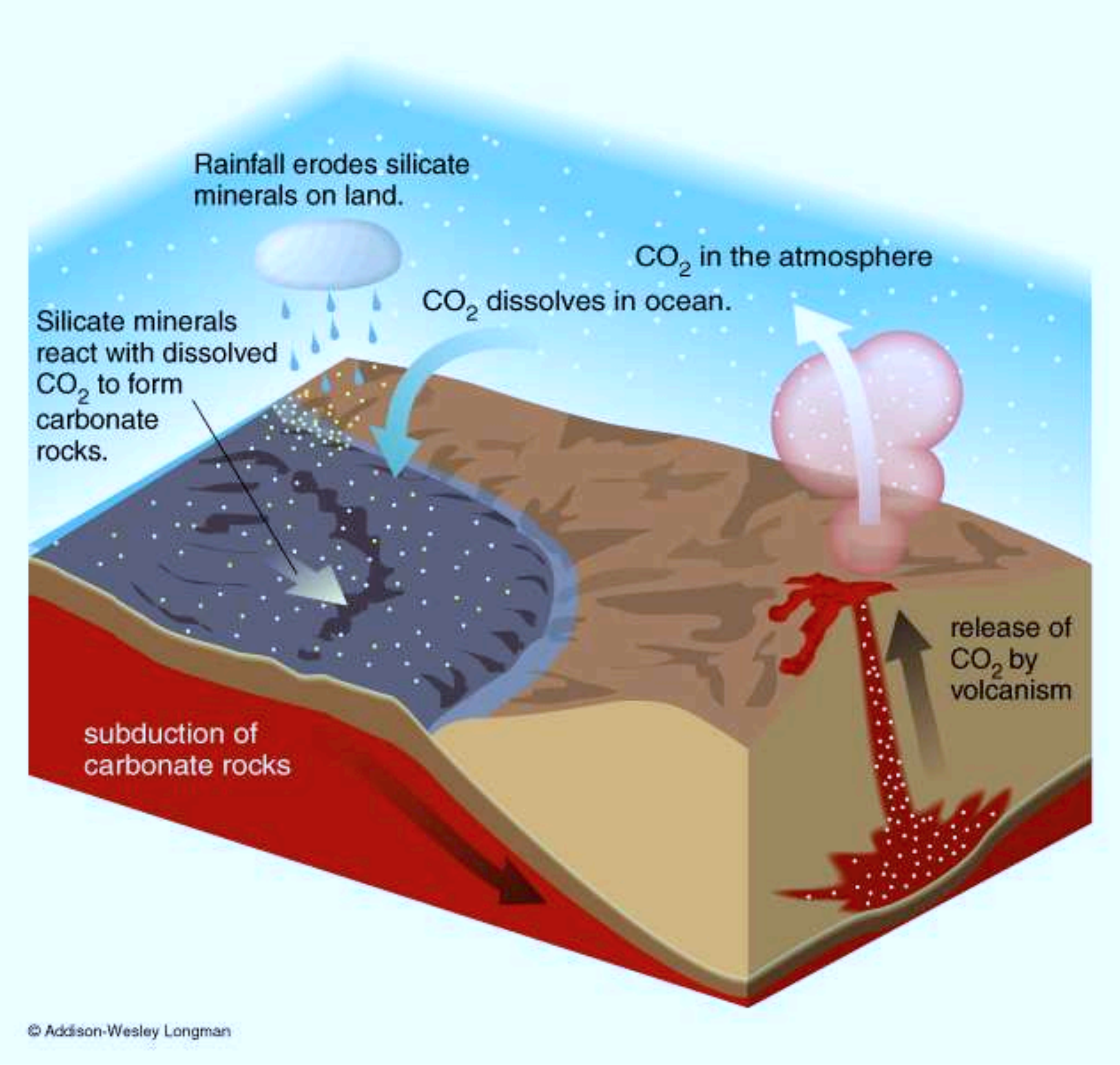
**The ocean sediments subduct and eventually resurface as rocks**

**Thus we have limestone at the surface**



**This is so a VERY slow process.**

# Silicate minerals follow much the same fate as Calcium



# Limestone cliffs (sedimentary rocks of $CaCO_3$)

Photograph by Sam Abell

# Limestone (left) versus marble (left and below)

Marble is crystalline $CaCO_3$

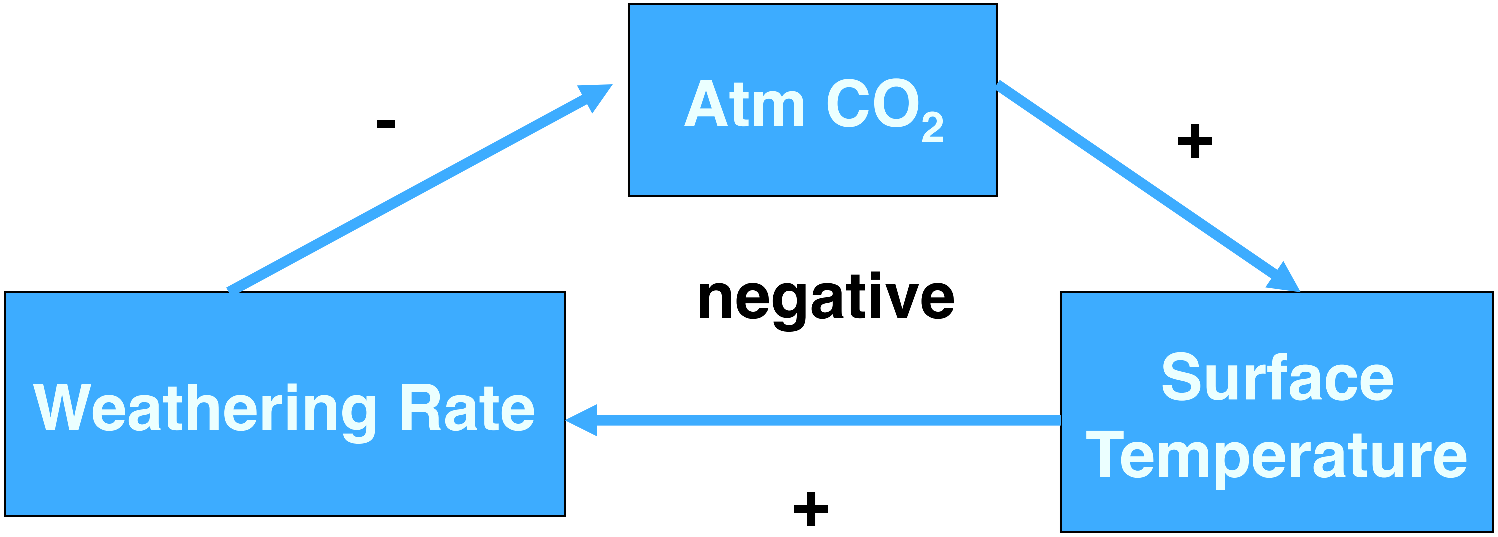
## Chemical Weathering

$CO_2$ dissolved in rain water makes carbonic acid, which then reacts with rocks.

Bad for the Taj Mahol

Weathering is higher with more atmospheric $CO_2$, warmer climate, freshly exposed rocks (mountains)

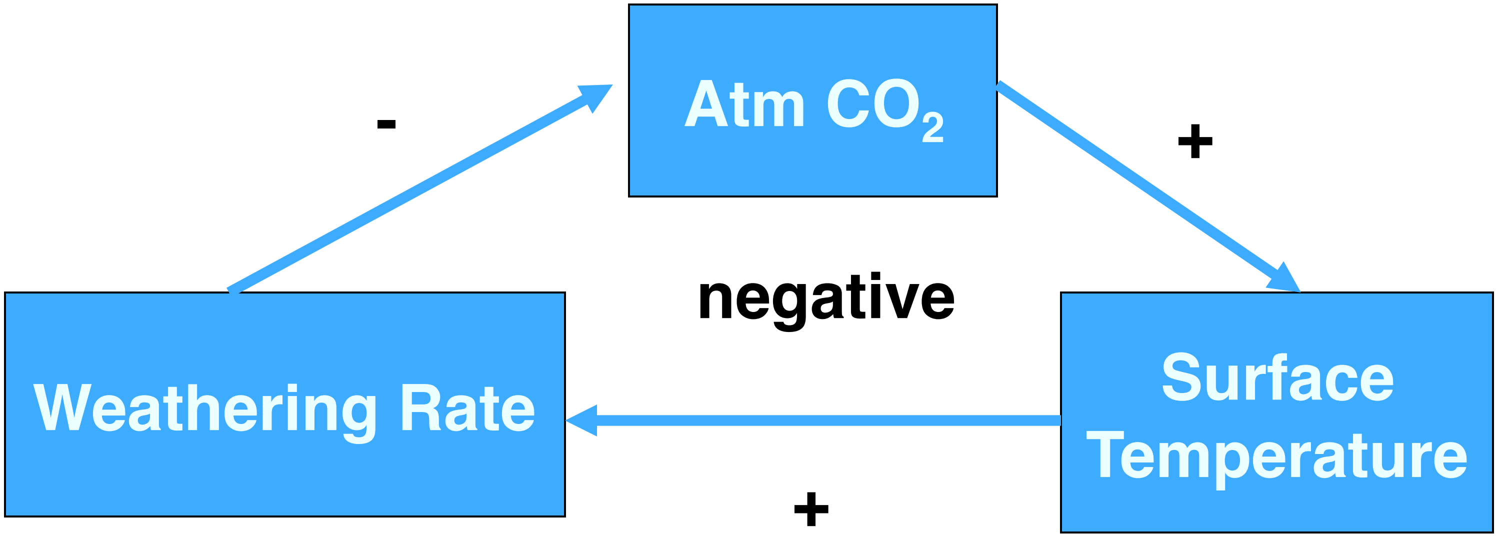
# Weathering Feedback Loop



Higher atmospheric $CO_2$ , warms planet, weathering rate increases. Now what?

What is the sign of the feedback?

# Weathering Feedback Loop



Atm $CO_2$

Surface Temperature

Weathering Rate

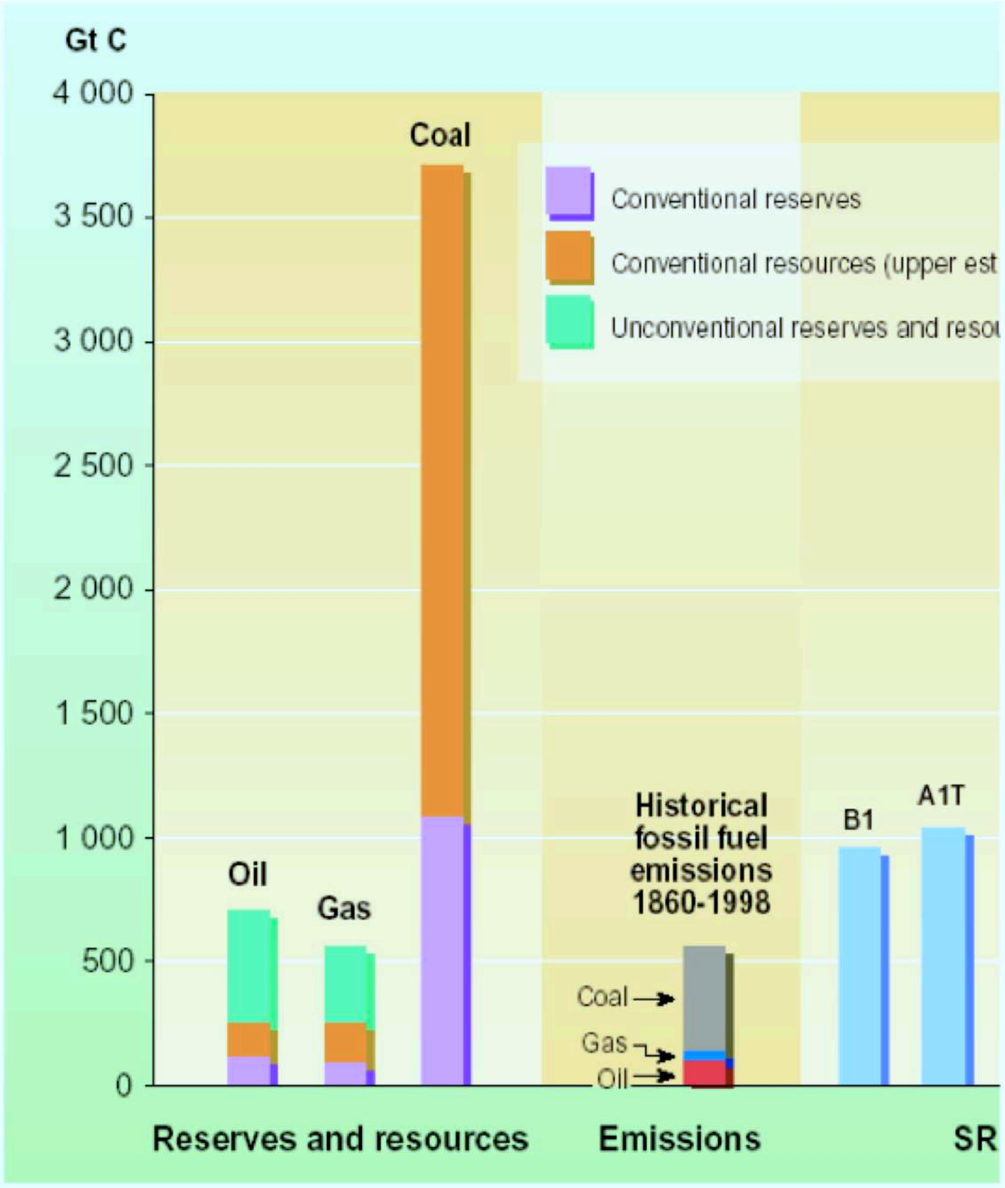
+

+

-

negative

**Makes climate stable on long time scales - millions of years**



Total known fossil fuel deposits  4500 Gt

# What are the implications for global warming?

Most of the carbon in the fossil fuel reservoir is in the form of coal.

Assuming zero uptake by the ocean/land, burning all known coal deposits would add to the atmospheric reservoir a mass of carbon roughly equivalent to 4 to 5 time the carbon presently in the atmosphere.

The true size of the fossil fuel reservoir may be larger but it’s hard to say by how much because we don’t know how much oil shale and methane hydrates we will be able to utilize.

Were it not for the biosphere, and especially the marine biosphere, most of the Earth’s carbon would be in the form of atmospheric CO2 as it is on Venus.

# Carbon cycle: reservoirs

| | Reservoir | Size (Gt C) | |
|---|---|---|---|
| 1 | Atmosphere | 750 | |
| | Land | 800 | |
| | Ocean Mixed Layer | 535 | 2 |
| 3 | Deep Ocean | 40,000 | |
| | Sediments/rocks | 70,000,000 | |

1. Coupled by biological processes and CO2 solubility in the ocean - fast
2. Coupled by sinking, mixing, upwelling processes - slow
3. Coupled by geological processes - very slow