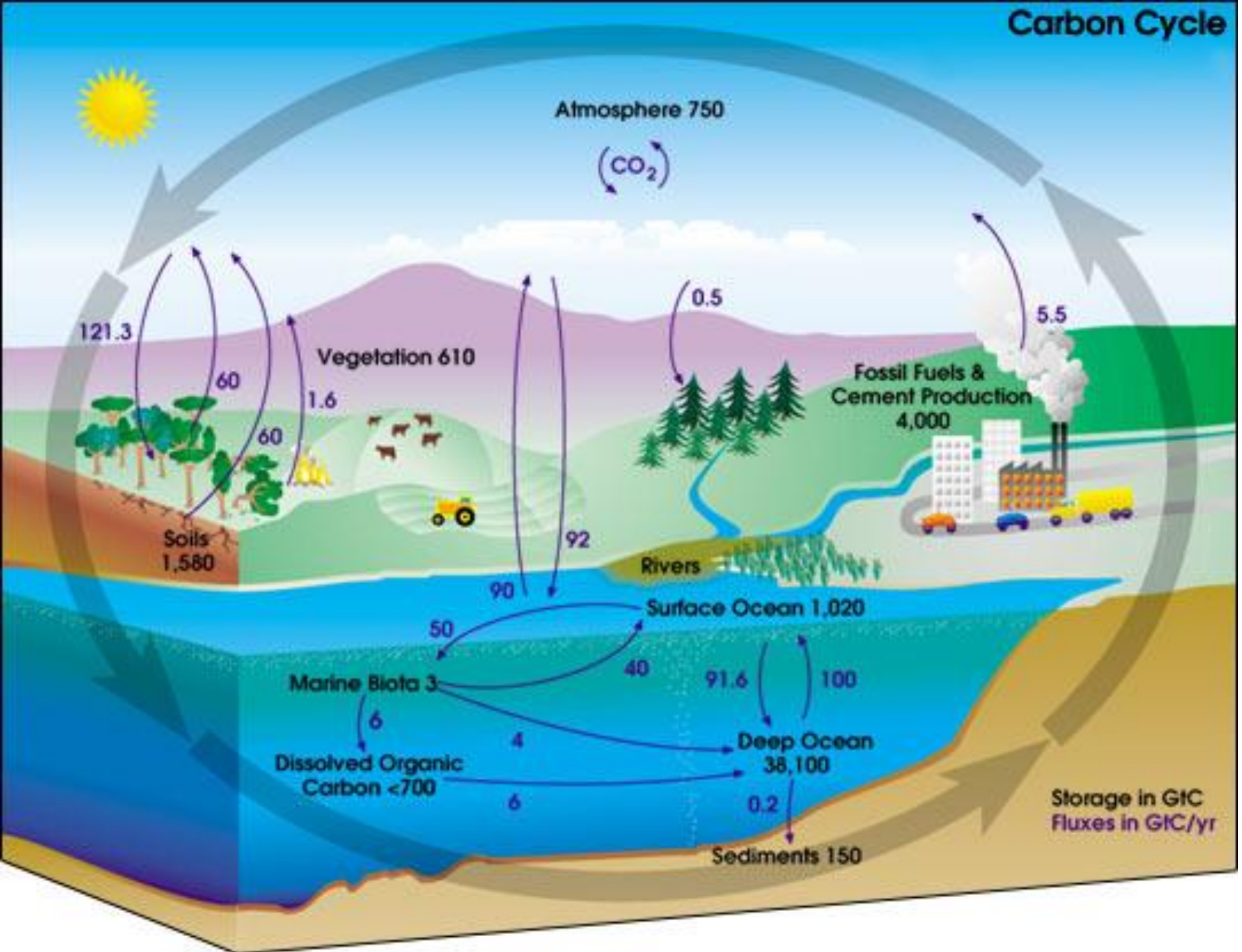


Inorganic carbon
(the ocean and rocks)

Carbon Cycle



Mass and concentration

- Atmospheric CO₂ is about 386 ppmv
- Total carbon in the atmosphere is about 760 Gt.
- *How are there two different?*
- 386 moles of CO₂ per million moles of air
- How many moles of air?
- How many moles of carbon?



Mole, not mole,

nor molé

- Recall molecular weight of carbon is 12.
(so, **12 grams per mole**)
 - Also, molecular weight of air is about 29.
- i.e., CO₂ concentration = moles of CO₂/moles of air

Mass of carbon = moles of carbon x molecular weight of carbon

Mass of air = moles of air x molecular weight of air



We know the mass of the atmosphere is 5.3×10^{18} kg
(Which is the same as 5.3×10^6 Pg)

So...

Concentration = moles of CO₂/moles of air

moles of carbon = Mass of carbon /
molecular weight of carbon

moles of air = Mass of air/
molecular weight of air

1 Gt C ~ 0.45 ppm.

For atmosphere of 760 GtC is 340 ppm
(i.e., about 1990 level)

Recall organic carbon cycle

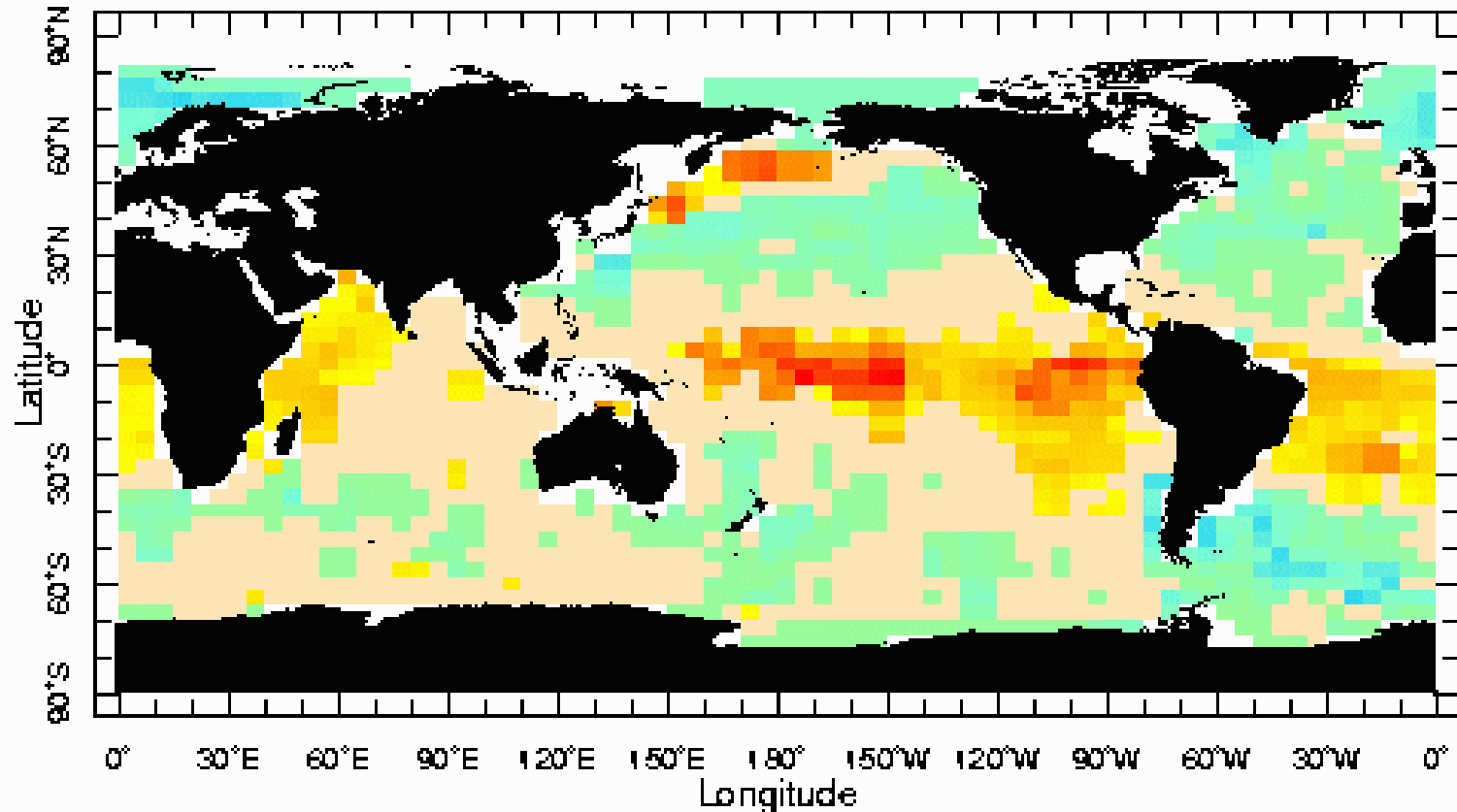
- Burial and sedimentation is the long time scale sink of CO₂
- Biological processes take up CO₂ from the atmosphere on land, and take up carbon from the ocean water in the ocean
- ... **Carbon dissolved in water (ocean) is mostly inorganic.**
- It gets there by a **physical processes** (compared to the biological processes needed for organic carbon)
- This inorganic carbon is chemically active and can take part in other chemical reactions, including biology.

Solubility depends on temperature

- Solubility is how well/easily something (e.g., CO_2) can be dissolved
- CO_2 is more soluble in colder water
- Consider a can of soda
 - Experiment (to try at home).
 - Take two cans of soda
 - Put one in a cold fridge, put the other in a warm sunny window
 - Shake both the hot and cold cans
 - Ask two friends to choose one each
 - Upon exclaiming “trick or treat” have them open the cans
 - Who ends up worst?
- More CO_2 dissolved in colder soda (water), so when pressure is released it comes out of solution in the WARM can.
- i.e., warm can has more bubbles escaping from solution
- Same for ocean. Colder ocean can store more CO_2
- **What if ocean warms up?**
- ***Release CO_2 !***



Partial pressure of CO₂ dissolved in the upper ocean (difference from atmosphere)

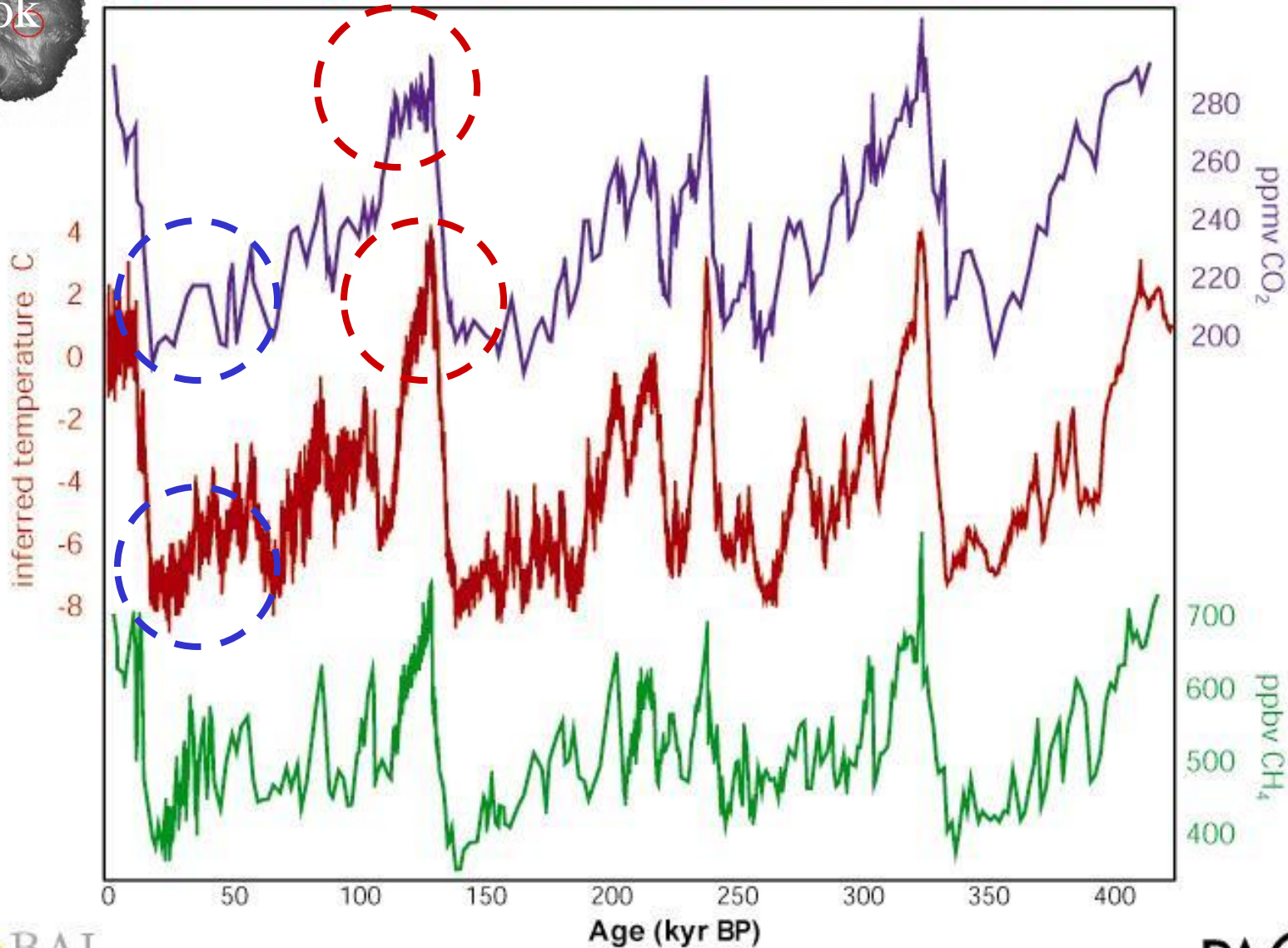


Jan 1990



Vostok

4 glacial cycles recorded in the Vostok ice core



CO₂ and temperature

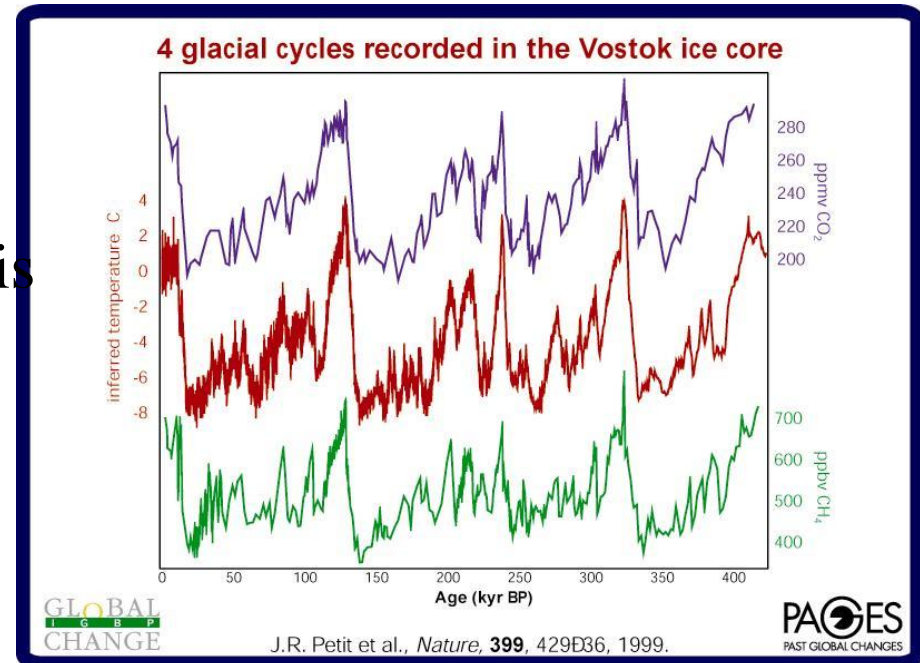
More CO₂, stronger greenhouse effect, so warmer

Or...

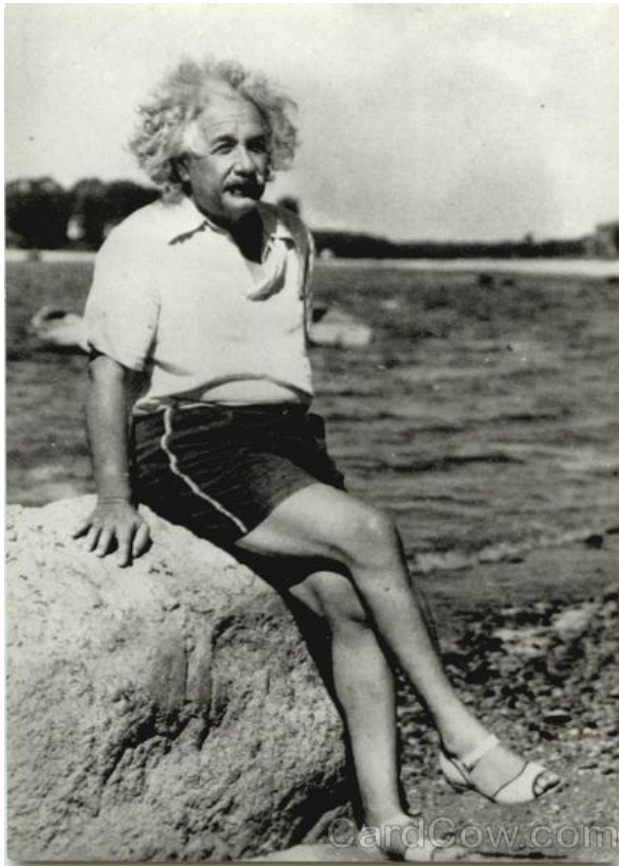
Warmer temperature, so ocean out gassing (like warmer soda), so higher CO₂.

Which is cause, which is effect?

Not clear on long time scales,
but certainly fossil fuel burning is
a cause is recent times.



What did Einstein ever do for me!?



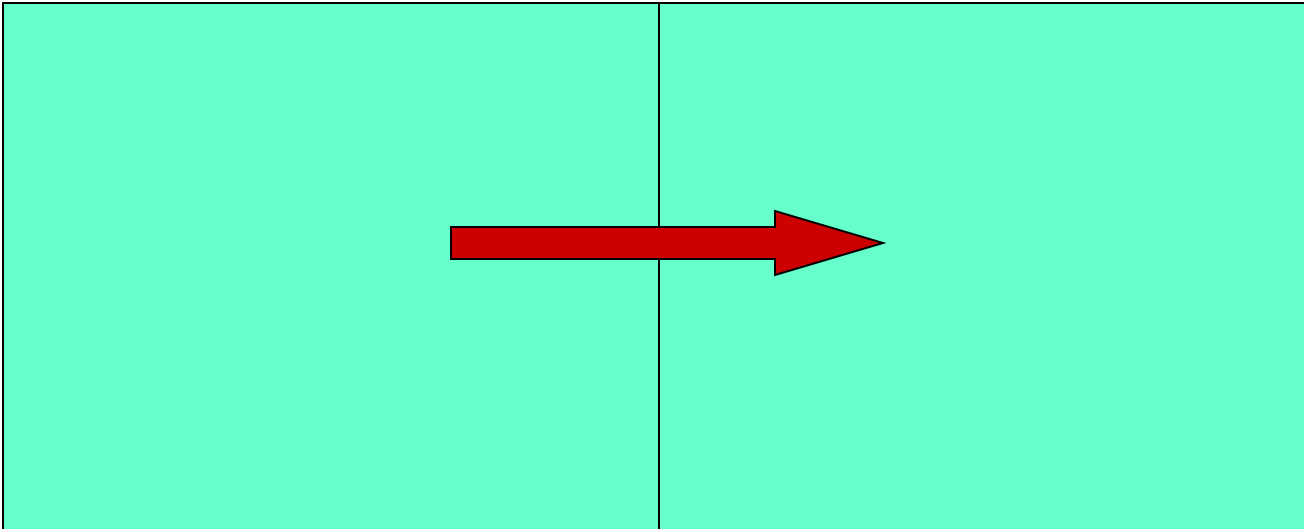
3 important papers in 1905

- Special relativity ($E = mc^2$)
- Heat capacity
(photoelectric effect – Nobel prize)
- Movement of molecules,
.... and diffusion...

Diffusion

- Gas high concentration spreads into regions with low concentration.
- Einstein is famous for showing that the diffusion flux of a gas into a vacuum can be expressed as:

flux = coefficient of diffusion x concentration difference

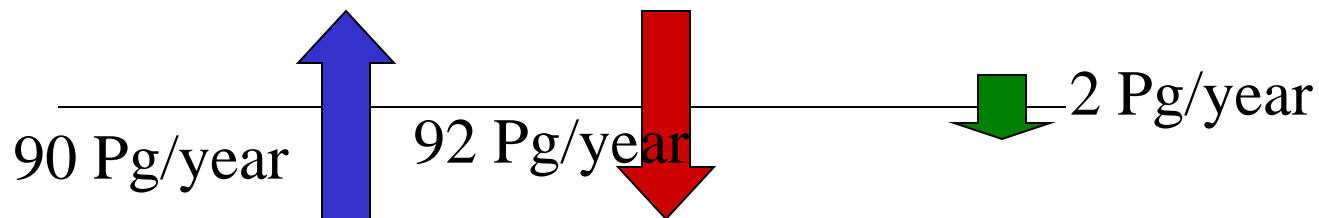


Net CO₂ flux between atmosphere and ocean

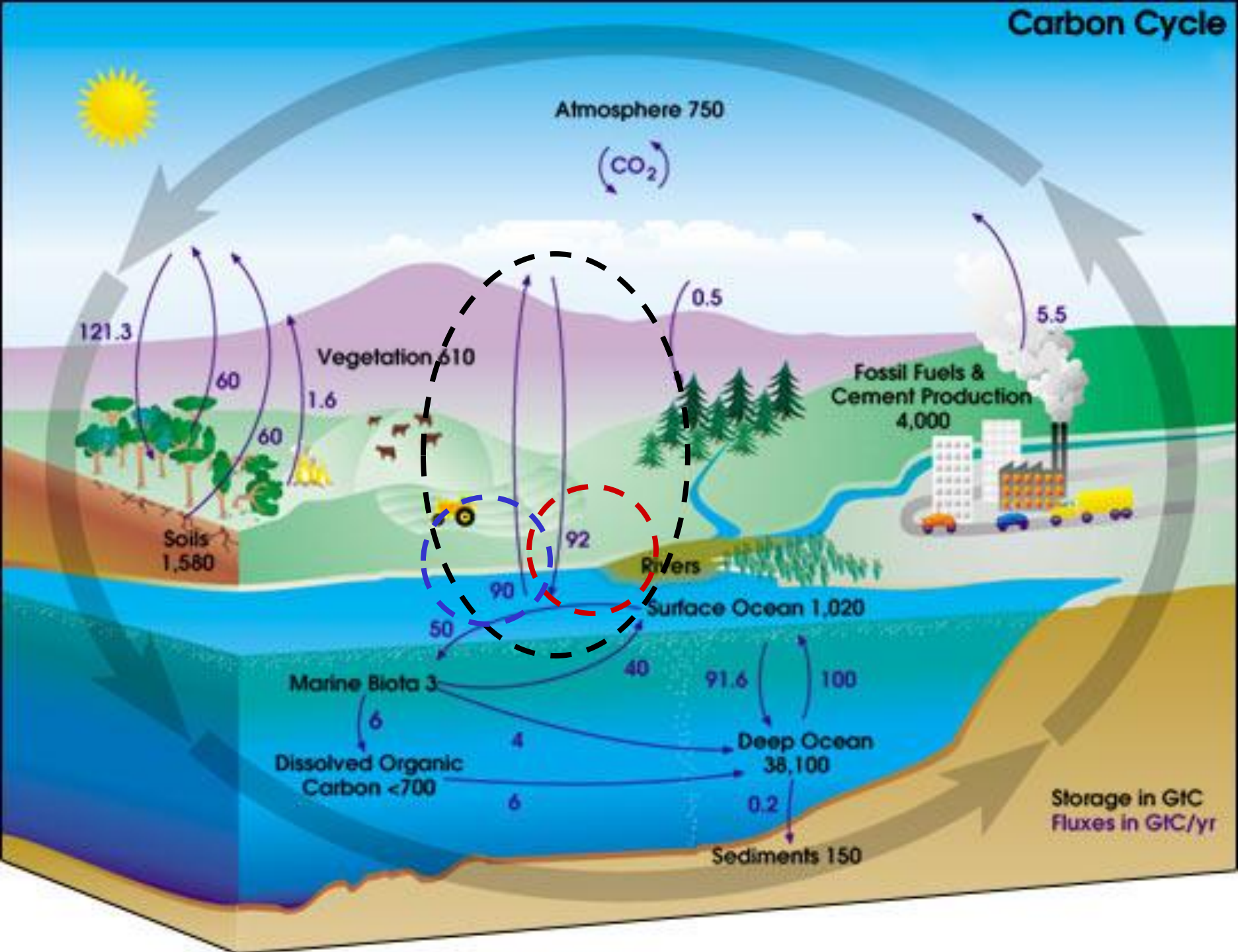
- Can imagine then that flux can be understood as being driven by the difference in concentrations
- That's is, a concentration gradient.
- In the atmosphere the CO₂ concentration is about 386 ppmv
- And we know the CO₂ concentration in the ocean (see earlier slide)
- So we can estimate the flux

(Thanks Einstein!)

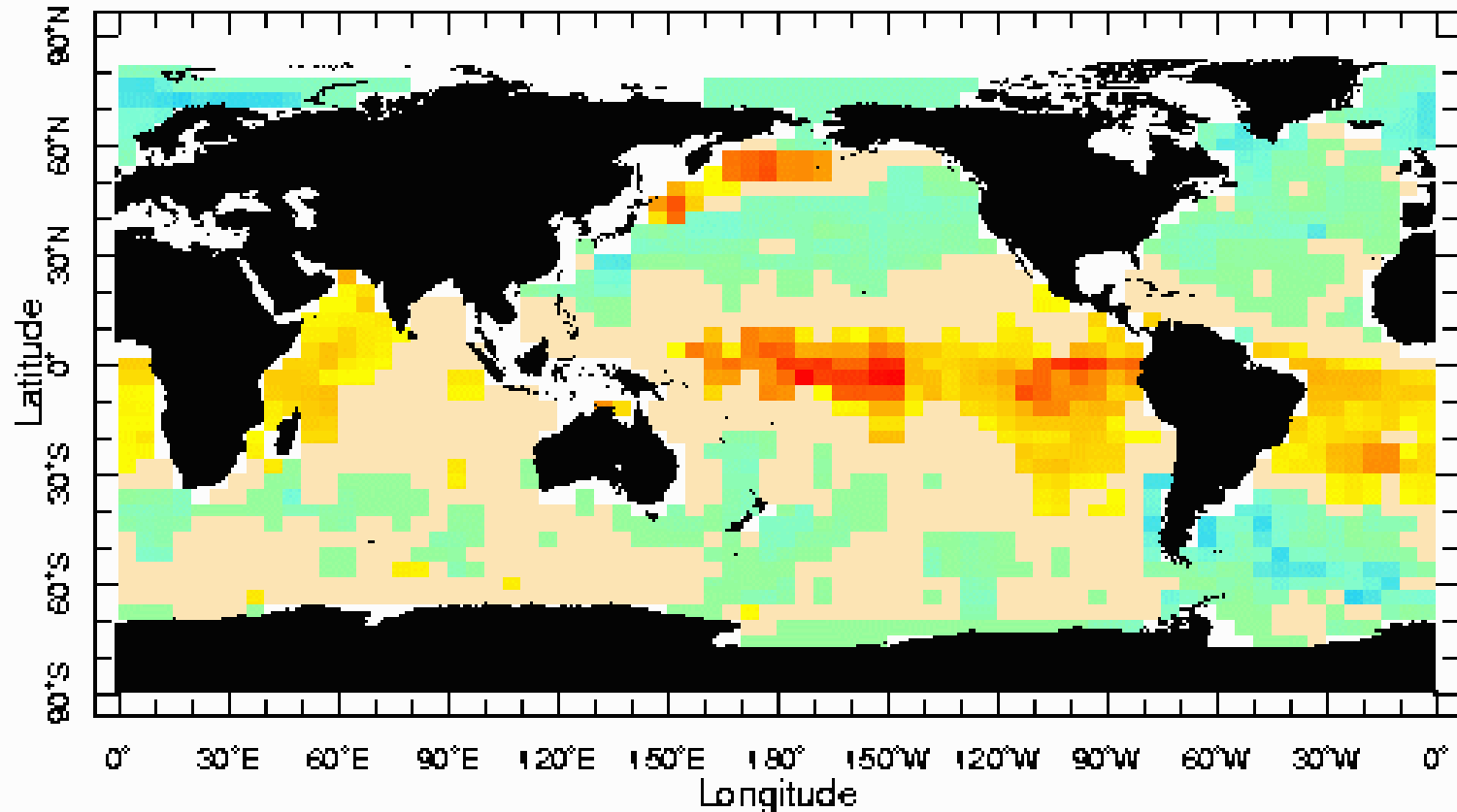
- Flux = coefficient x (CO₂ ocean – CO₂ atmosphere)



Carbon Cycle



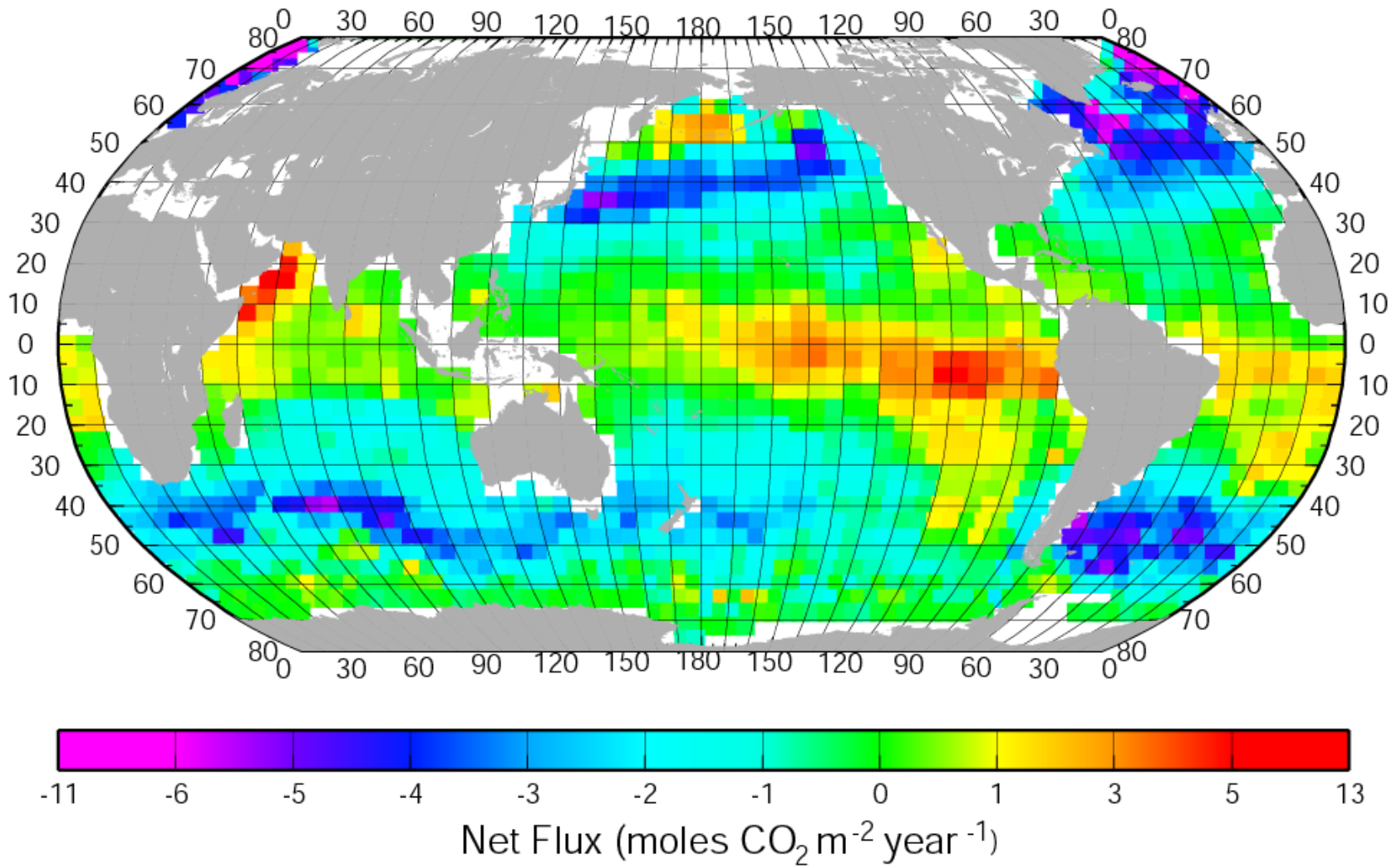
Partial pressure of CO₂ dissolved in the upper ocean (difference from atmosphere)



Jan 1990



Net CO₂ Flux from Takahashi et al., 2002



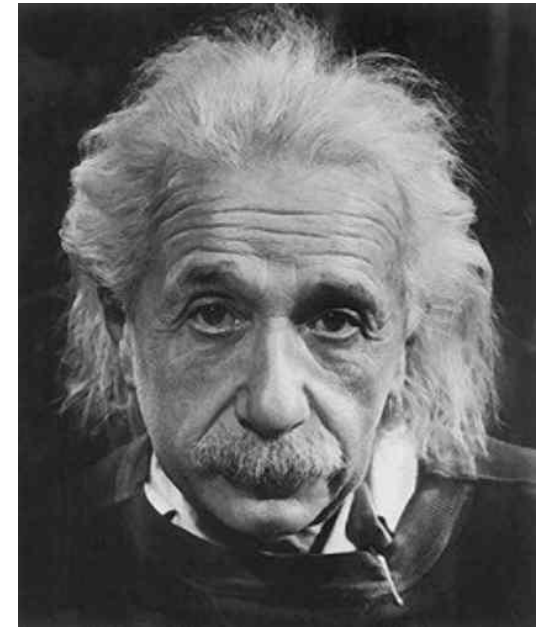
Thought experiment

“*Gedankenexperiment*”

Einstein would be proud

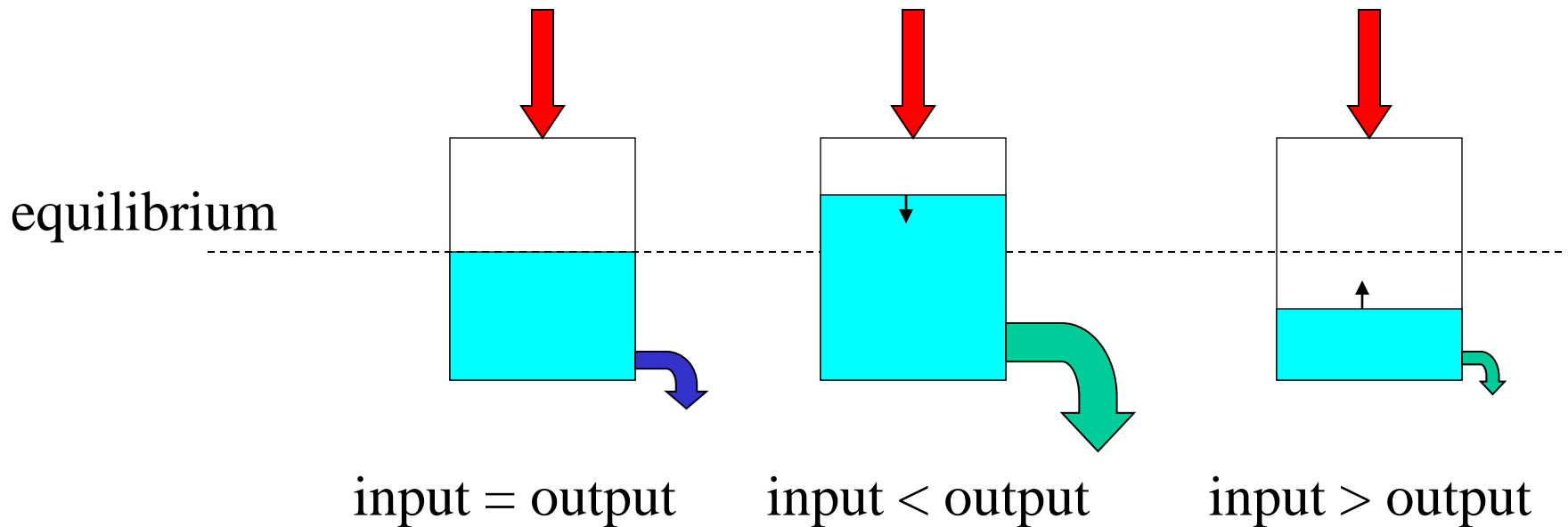
- Imagine we put CO₂, which is a greenhouse gas, into the atmosphere
- This would warm the earth’s surface, and the would warm up the ocean
- What would happen to the CO₂ in the ocean?

Positive feedback?



Thought experiment (1)

Bucket with a hole in it: Drains faster if fuller



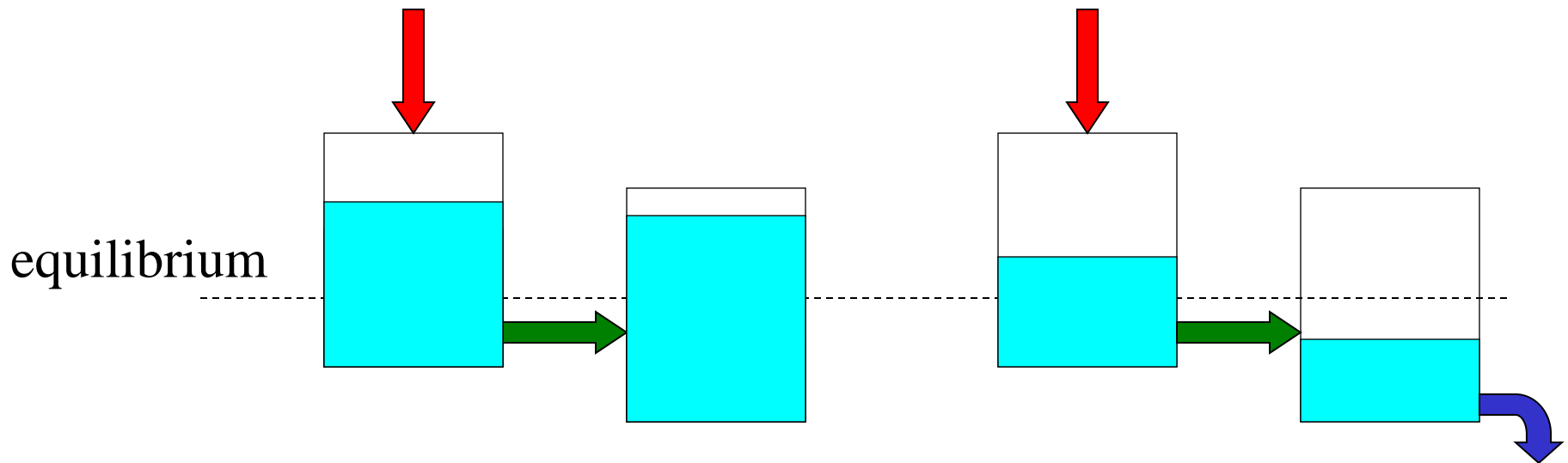
Flux depends on: size of hole, and height of water

$$F = c (h_{\text{top}} - h_{\text{bottom}}) = \text{change in height (h)}$$

Normal example of a *negative feedback*

Thought experiment (2)

What about the outflow? Another bucket!



How can we keep the flow going?

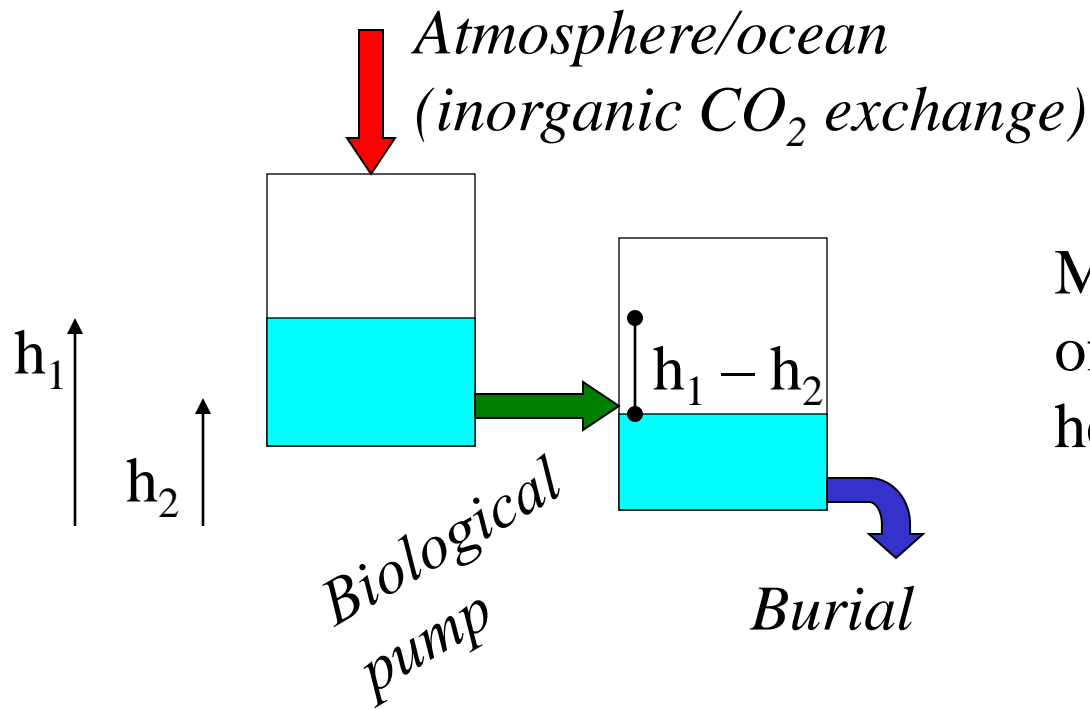
input = output

Obviously, must continue to drain the second bucket.. Duh!

Notice: the equilibrium now has 2 different levels!

The three fluxes (in, middle and out) are all equal

Balanced buckets of carbon



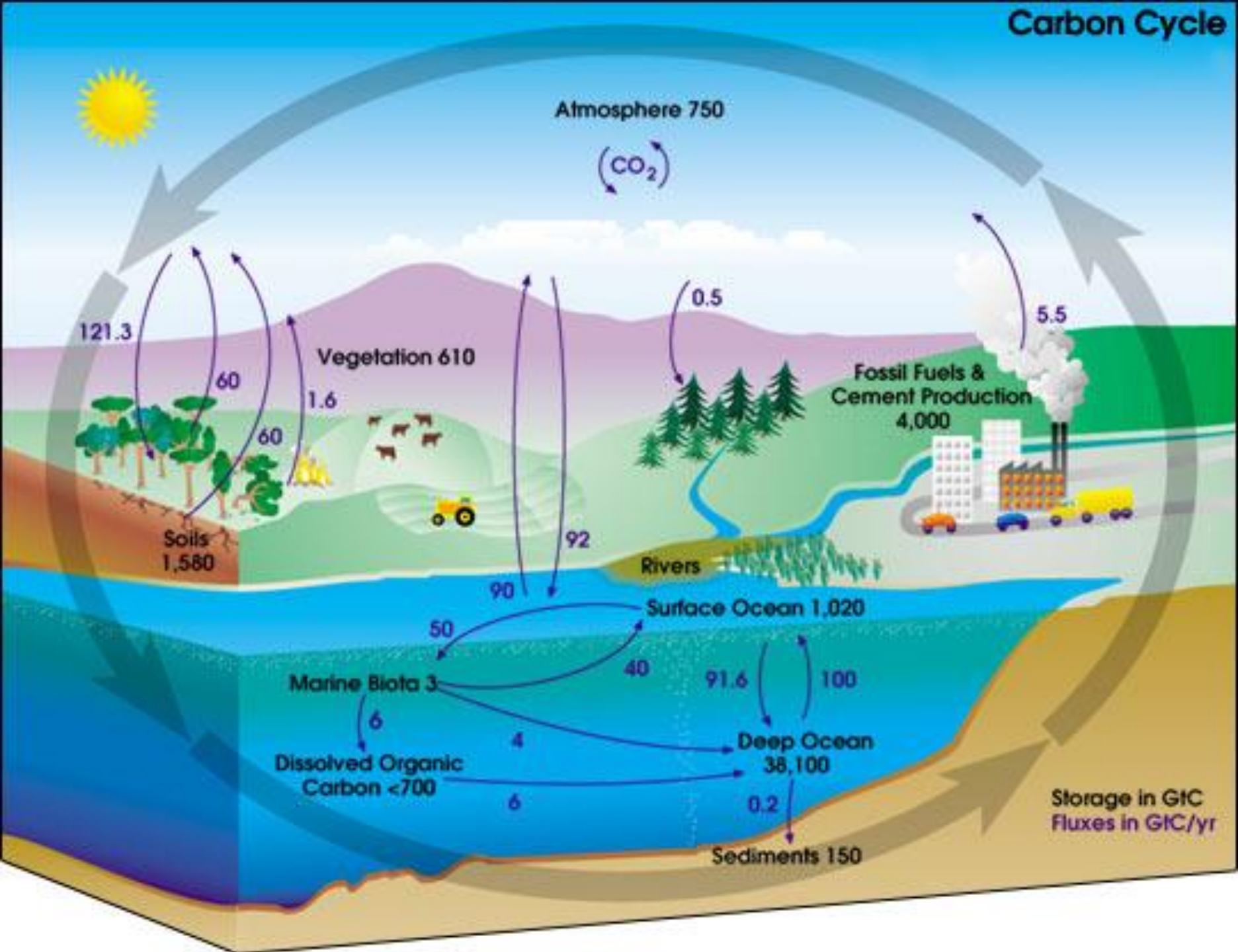
Middle flux depends on: size of hole, and DIFFERENCE in height of water

$$F_{\text{middle}} = c (h_1 - h_2)$$

This is like the upper ocean.

The atmosphere/ocean flux can only continue if there is a removal of CO_2 from the upper ocean (by biology... fish poop)

Carbon Cycle

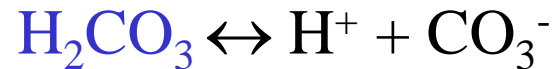


Carbon dissolved in water

- $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$
- Forms carbonic acid
- Notice this is an *equilibrium* reaction.
- More $\text{CO}_2 + \text{H}_2\text{O}$ gives more H_2CO_3
... but more H_2CO_3 , gives more $\text{CO}_2 + \text{H}_2\text{O}$

What next?

- Carbonic acid can dissociate into ions



H^+ Hydrogen cation

(means lacks an electron, so has a net positive charge)

CO_3^- Bicarbonate anion

(has one extra electron, so has a net negative charge)

- Notice again this is an equilibrium reaction
So more H^+ ions will mean there are more H_2CO_3 molecules,
.... And so more $\text{CO}_2 + \text{H}_2\text{O}$

But wait there's more...

- Bicarbonate can dissociate further
- $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$

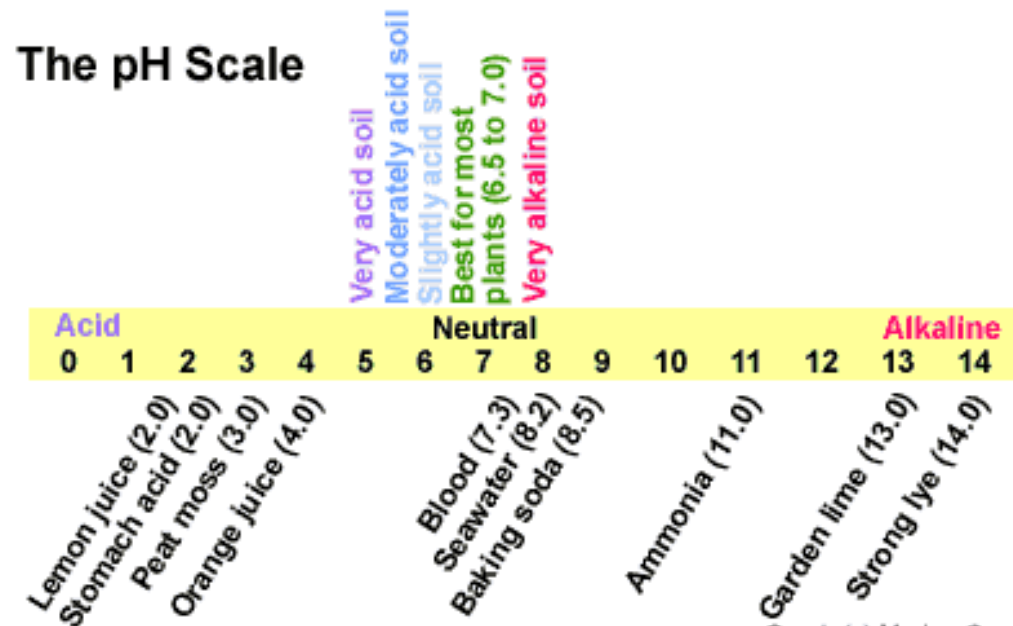
..... to *carbonate*

Notice all the H^+ .

The amount of these is determines
the acidity of the ocean.

Acidity is measured with the pH
scale

pH of 7 means “normal”

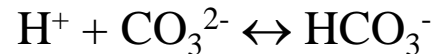


Adding CO₂ to the atmosphere

Consider the sequence of reactions...



So, *more dissolved CO₂ leads to more acidic ocean water*



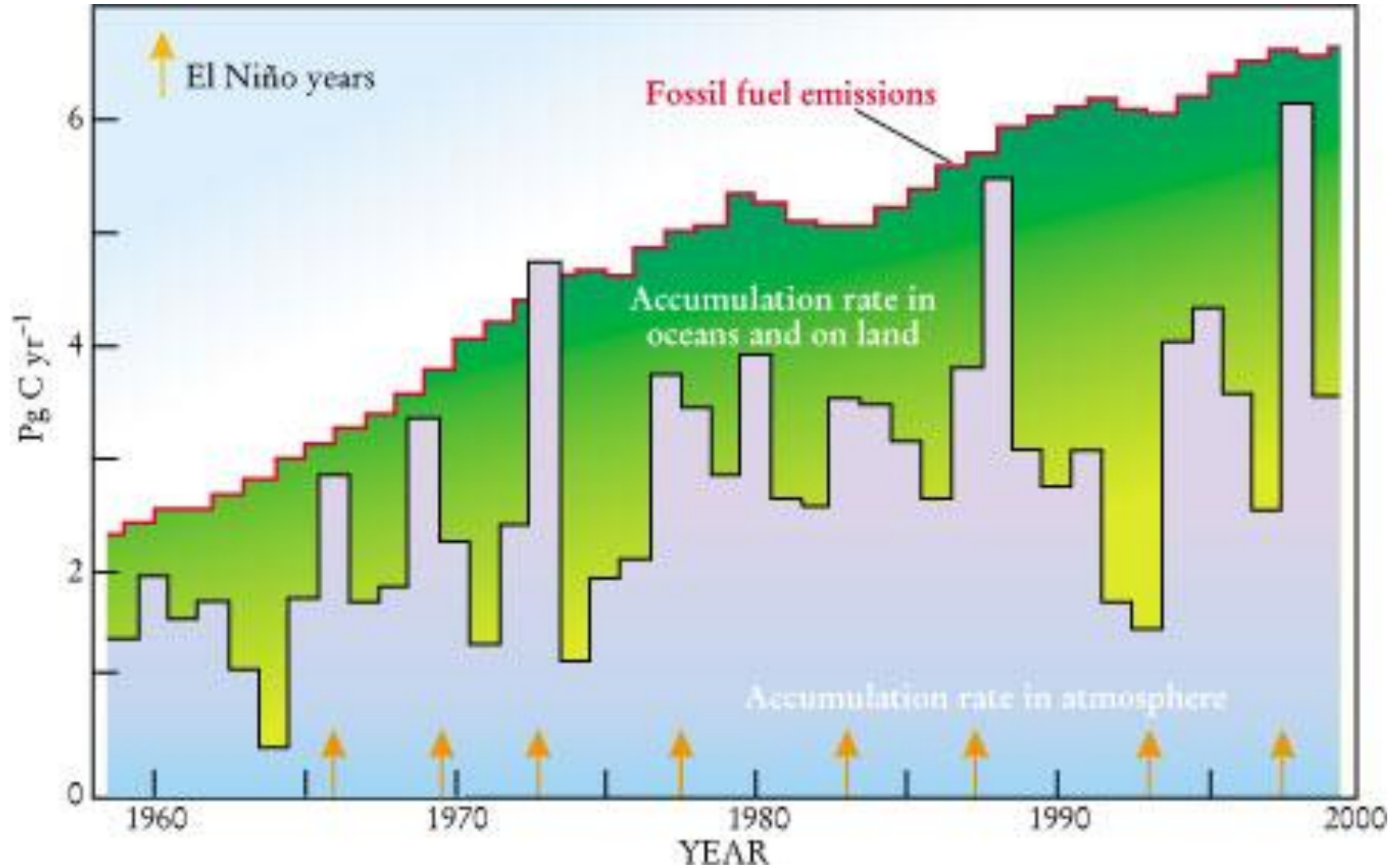
So *more acidic ocean leads to less carbonate*

Combine both



- Recall we claimed that with more CO₂ in the atmosphere, we can have more flux to the ocean.
- This new result shows that uptake limited by ocean chemistry.
- Specifically, uptake is *limited by carbonate amounts!*
- Imagine adding CO₂ to the atmosphere, some of this could end up in the ocean.
- However less carbonate in ocean than fossil fuels, so ocean can not soak up all of the fossil fuels that we have emitted.

Observed increase in atmospheric CO₂



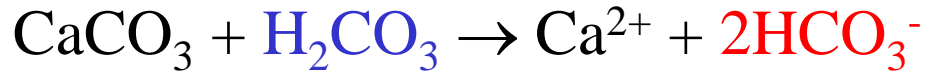
Increase due to adding fossil fuels

But some (about a third) of this has gone in the ocean

Calcite and silicate

Crustal rocks have plenty of silicate and calcite

Calcite weathering



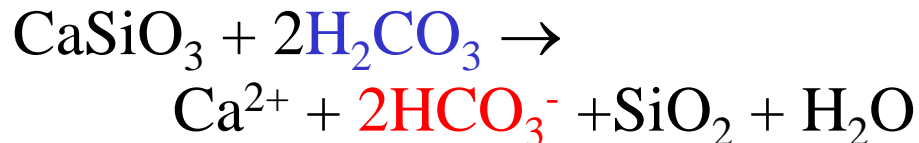
Small amounts of carbonic acid in rain water.

Carbonate supplied to ocean by rivers



Example of silicate rich rock

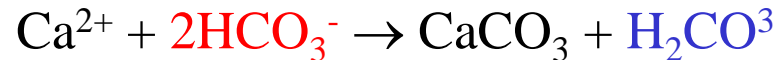
Silicate weathering



Carbonate supplied to ocean by rivers

Carbonate deposition

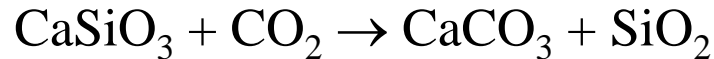
In ocean formation of shells and skeletons leads to carbonate deposition



Just the reverse of weathering, *so no net effect*

However, with silicate weathering, and carbonate precipitation there is an extra carbonate.

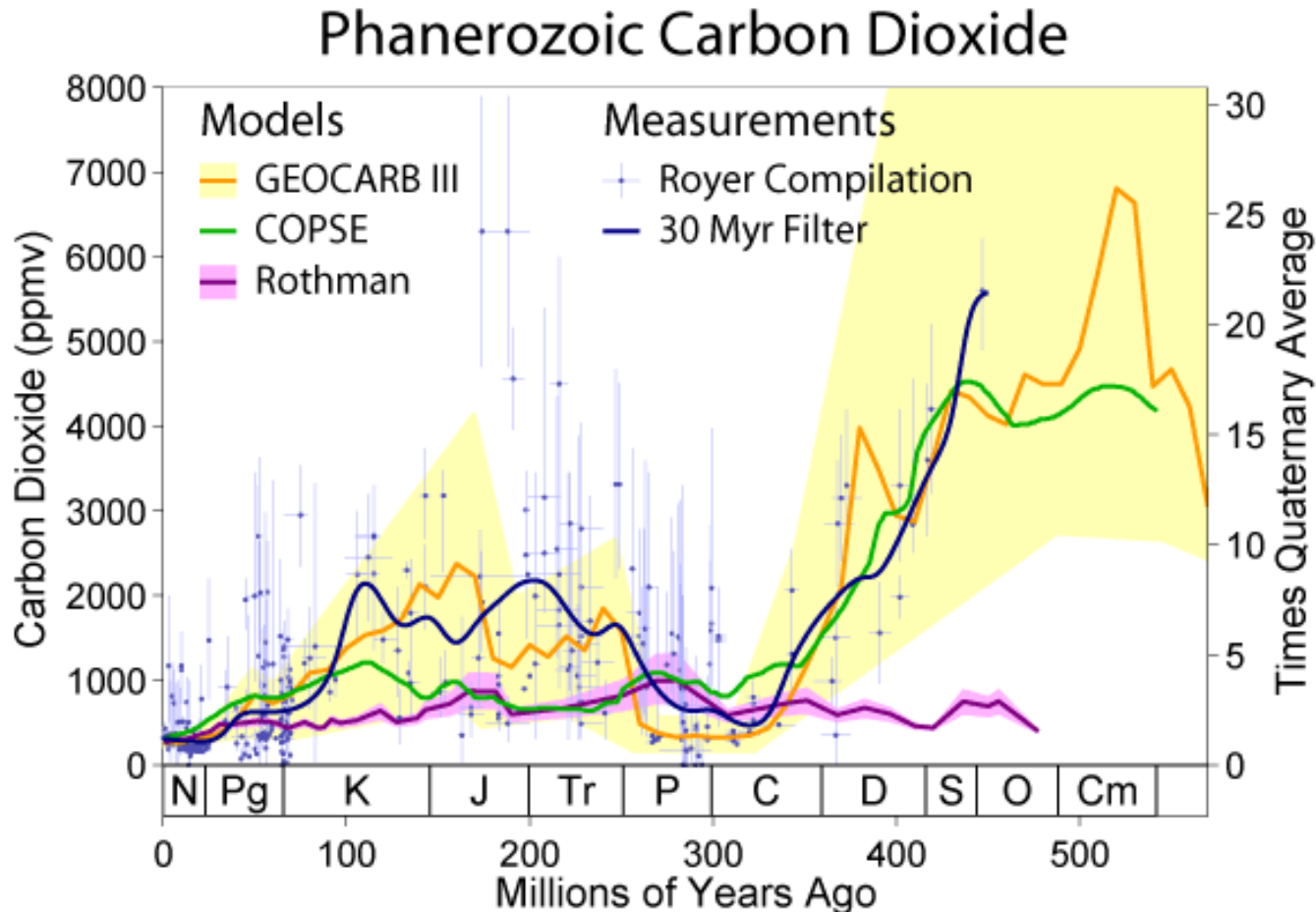
This extra carbonate can be used to make more calcium carbonate (shells)...



... and thus removes of CO_2 from the ocean.

Since this CO_2 comes from exchange with the atmosphere,
silicate weathering can drive a reduction in atmospheric CO_2
(on geological time scales)

Change in CO₂ over millions of years



Time scale similar to changes in continent locations.

Decrease thought to be due to increased weathering of silicate rocks when mountains (e.g., Himalaya, Rockies) are created.

Key points

- Physical gas **exchange due to difference in CO₂ concentration**
- ***Colder water can hold more CO₂***
If ocean **cools**, can **take up CO₂**
If ocean **warms**, can **give up CO₂**
- Adding CO₂ to the atmosphere makes **ocean more acidic** (uptake and dissolution as carbonic acid)
- Amount of CO₂ that the ocean can take up is **limited (controlled by)** the amount of **carbonate ions**
- Bicarbonate used by biology to make shells/skeletons, which are deposited
- Carbonate supplied to ocean by weathering of rocks (mountains), with river runoff
- Since silicate weathering introduces an extra bicarbonate, silicate weathering can act to reduce atmospheric CO₂
- Changes in ocean H⁺, means the acidity. Changes the ability of biology to make shells – including coral reefs

