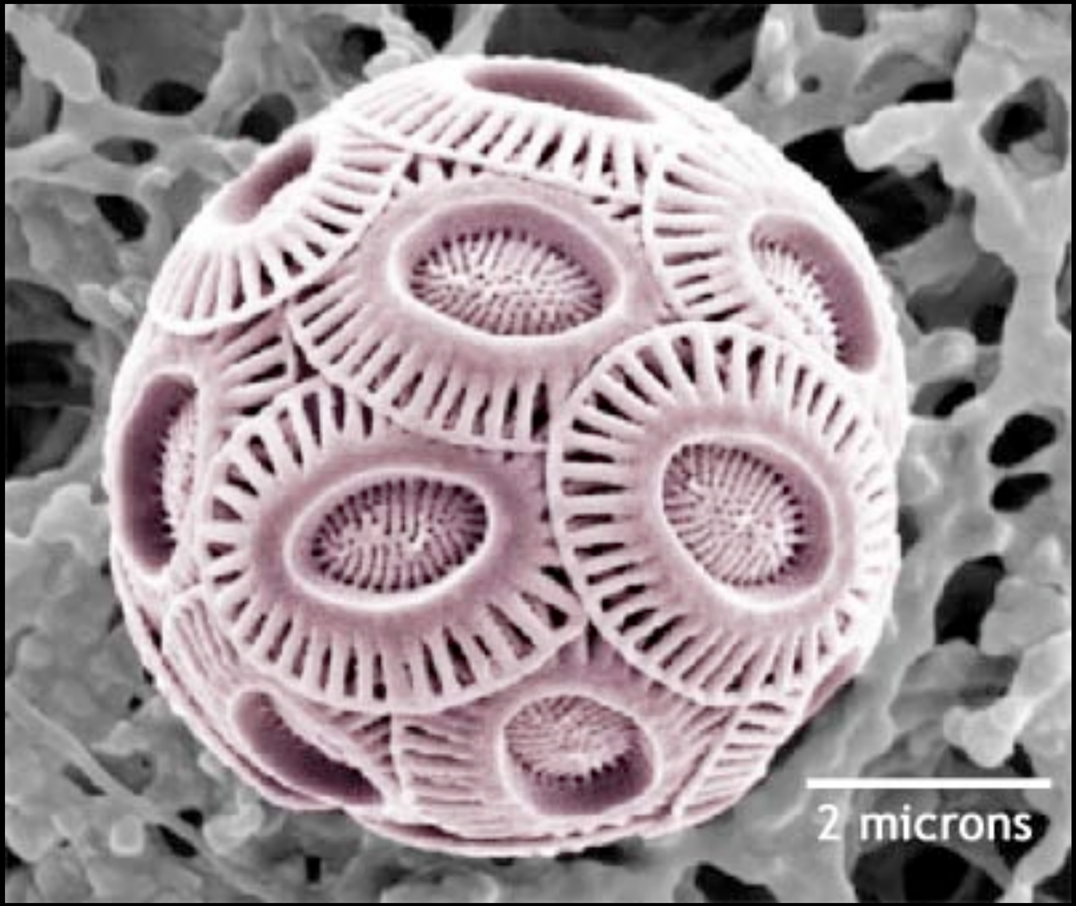
XI. the natural carbon cycle



with materials from
J. Kasting (Penn State)

outline

- properties of carbon
- the terrestrial biological cycle of carbon
- the ocean cycle of carbon
- carbon in the rock cycle
- overview of carbon stocks and exchanges
- timescales of exchange and renewal
- the silicate weathering “thermostat”

the carbon cycle

- flow of matter and energy between reservoirs (stocks and flows naturally in or near balance)

- linked to other biogeochemical and life cycles thru nutrient and energy flows

- linked to climate via greenhouse effect (and direct influence of vegetation on climate)

- to understand, first need to know something about carbon itself

organic and inorganic carbon

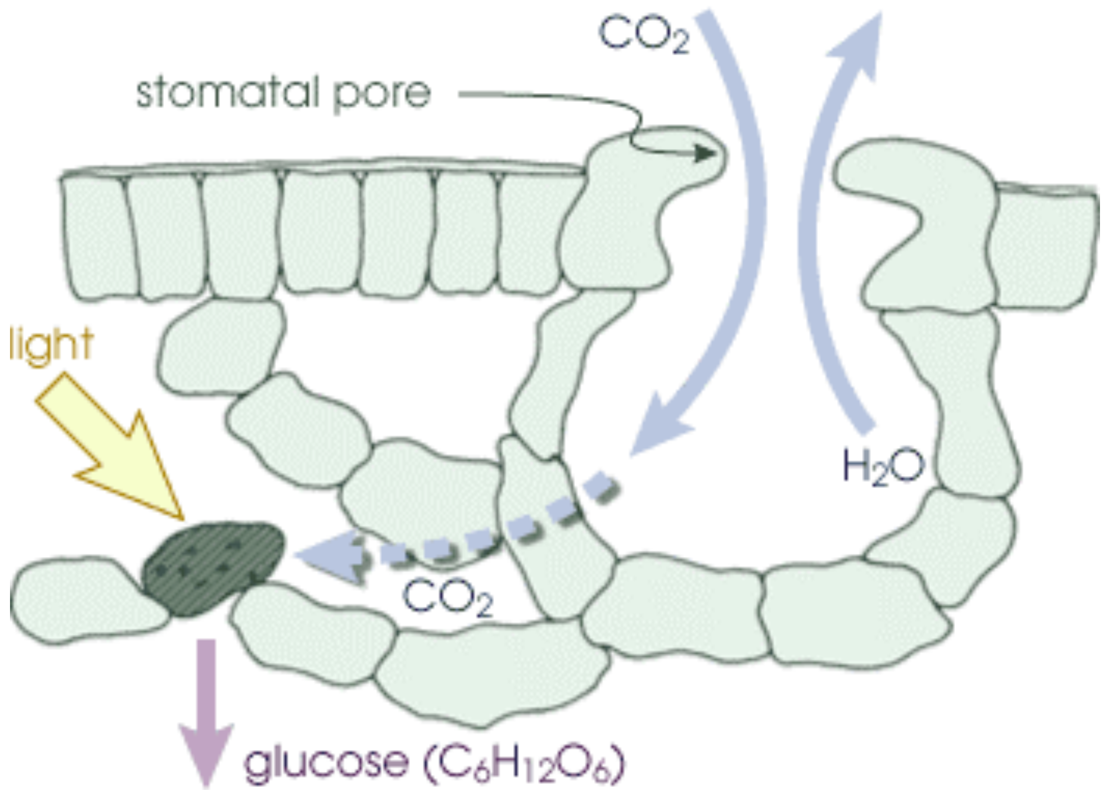
C is cycled between <u>reduced</u> and <u>oxidized</u> forms by natural processes

organic carbon (reduced)	inorganic carbon (oxidized)		
'CH$_2$O'	CO_2	carbon dioxide	
	H_2CO_3	*carbonic acid*	*"DIC"*
example:	HCO_3^-	*bicarbonate ion*	*"DIC"*
Glucose -- $C_6H_{12}O_6$	$CO_3^=$	*carbonate ion*	*"DIC"*
	$CaCO_3$	calcium carbonate	

example of transfer of oxidized to reduced C that also involves a flow of energy?

photosynthesis

$$\text{energy} + CO_2 + H_2O \rightarrow CH_2O + O_2$$



plants harness sun's energy to make chemical energy (carbohydrate) from inorganic CO_2 (& water)

photosynthesis

$$\text{energy} + CO_2 + H_2O \rightarrow CH_2O + O_2$$

$$\text{energy} + CO_2 + H_2O \leftarrow CH_2O + O_2$$

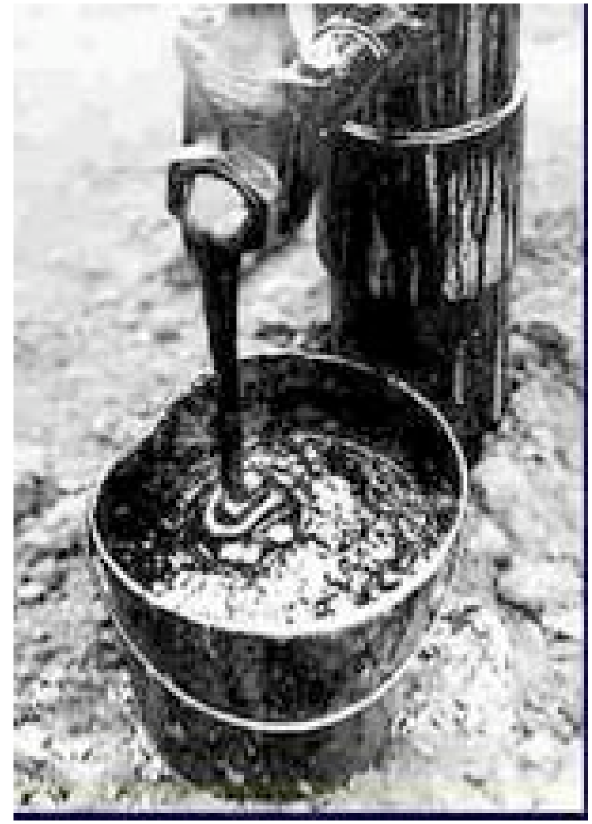
respiration and decay

photosynthesis requires an input of (light) energy, respiration and decay release stored chemical energy

(on land, photosynthesis is roughly balanced by respiration and decay….)

coal

biomass



crude oil

organic carbon

(reduced)

as biomass ages it takes on different forms

inorganic carbon

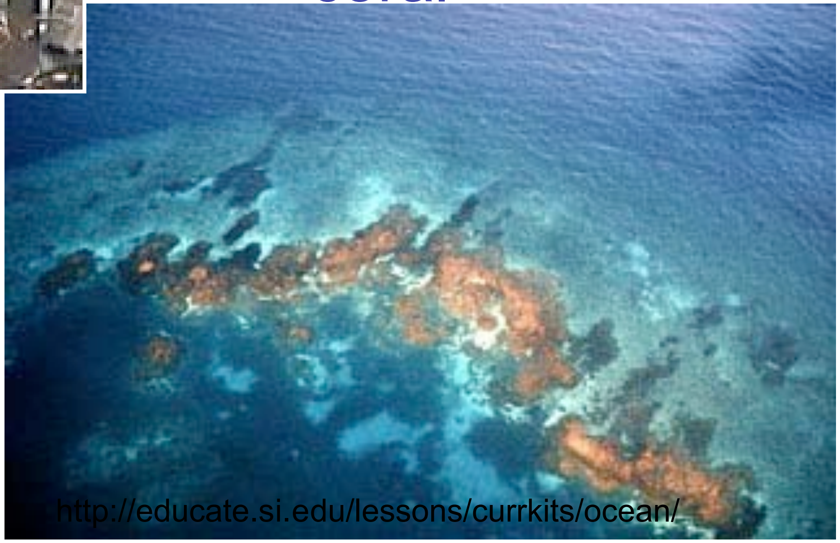
(oxidized)

limestone

CO_2, *DIC*

seashells

coral

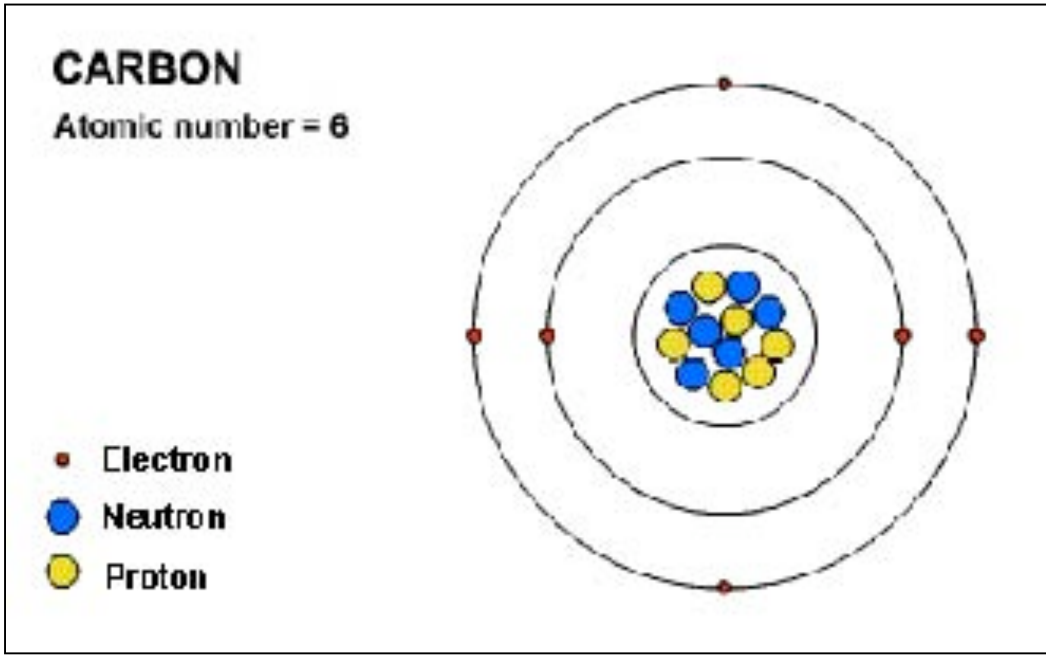


carbon

•can bond <u>readily</u> and <u>reversibly</u> with H, O, N and any number of additional carbon atoms

•provides molecular "backbone" for life

•can store and release energy via change in "oxidation" state



oxidation state

	oxidized	intermediate	reduced
simplest example	CO_2	CH_2O	CH_4
carbon oxidation state	+4	0	-4
general category	inorganic carbon	carbo-hydrate	hydro-carbon

$$\underbrace{\text{carbohydrate} \quad \text{hydrocarbon}}_{\text{organic carbon}}$$

oxygen is hungry for electrons and generally leaves bonded atoms depleted in electrons and therefore positively charged

oxidation state

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carbon oxidation state	+4	0	-4
general category	inorganic carbon	carbo-hydrate	hydro-carbon

$$\underbrace{\text{carbo-hydrate} \quad \text{hydro-carbon}}_{\text{organic carbon}}$$

oxidized state most stable, so organic C will tend to move to this state over time

the terrestrial biological C-cycle

photosynthesis

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

respiration and decay

- on land, production of organic carbon by photosynthesis is largely balanced by respiration and decay

-- respiration: used by *both plants and animals* to to produce energy for metabolism

-- decay: consumption of dead organic matter by (aerobic or anaerobic) micro-organisms

natural carbon stocks and flows

on a global scale, we measure quantities of carbon in **gigatons (Gt)**

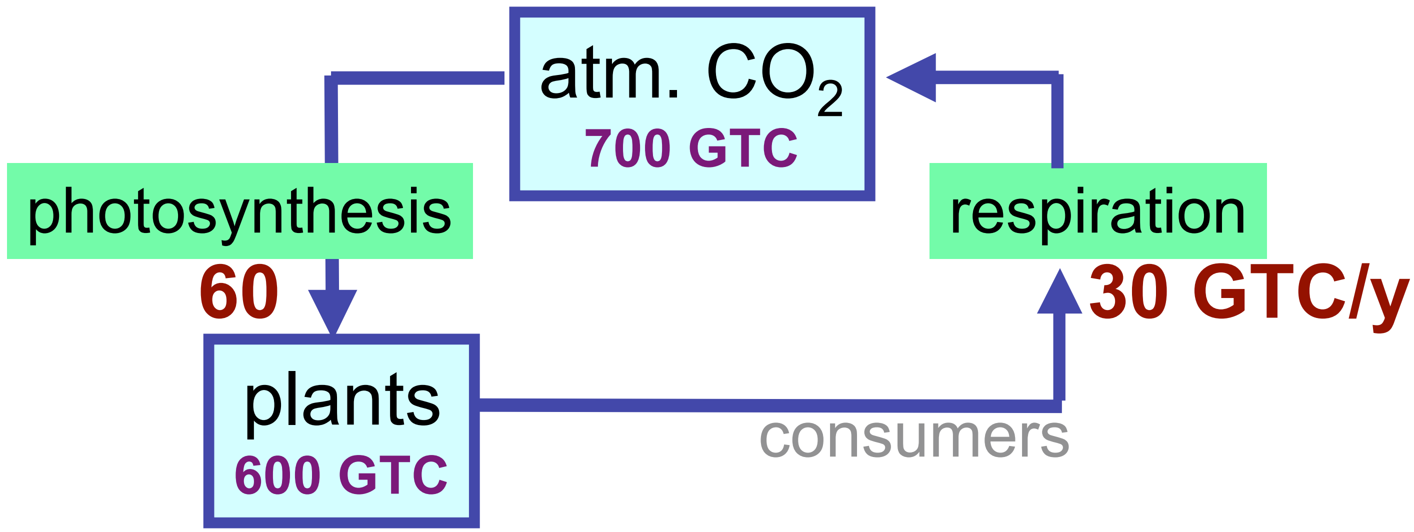
1 Gt = 1 billion metric tons

1 metric ton = 1,000 kilograms

(so, 1 Gt = 10^{15} grams)

Typically, we only count the weight of the carbon itself, *i.e.*, for CH_2O we neglect the weight of the H_2O. So, we write these units as Gt(C) or GTC.

the terrestrial biological C-cycle

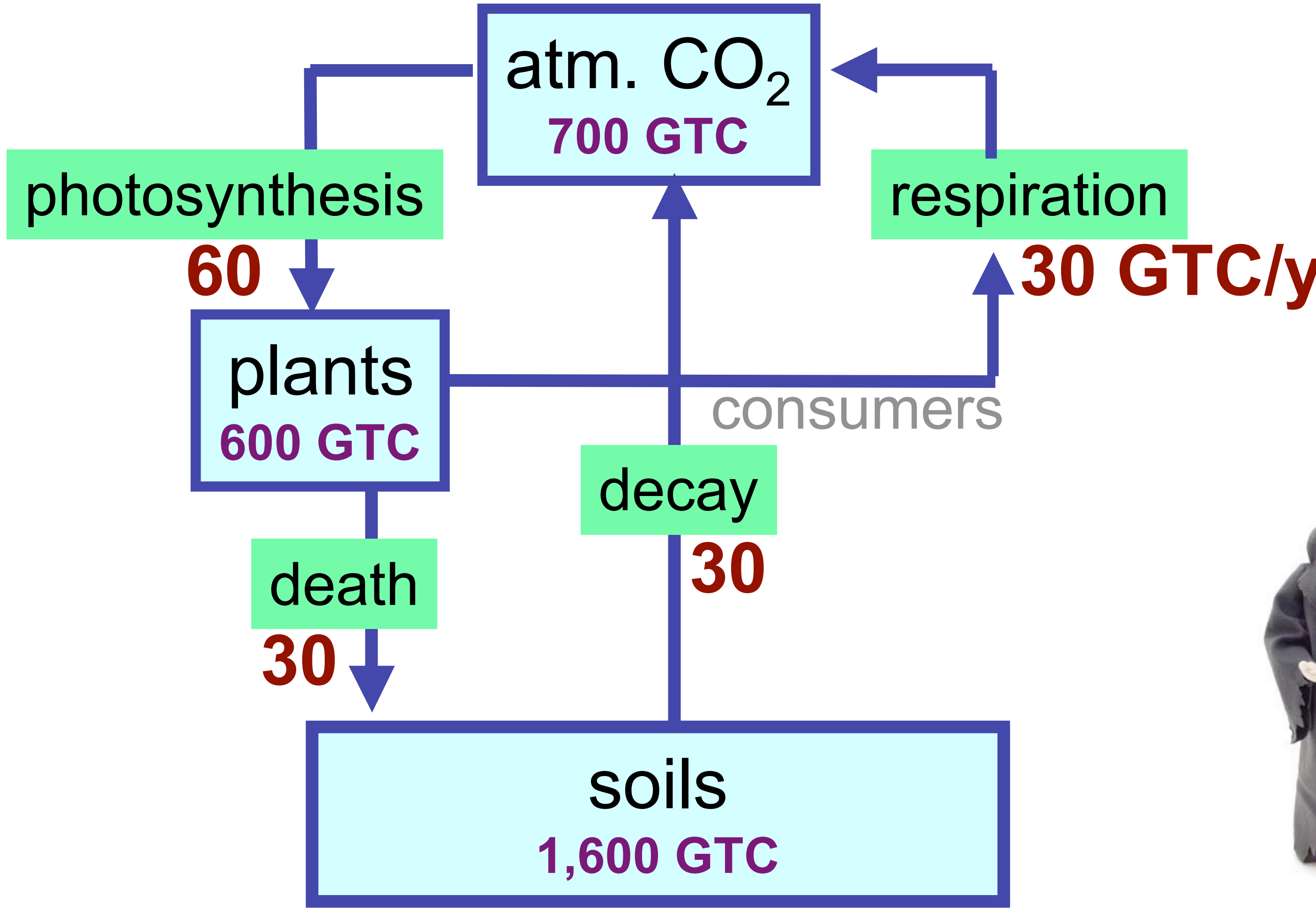


flows in GTC/year

balanced?

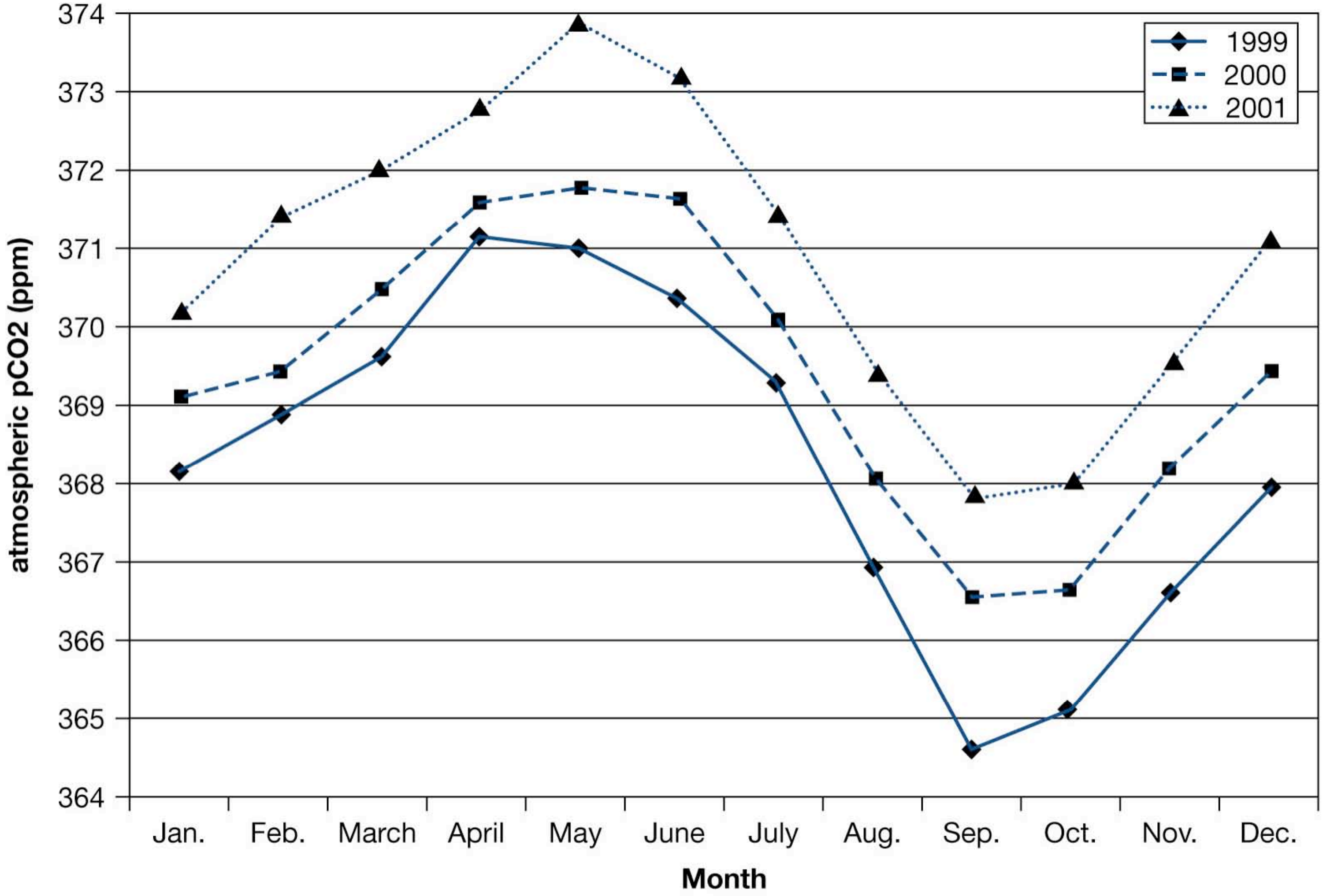
Plants respire all the time, offsetting much of new photosynthesis. The values here are for net photosynthesis which is offset by respiration by consumers on various timescales.

the terrestrial biological C-cycle



not all new plant tissue survives- about as much new dead plant material enters soils as is lost from soils by decay (mostly oxidation)

seasonal var. in CO_2



season to season "breathing" of biosphere (~+/- 60 GTC/yr) leads to clear seasonal var. in amount of atmospheric CO_2

clicker question:

the change in overall CO_2 amount from 1999 to 2000 and 2001 is due primarily to:

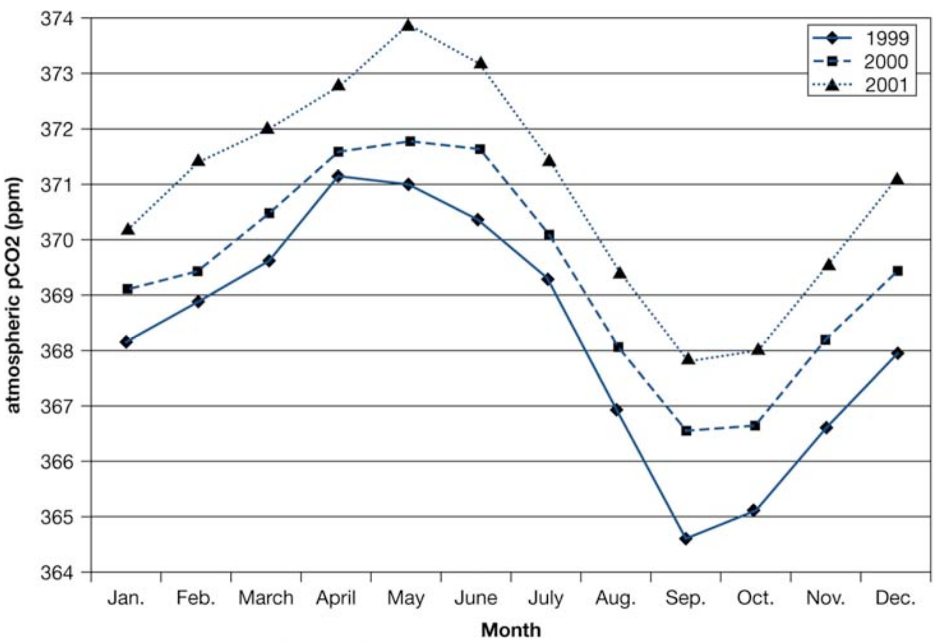
a) more respiration

b) less photosynthesis

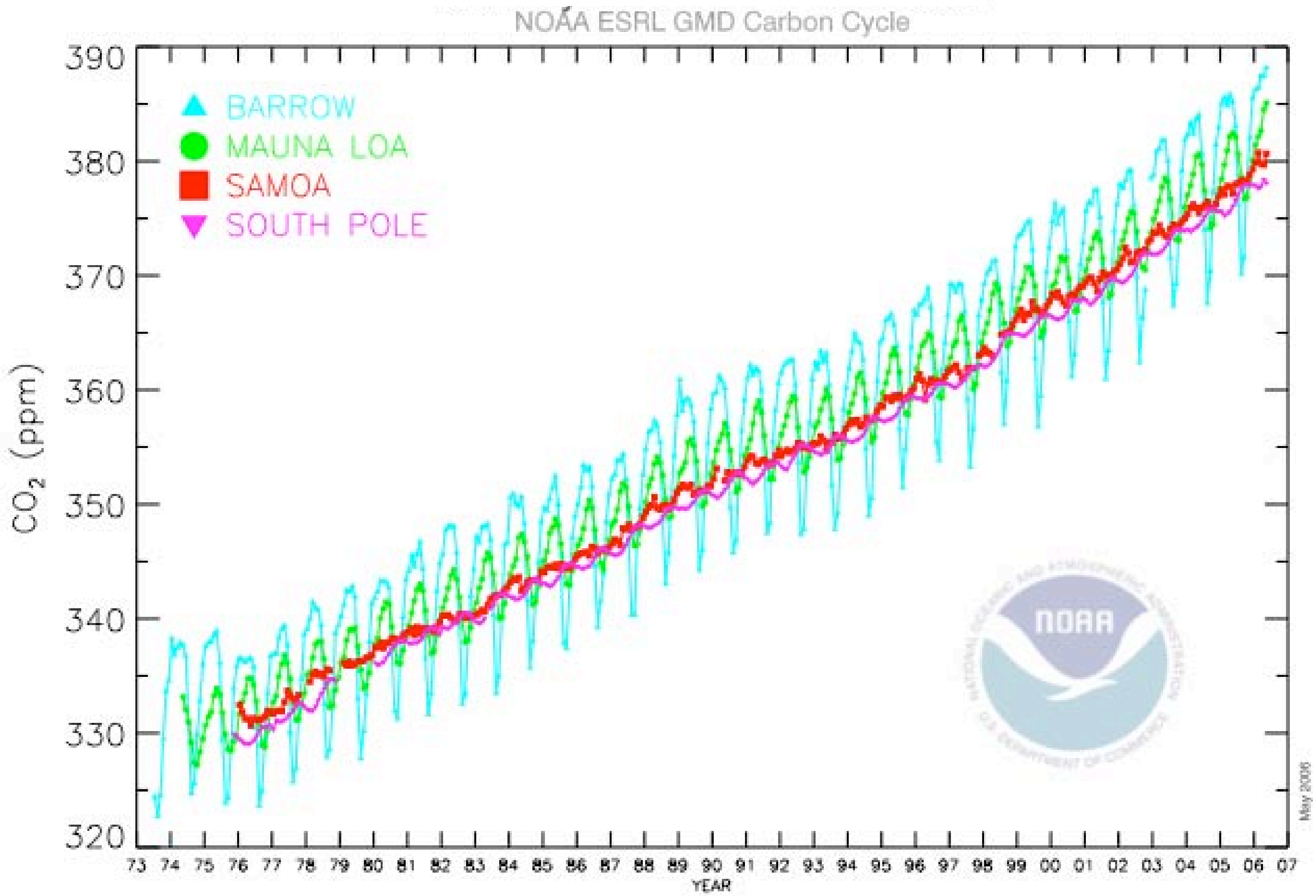
c) more decay

d) <u>burning of fossil fuels</u>

e) none of the above



monthly mean CO_2



the terrestrial biological C-cycle

output $\longleftarrow$ atm. CO_2 $\longleftarrow$ input

photosynthesis
60 GTC/yr

respiration & decay
60 GTC/yr

CO_2 reservoir size: 700 GTC

residence time: $\dfrac{\text{700 GTC}}{\text{60 GTC/yr}}$ = **~11.7 yr**

approx. lifetime of CO_2 molecule in atmosphere if there were no exchange with slowly moving deep ocean, sediments and rocks

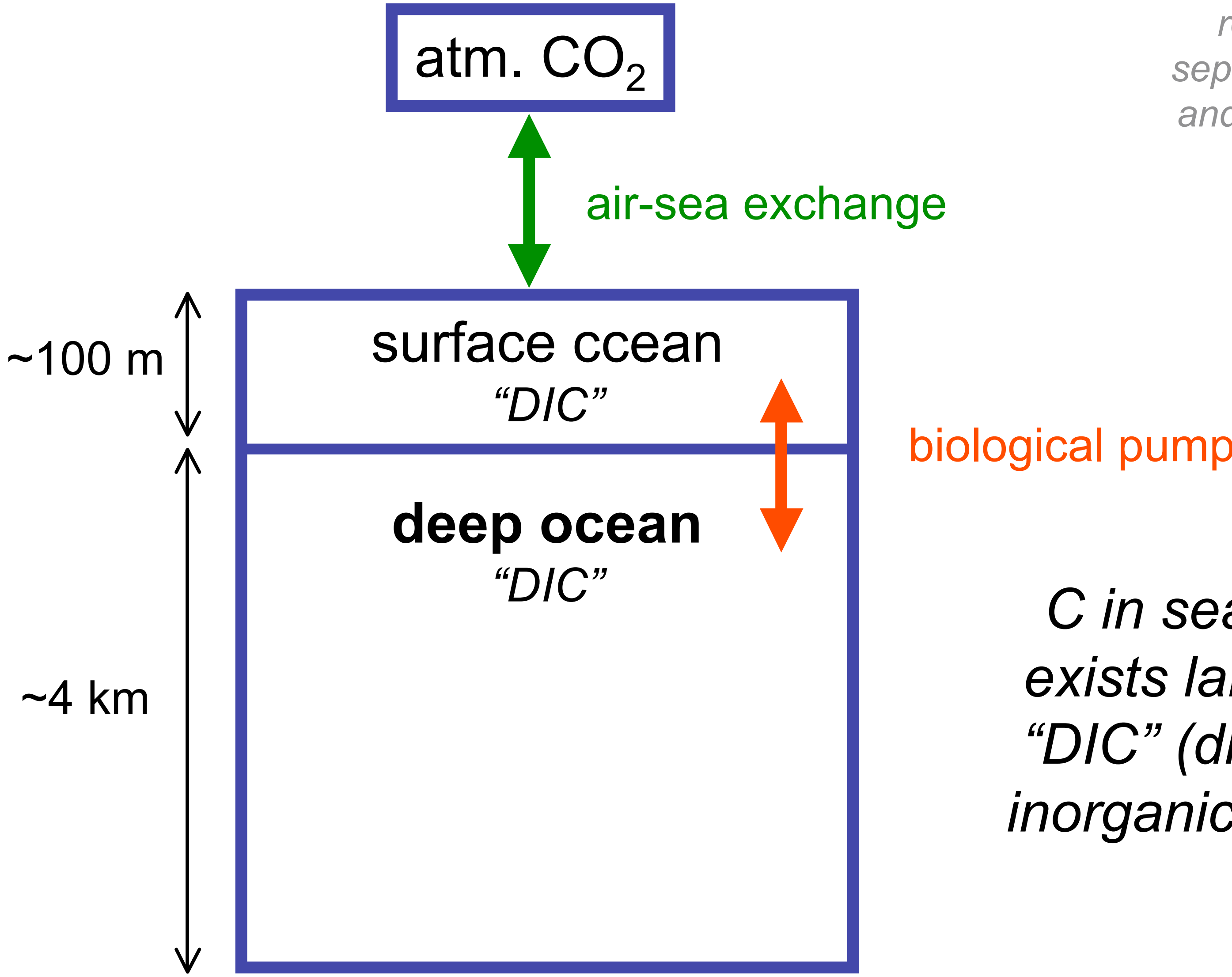
the ocean C-cycle

carbon uptake and release by the oceans:

1. exchange of CO_2 gas across air-sea interface

2. the "biological pump"

the ocean C-cycle



recall phys. separation upper and deep ocean

C in sea water exists largely as "DIC" (dissolved inorganic carbon)

biological activity transfers C from upper O. to deep O., leading to different [DIC] and pCO_2 in upper and deep O.

the ocean's biological pump

surface water

photosynthesis

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

sinking particles

respiration

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

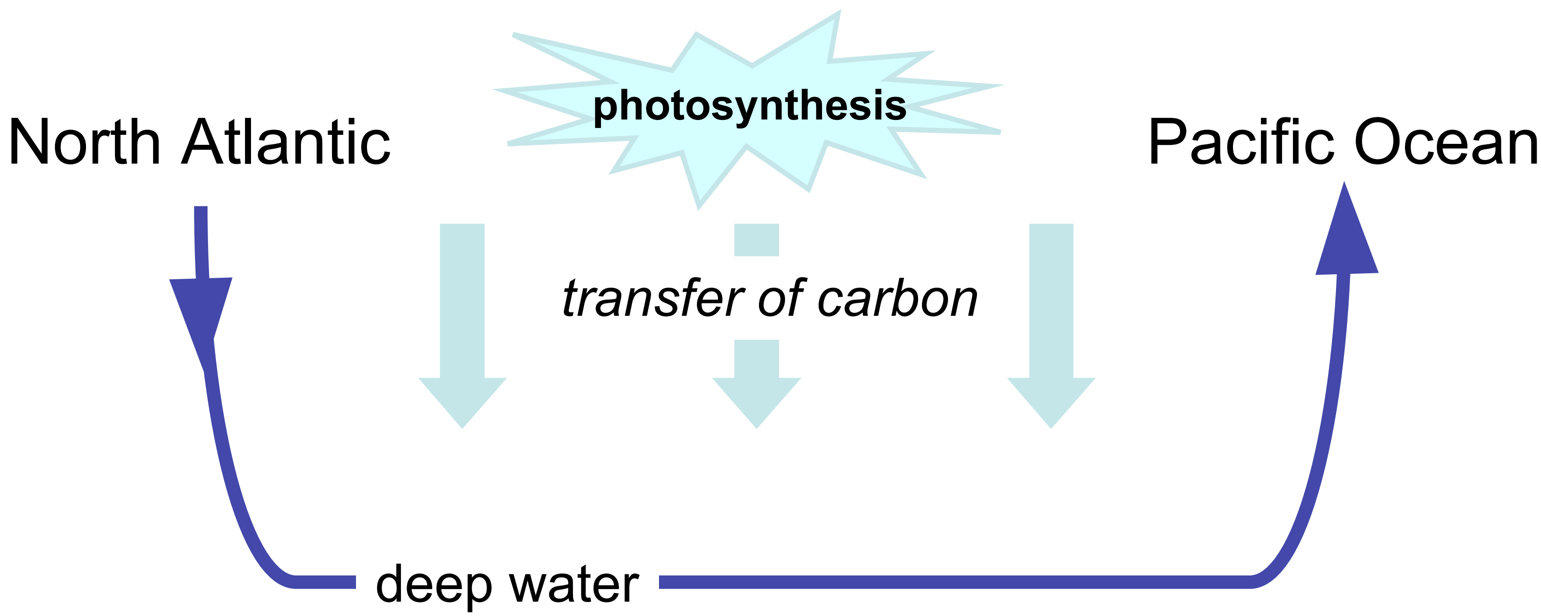
deep water

This pumps up the CO_2 of deep water…

the ocean's biological pump

transfer of CO_2 to the deep ocean:

photosynthesis creates organic matter; this sinks to the deep ocean, where it decays back to CO_2



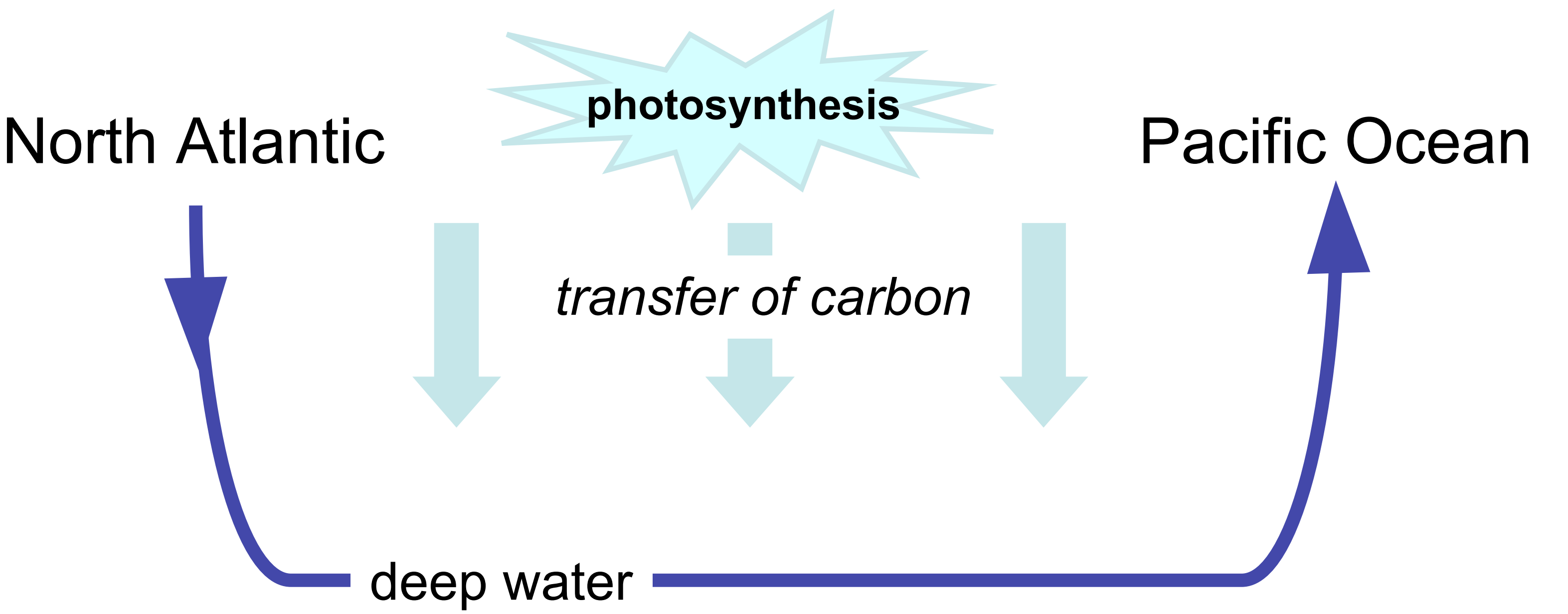
the ocean's biological pump

transfer of CO_2 to the deep ocean:

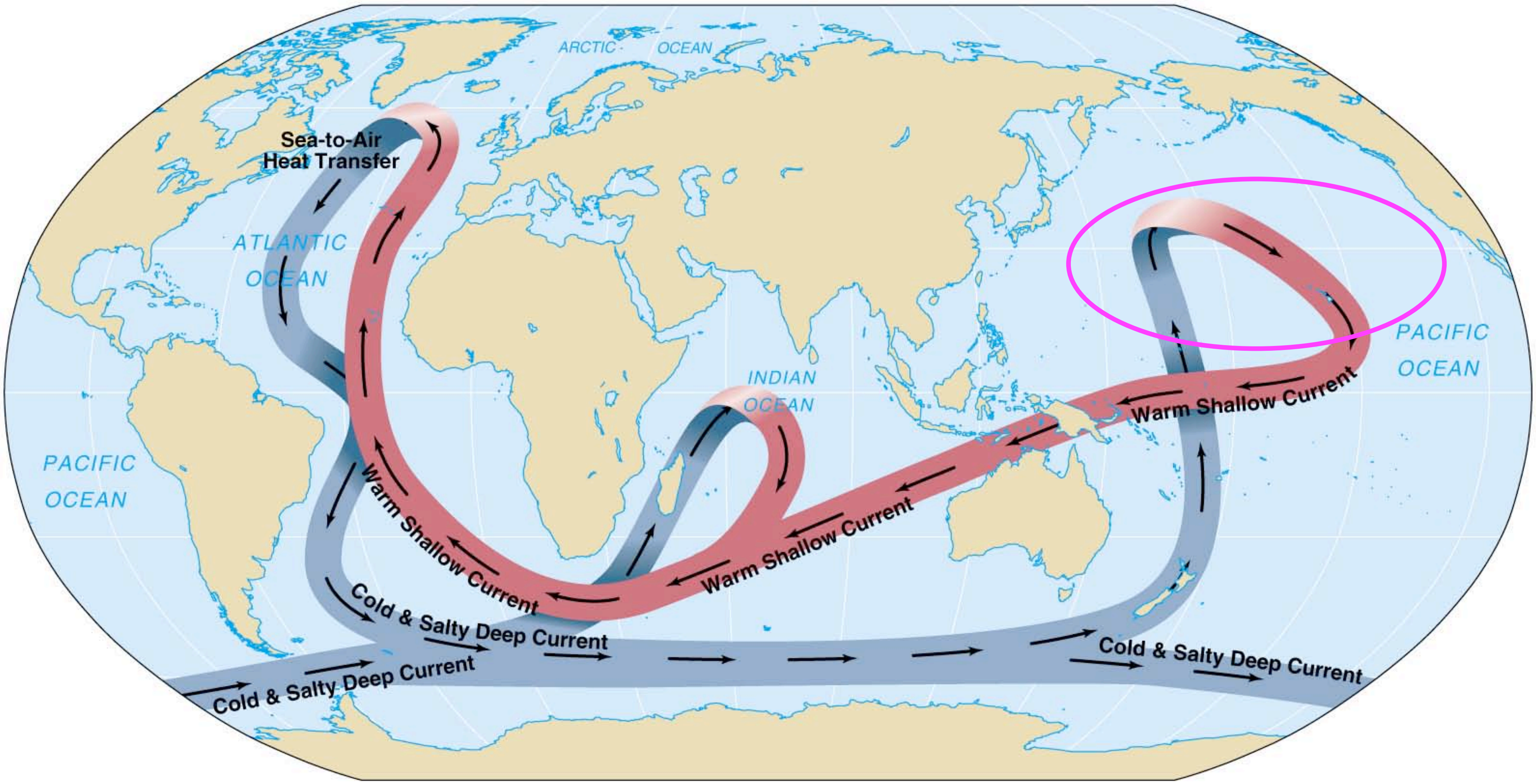
deep water becomes enriched in CO_2

the carbon is recycled to the surface in ~1,000 years

i.e. approx. residence time deep water from ^{14}C

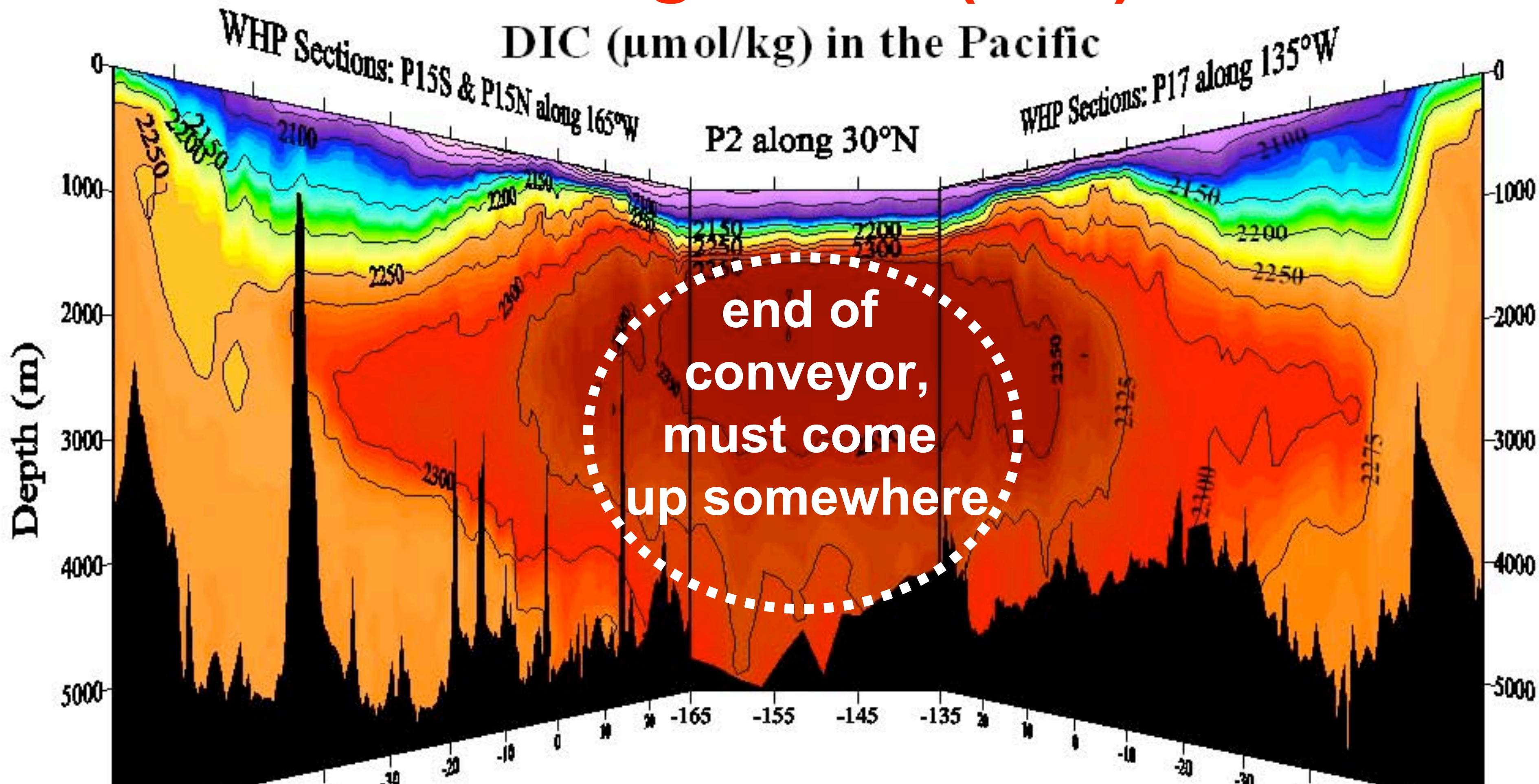


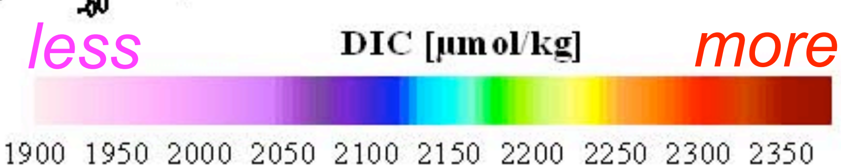
recall ocean "conveyor belt"

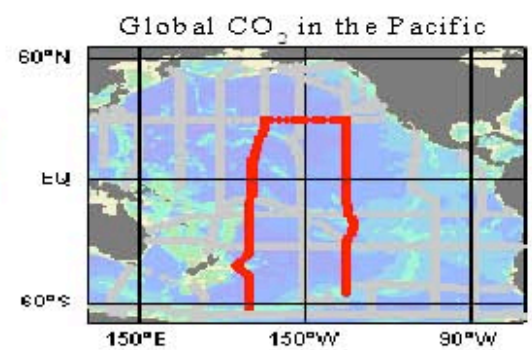


deep circulation dominated by a continuous circuit associated with formation of deep water in the N. Atlantic (i.e. NADW)

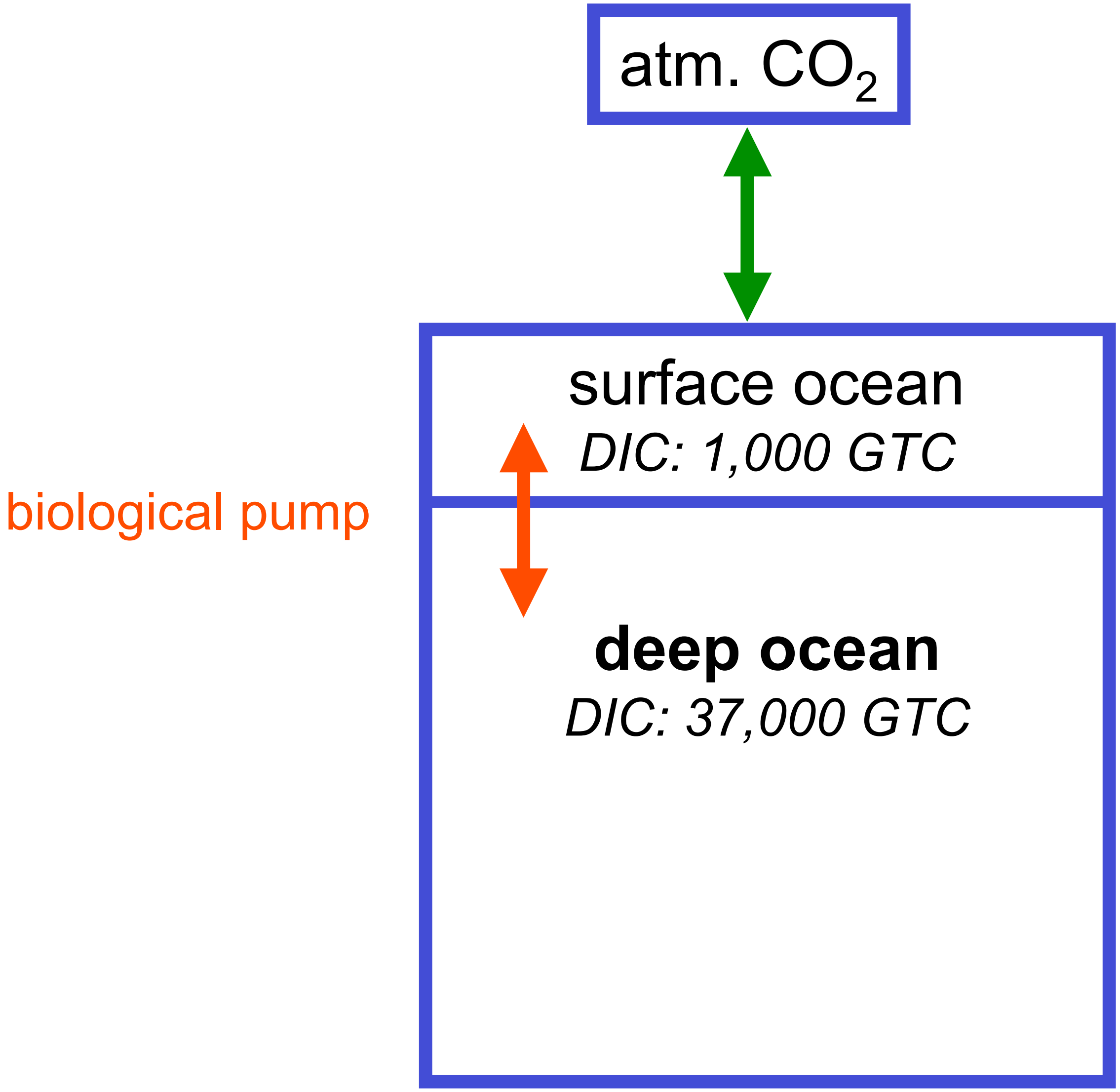
Dissolved Inorganic C (DIC), Pacific







pls. see later note on molar units



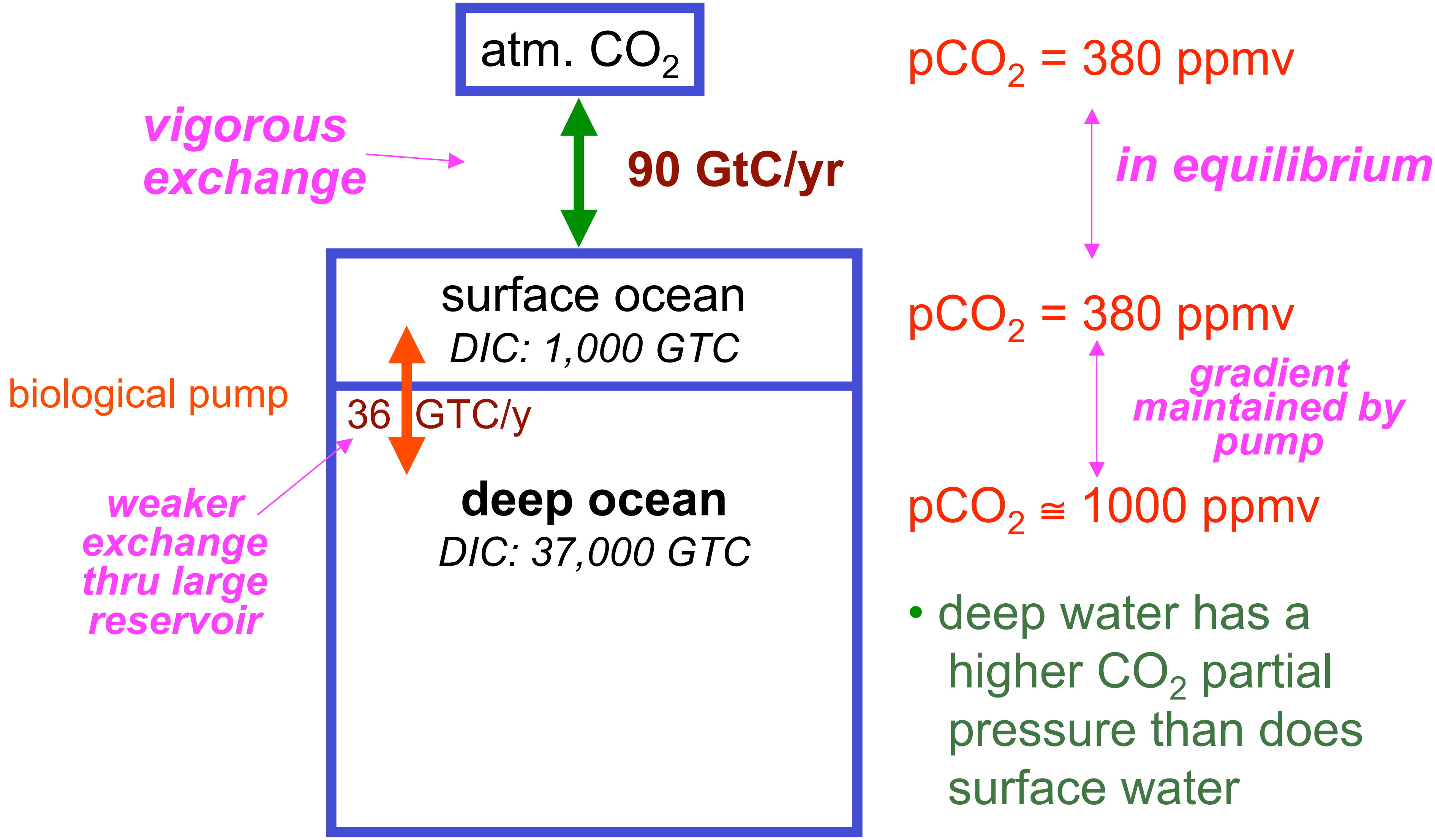
pCO_2 = 380 ppmv

pCO_2 = 380 ppmv

$pCO_2 \cong$ 1000 ppmv

- deep water has a higher CO_2 partial pressure than does surface water

The biological pump increases the [DIC] and pCO_2 of the deep ocean. When deep water upwells to surface, some excess CO_2 escapes to atmosphere, but most is taken back up by the biological pump….



- deep water has a higher CO_2 partial pressure than does surface water

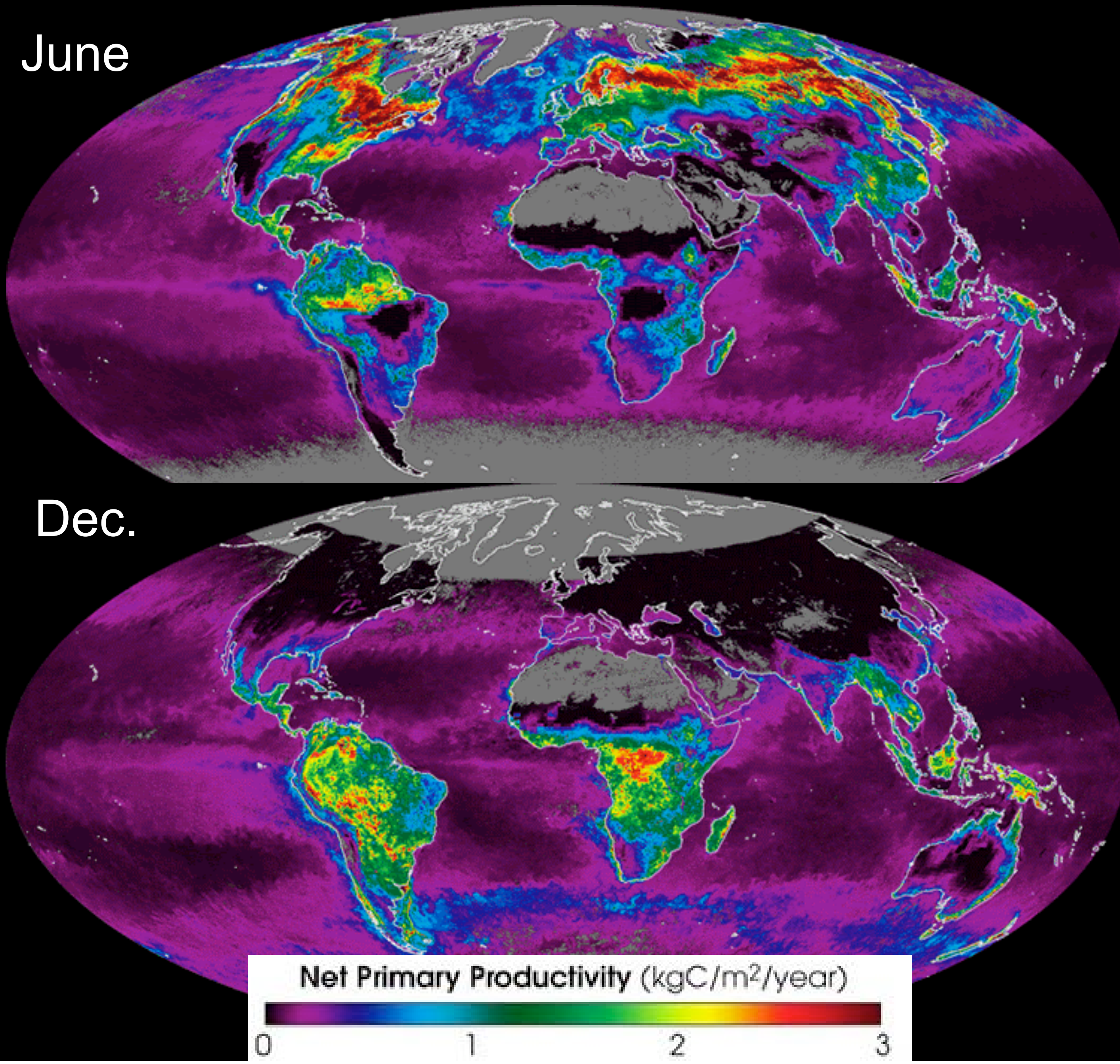
Can say that the partitioning of C between surface and deep ocean by the biological pump helps to set the atmospheric concentration (in unperturbed C-cycle)…

the ocean timescale(s)

the surface ocean-to-atmosphere exchange is large with respect to the size of the atmospheric reservoir, but does not tug on the atmospheric concentration seasonally, because:

•unlike land, there is not a strong hemispheric or seasonal bias in biological production over the ocean (slide)

new production ocean vs. land



the ocean timescale(s)

the surface ocean-to-atmosphere exchange is large with respect to the size of the atmospheric reservoir, but does not tug on the atmospheric concentration seasonally, because:

•unlike land, there is not a strong hemispheric or seasonal bias in biological production over the ocean

•it takes hundreds of years for all ocean water to contact the atmosphere due to slow overturning timescale of the conveyor (~1000 yrs)

•most importantly, reactions between the CO_2 and DIC make it hard to change seawater pCO_2 (see next lecture on the perturbed C-cycle..)

ocean breathes on timescale of 5,000 year set by slow overturning and chemical reaction with sea sediments (see a later lecture on Ice Age mysteries…)

natural carbon stocks and flows

land:

600 GTC living
1500 GTC dead (soils and sediments)

ocean:

1 GTC living
600 GTC dead (organic)
38,000 GTC inorganic

atmosphere:

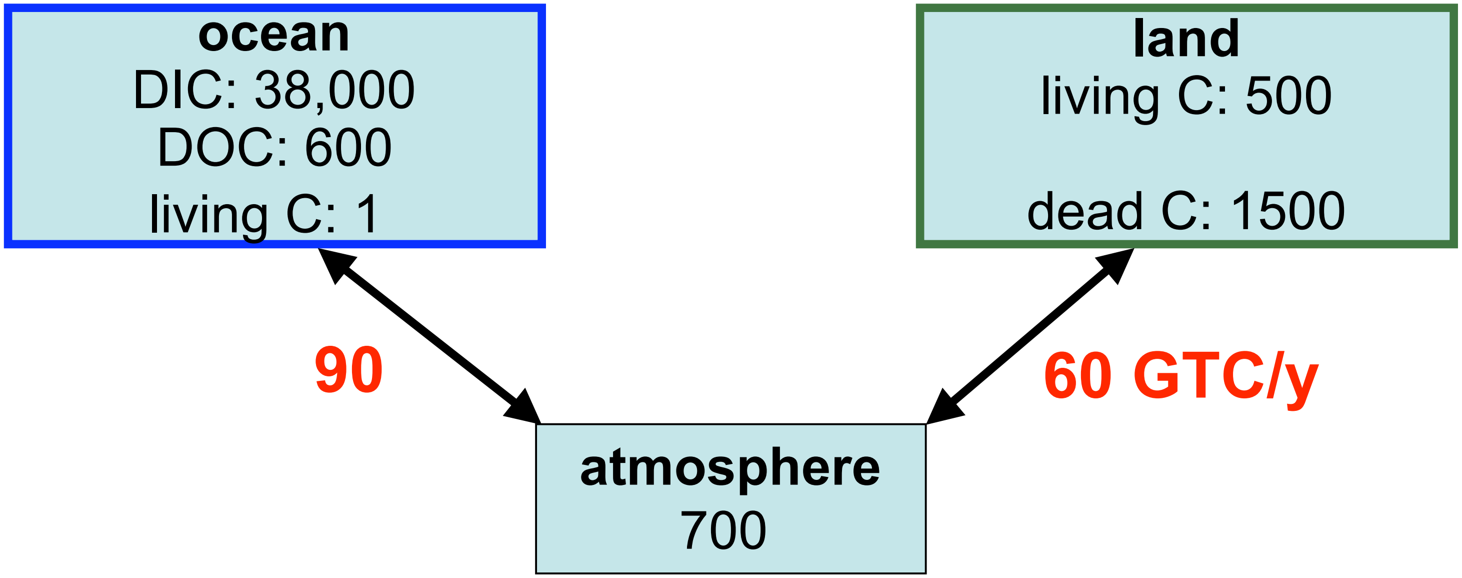
700 GTC inorganic (pre-industrial)

rocks:

50,000,000 GTC inorganic + organic
5,000 GTC conc. organic (fossil fuel!)

values are approximate

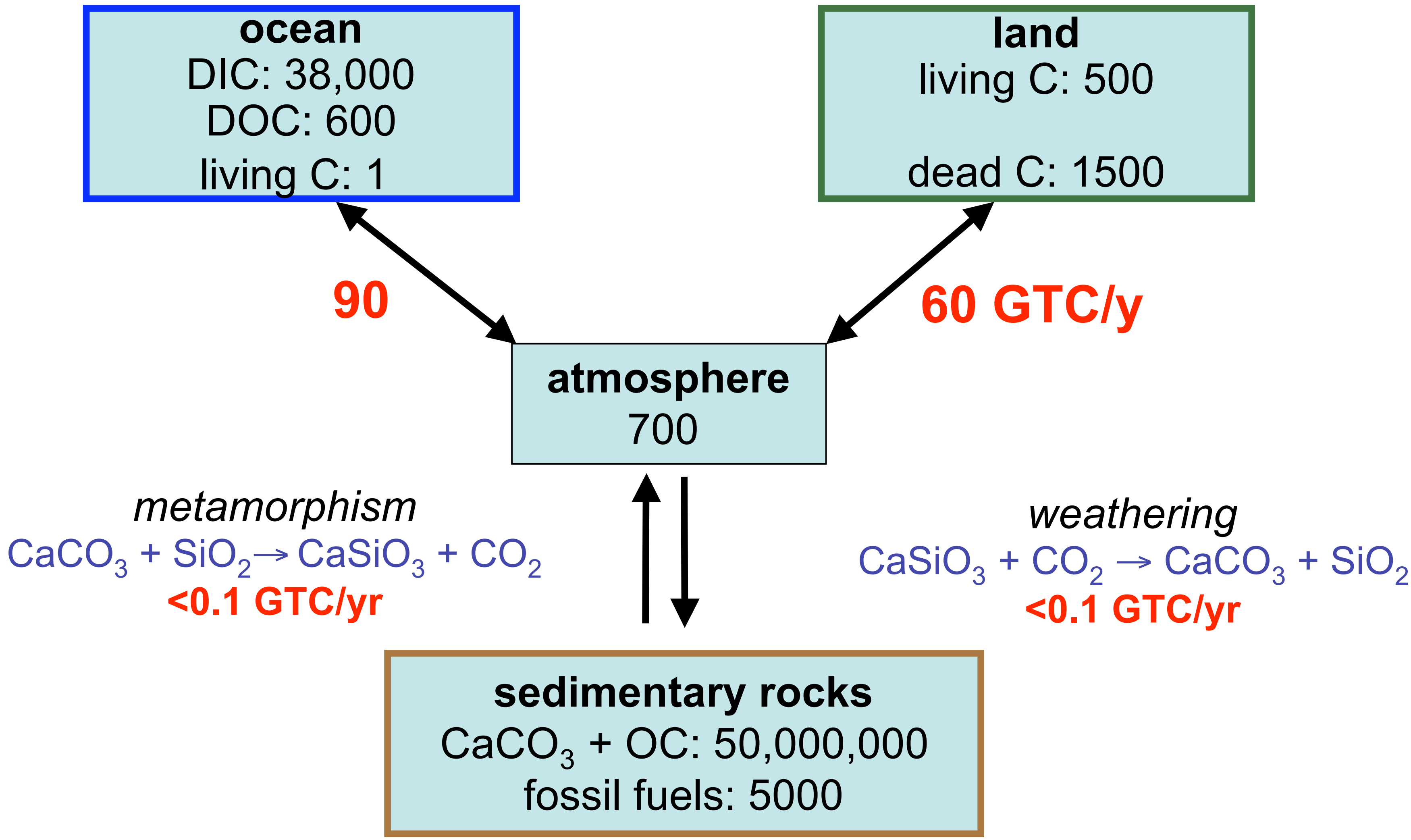
natural carbon stocks and flows



stocks in GTC (gigatons C = 10^{15} g C)

transfer fluxes in GTC/year

natural carbon stocks and flows



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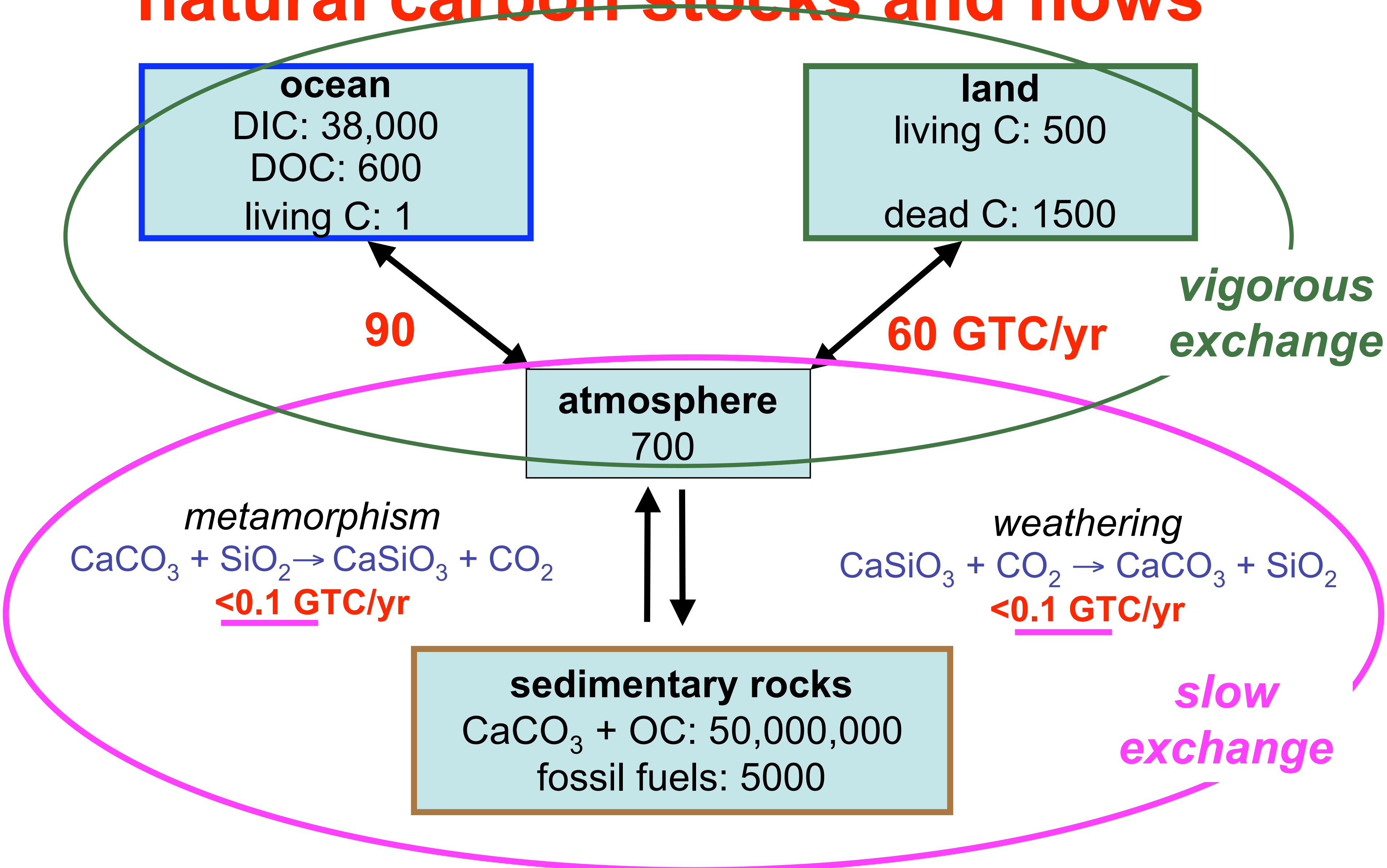


stocks in GTC (gigatons C = 10^{15} g C)

transfer fluxes in GTC/year

the long term “rock” C-cycle

- ***dominated by the <u>weathering</u> of Ca-containing silicate minerals and the subsequent use of Ca by organisms to build calcium carbonate shells***

- ***the <u>net</u> result of the two reactions is the uptake of CO_2***

silicate rock weathering:

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

carbonate formation:

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

silicate rock weathering:

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

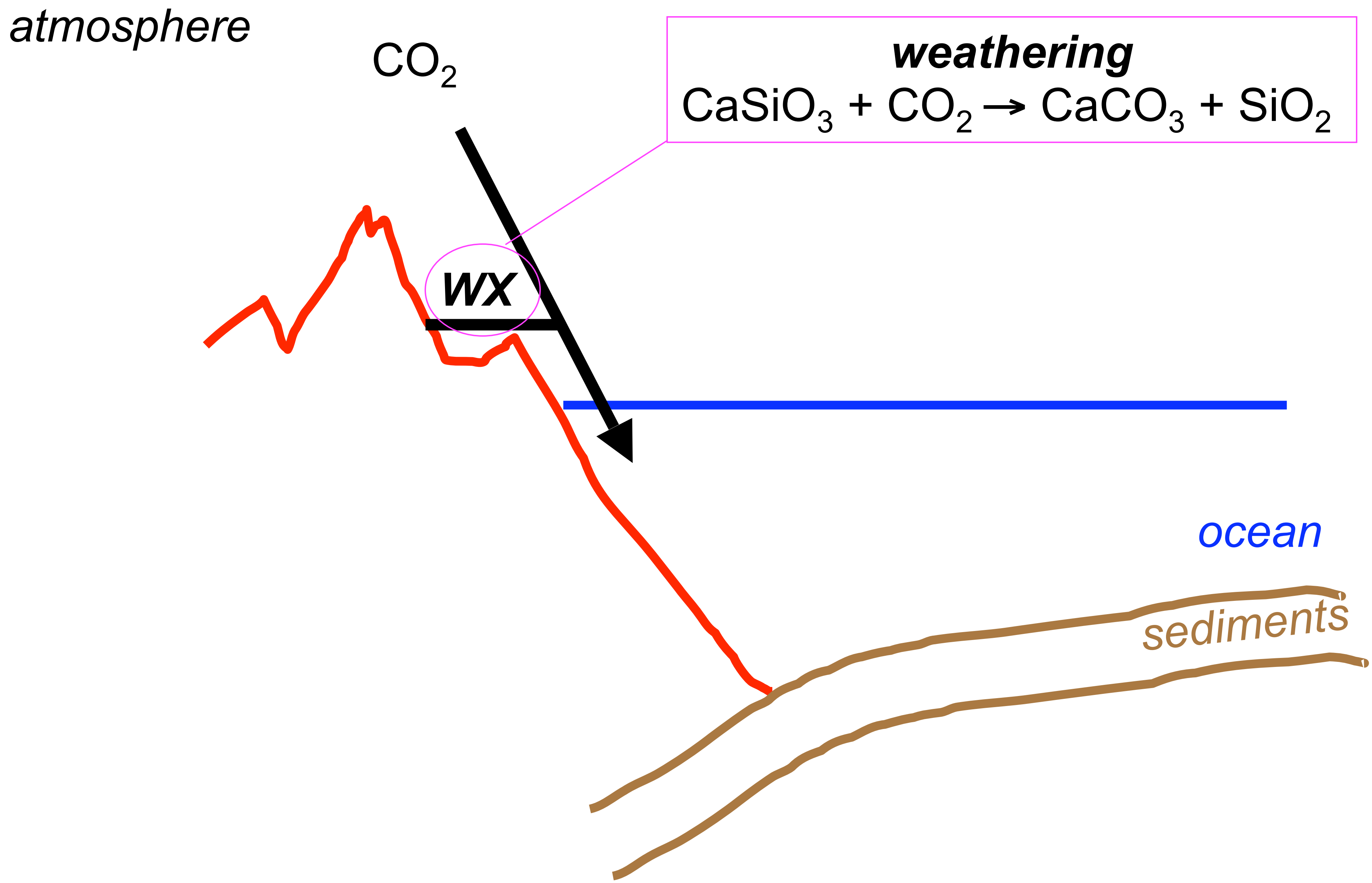
carbonate formation:

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

net reaction:

$$\boxed{\mathbf{CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2}}$$

the long term “rock” C-cycle



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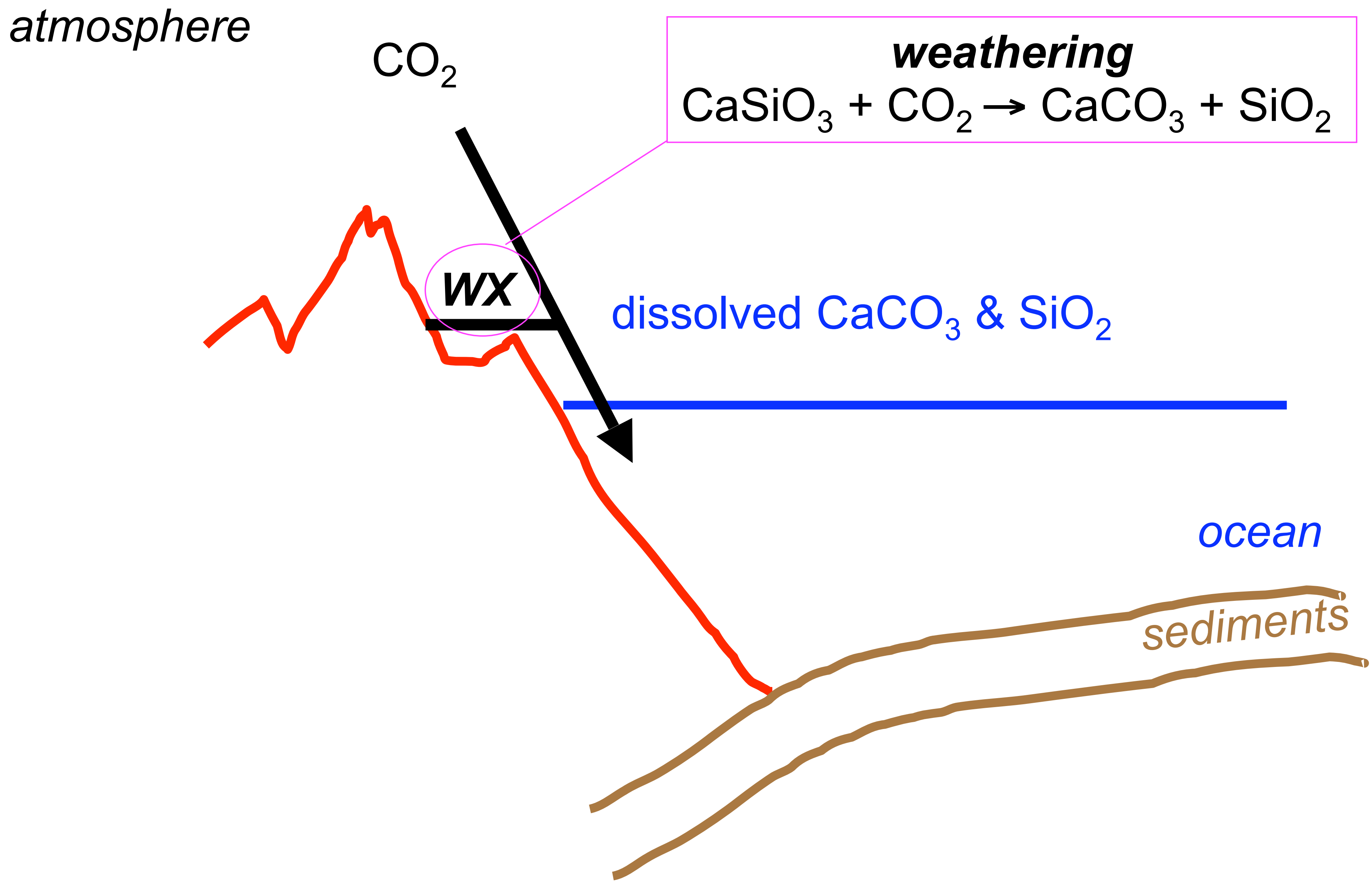

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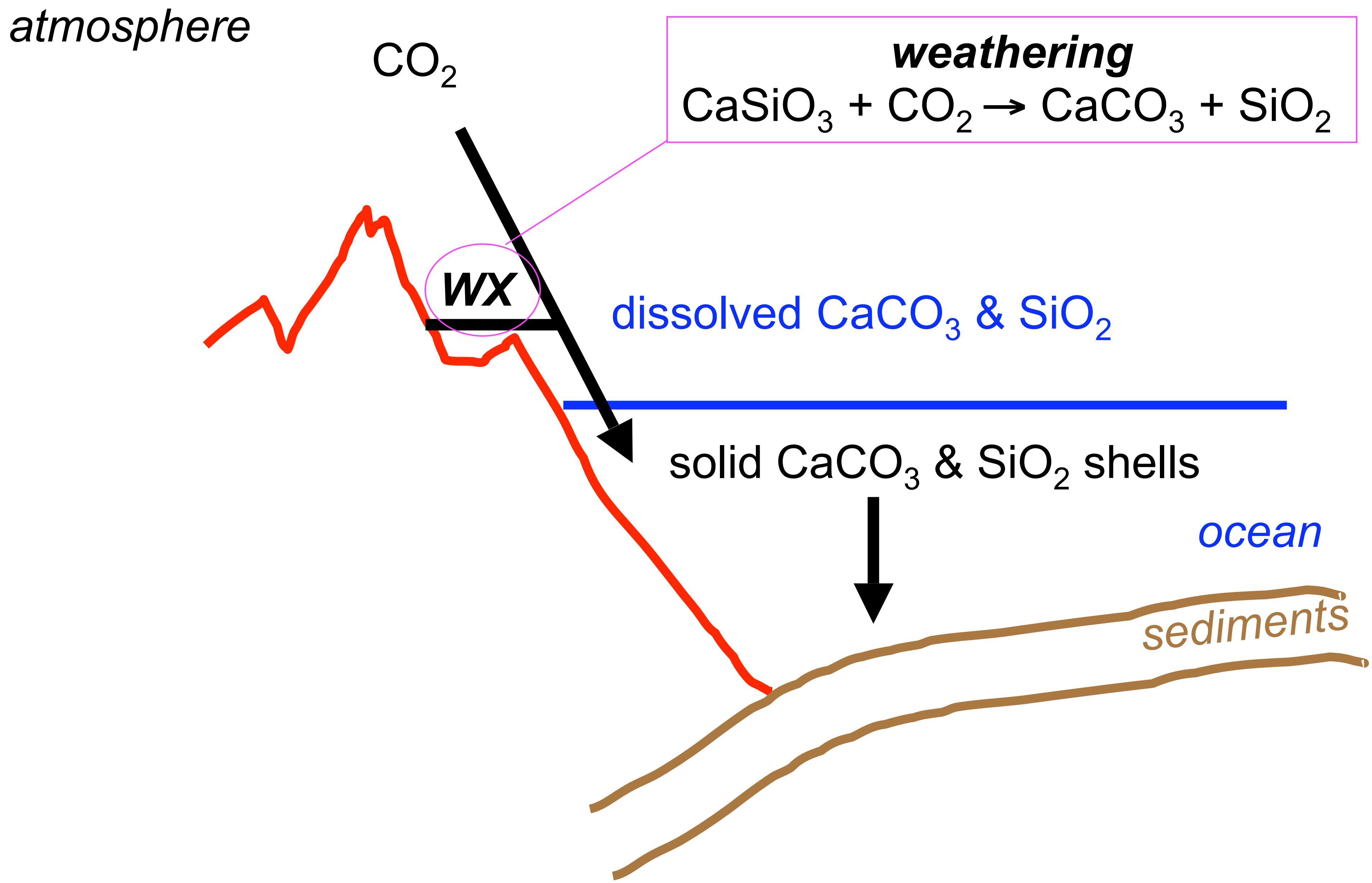

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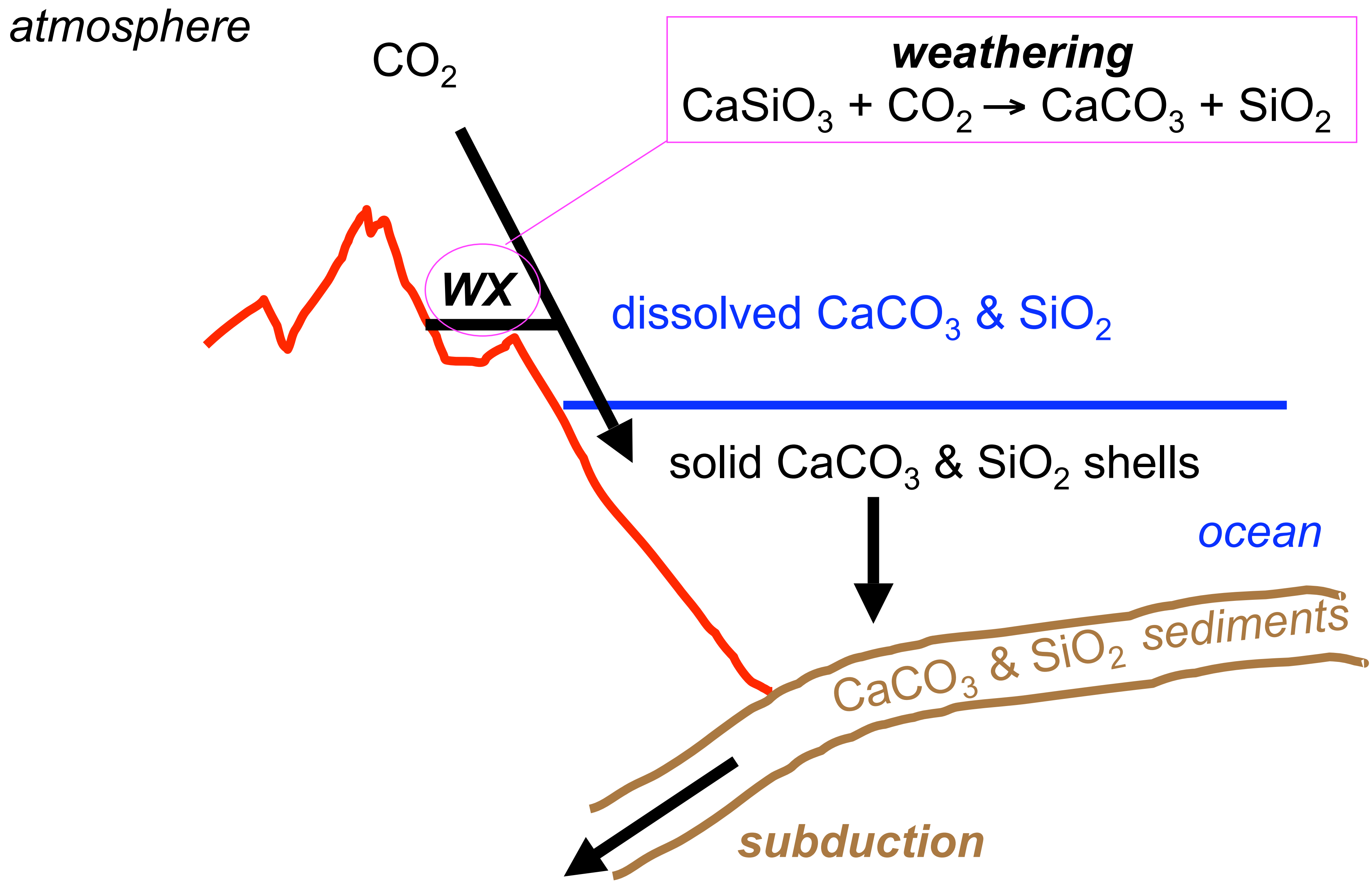
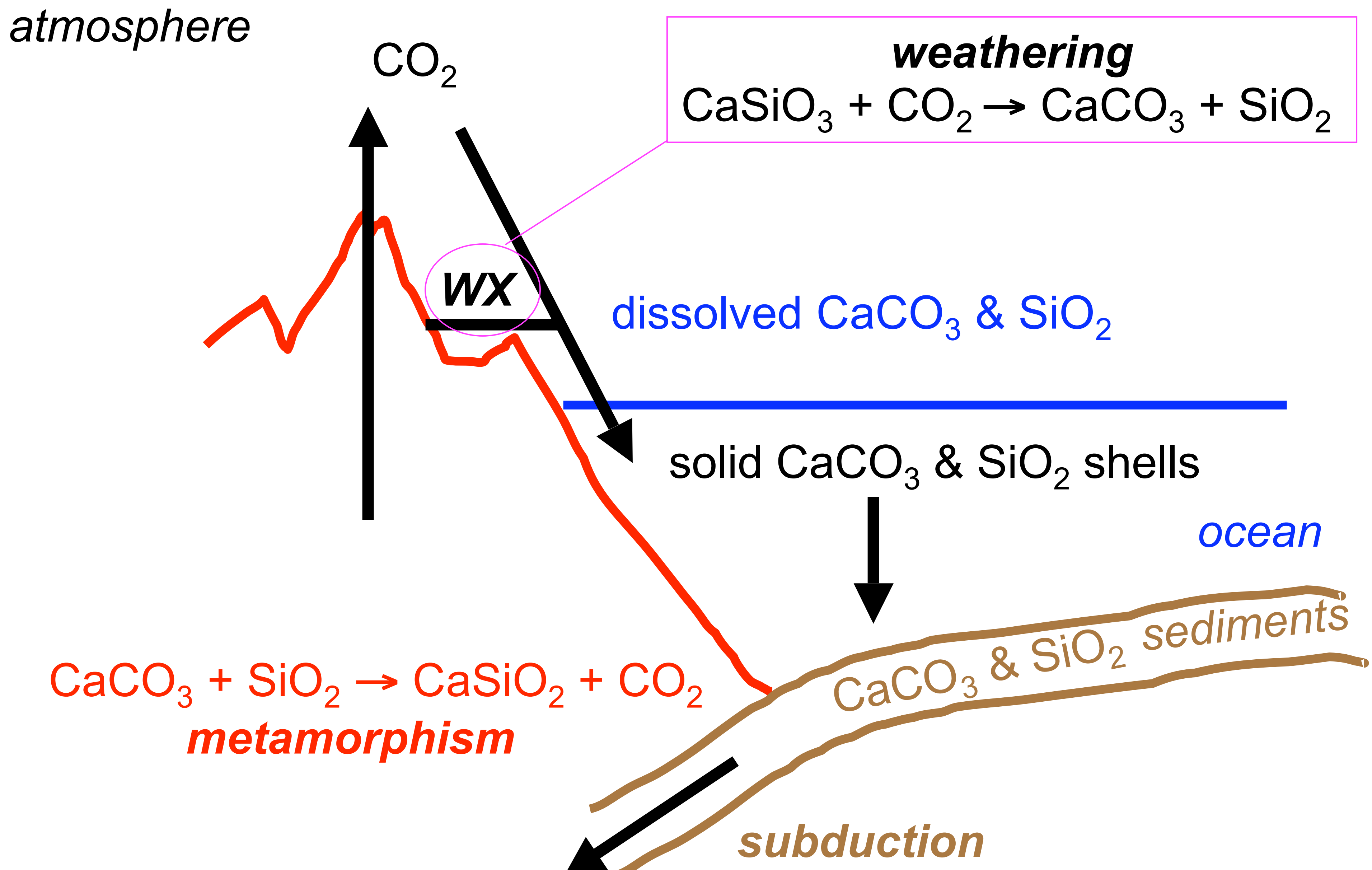
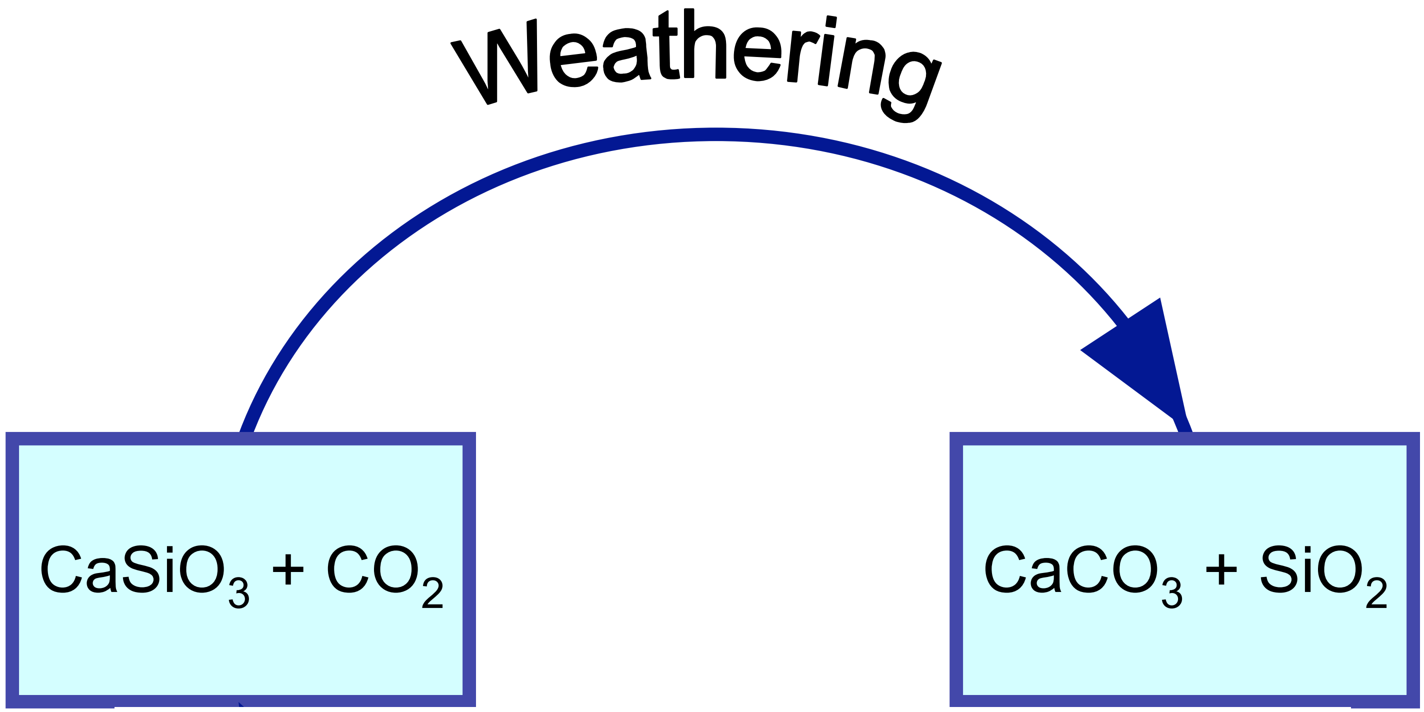


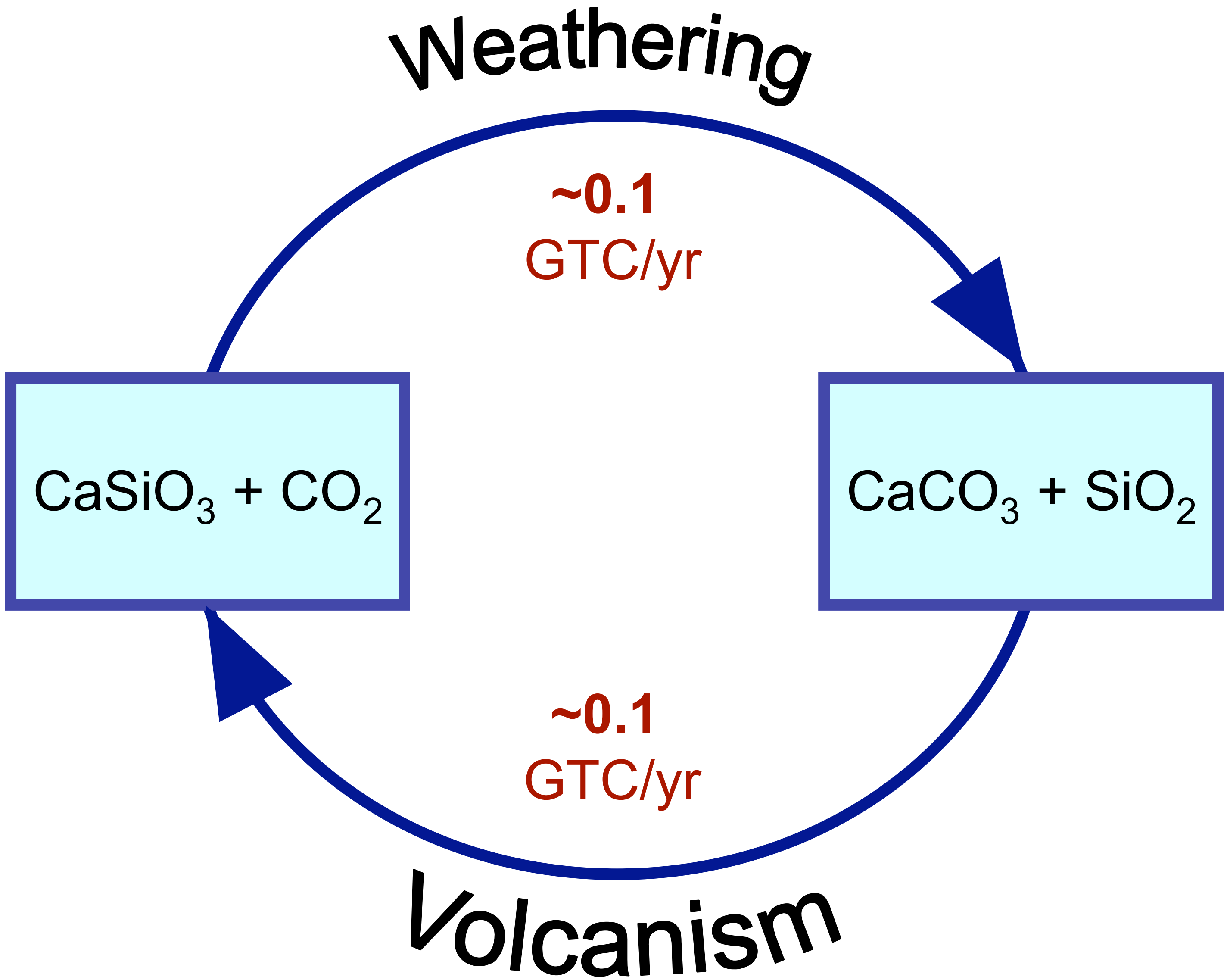
the long term "rock" C-cycle



long term "rock" inorganic C-cycle



long term "rock" inorganic C-cycle



What controls silicate weathering rates?

•time

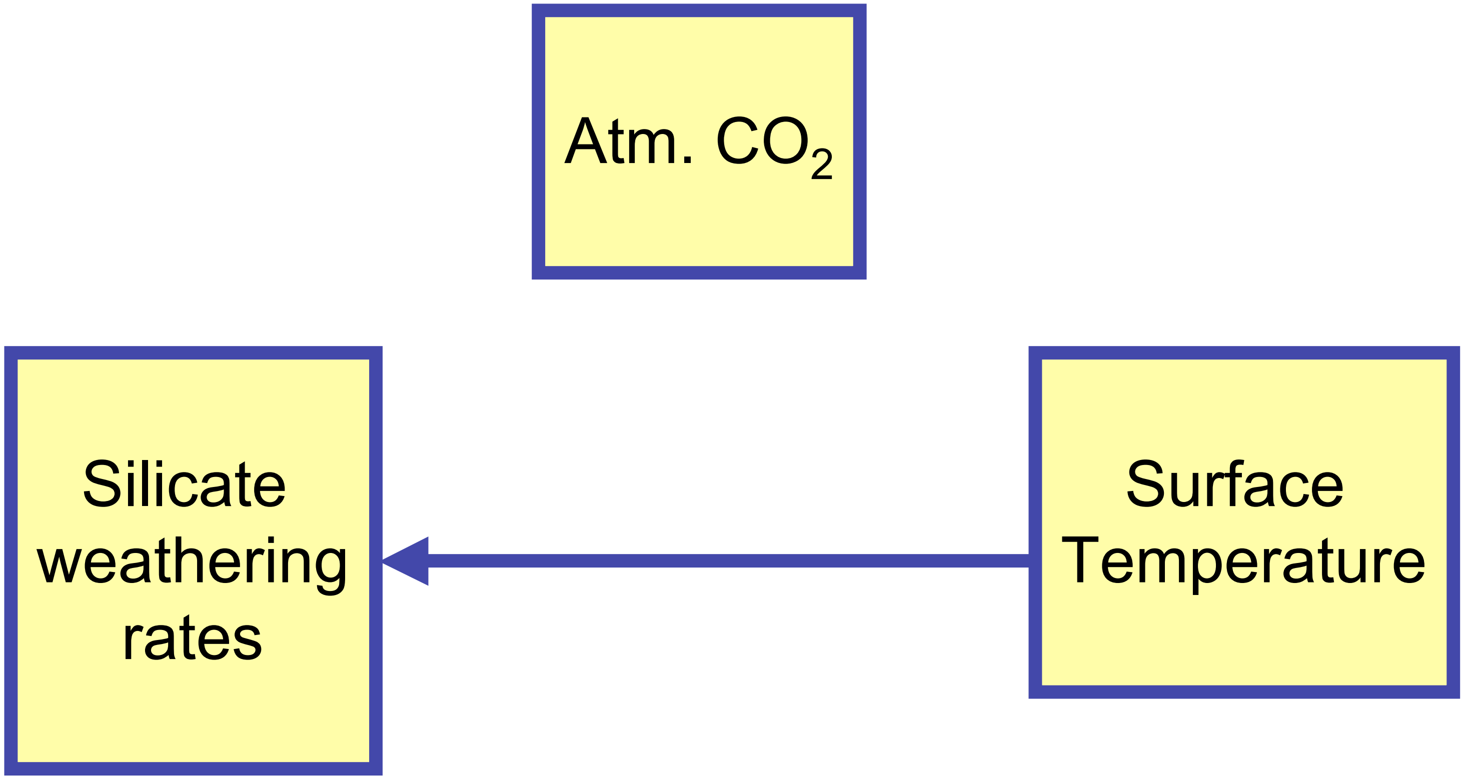
•temperature

•rainfall

•exposure of fresh rock surfaces

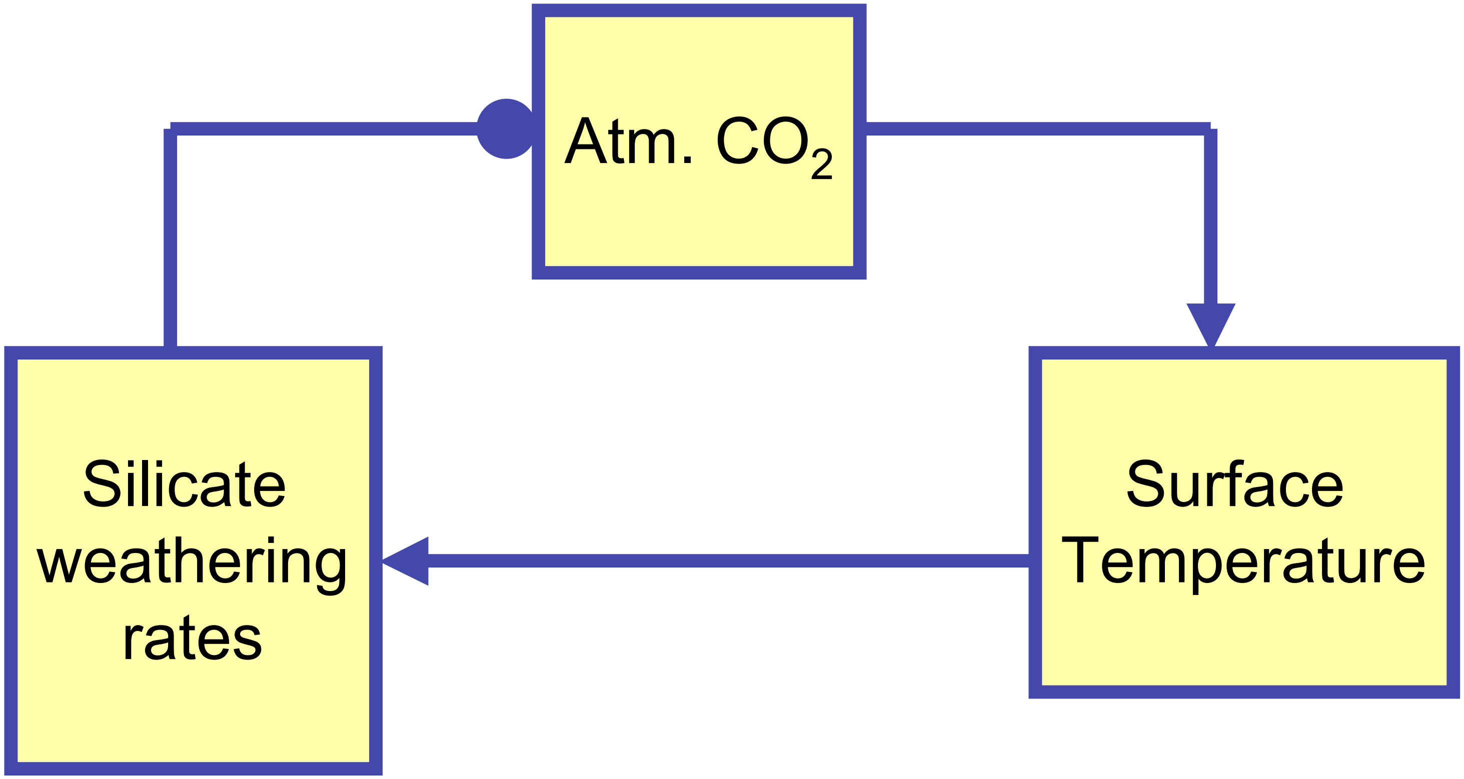
•vegetation (roots provide acid)

weathering feedback loop



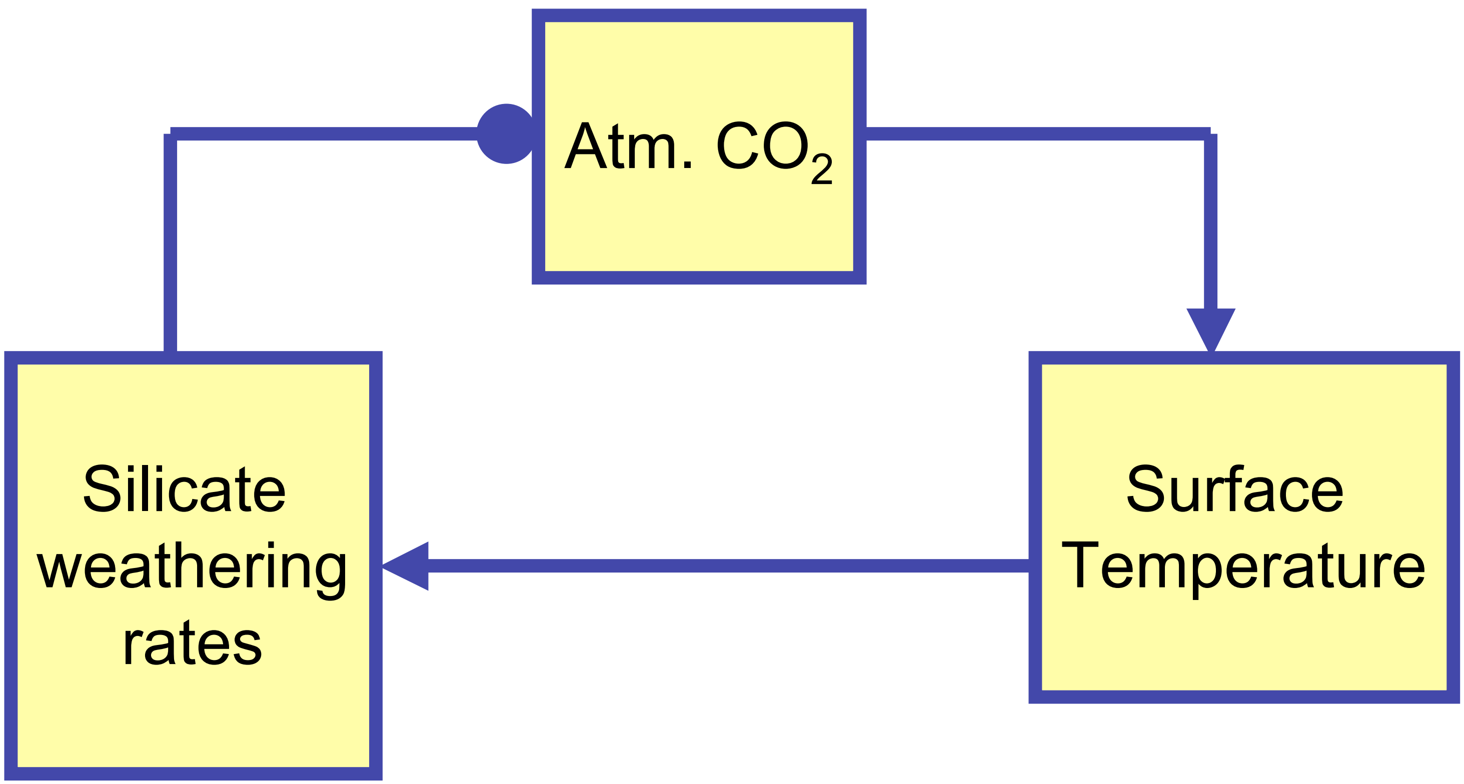
weathering rates increase with increased temperature

weathering feedback loop



weathering reactions remove CO_2, and as CO_2 declines, planet temperatures go down

weathering feedback loop



this is a negative feedback loop and a key factor in helping to stabilize climate and CO_2 over long time scales (i.e., millions of years)

key points

- **carbon cycle includes atmosphere, ocean, biosphere and lithosphere, but *each has different time scale***
- **time scales depend on *size of flux*, and *size of reservoirs***
- **the *terrestrial biosphere* is responsible for seasonal variations in CO_2**
- **other reservoirs must be responsible for longer time scale changes in CO_2**
- **as we will see, human activity and burning of fossil fuels connects the very long time scale of the rock cycle with the much shorter time scales of the atmosphere, ocean and biosphere**

the long term "rock" C-cycle

- A small flux of **organic** carbon (0.05 Gt/yr) is also buried in sedimentary rocks, mostly on continental shelves.

- Over time, this small flux has accumulated to create a large reservoir: ~10,000,000 (or 1×10^7) Gton C.

- Concentrations of this buried organic carbon include coal, oil and gas--but most carbon is <u>not</u> concentrated.

- Organic carbon in sedimentary rocks is ultimately returned as CO_2 resulting from <u>oxidation</u> by exposure to O_2.

- This oxidation is also a *weathering* process.

the natural fate of fossil fuels

- **weathering of rocks will ultimately allow the release of fossil fuels as CO_2**
- **this would normally occur over 100s of millions of years**
- **humans simply speed up this process by burning fossil fuels (10s of years)**
- ***as such, rapid burning of fossil fuels puts the carbon cycle out of balance***

concept of the mole

- the last slide gave the sea water concentration of Dissolved Inorganic Carbon (DIC) in *moles* (i.e. as micro-moles of DIC per kilogram of sea water)

- the number of *moles* is directly related to the number of molecules of a substance

- 1 *mole* is $6x10^{23}$ molecules

- the *molar mass* of C is 12 (‘formula weight’), so 1 *mole* of C weighs 12 g

- the *molar mass* of CO_2 is 44 (‘formula weight’), so 1 *mole* of CO_2 weighs 44 g

- the molar mass of $CO_3^{=}$ is 60 (‘formula weight’), so 1 *mole* of CO_2 weighs 60 g

- *the amount of C is the same in each…..*

learning goals

- be familiar w/ the special chemical attributes of C and how the stability of molecular C relates to its "oxidation" state
- be able to describe the photosynthesis/respiration reaction
- be able to describe the ambient Earth reservoirs of C, their relative sizes (or rank) and the sizes (or rank) of flows between them
- be able to determine a *residence time* from reservoir size and rate of in/output
- use this knowledge to determine which reservoirs exert the greatest influence on atmospheric CO_2 on brief (year to year) vs. very long (million year plus) timescales
- be able to describe the roles of *silicate weathering* and *metamorphism* and *volcanism* in the natural cycling of C
- be able to describe where sedimentary C and fossil fuel C come from