The Earth's Carbon Cycle

12.340 Global Warming Science

March 22, 2012

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Main topics

- How negative feedbacks in the carbon cycle are thought to lead to long-term (Myr-scale) climate stability
- Short-term (kyr or less) cycling of carbon
- Interactions between human activities and the carbon cycle, including:
  - Present uptake of anthropogenic CO_2 by the ocean and terrestrial biosphere
  - Long-term fate of anthropogenic CO_2

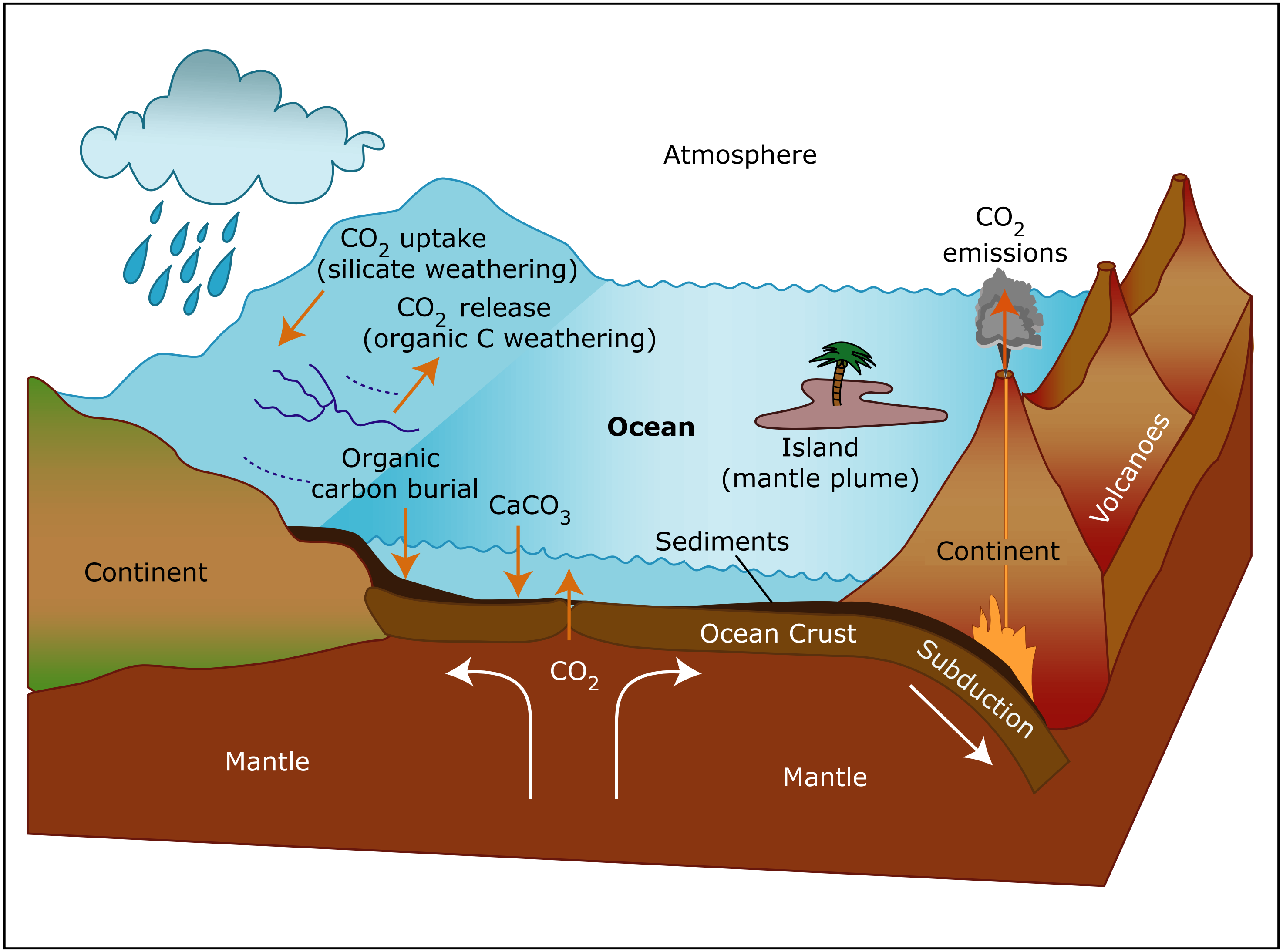
Global carbon reservoirs

Table: Carbon budget for the Earth in the pre-industrial era (Sarmiento and Gruber, 2002; Tyrell and Wright, 2001)

Reservoir	Mass of Carbon (10^{15}g=Pg)
Atmosphere	600
Fossil Fuels	3,700
Ocean	38,000
Rocks (as calcium carbonate)	60,000,000
Rocks (organic)	14,000,000
Vegetation/Soils	2,000

Image by MIT OpenCourseWare.

Geologic timescales



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Long-term sinks for atmospheric CO_2

- <u>Burial of organic carbon produced by photosynthesis</u>

  Idealized as

  $$CO_2 + H_2O + \text{photons} \longrightarrow CH_2O + O_2$$

  Most organic carbon is quickly respired, but some is buried in marine sediments, peat bogs, swamps, etc.

- <u>Silicate weathering and calcium carbonate burial</u>

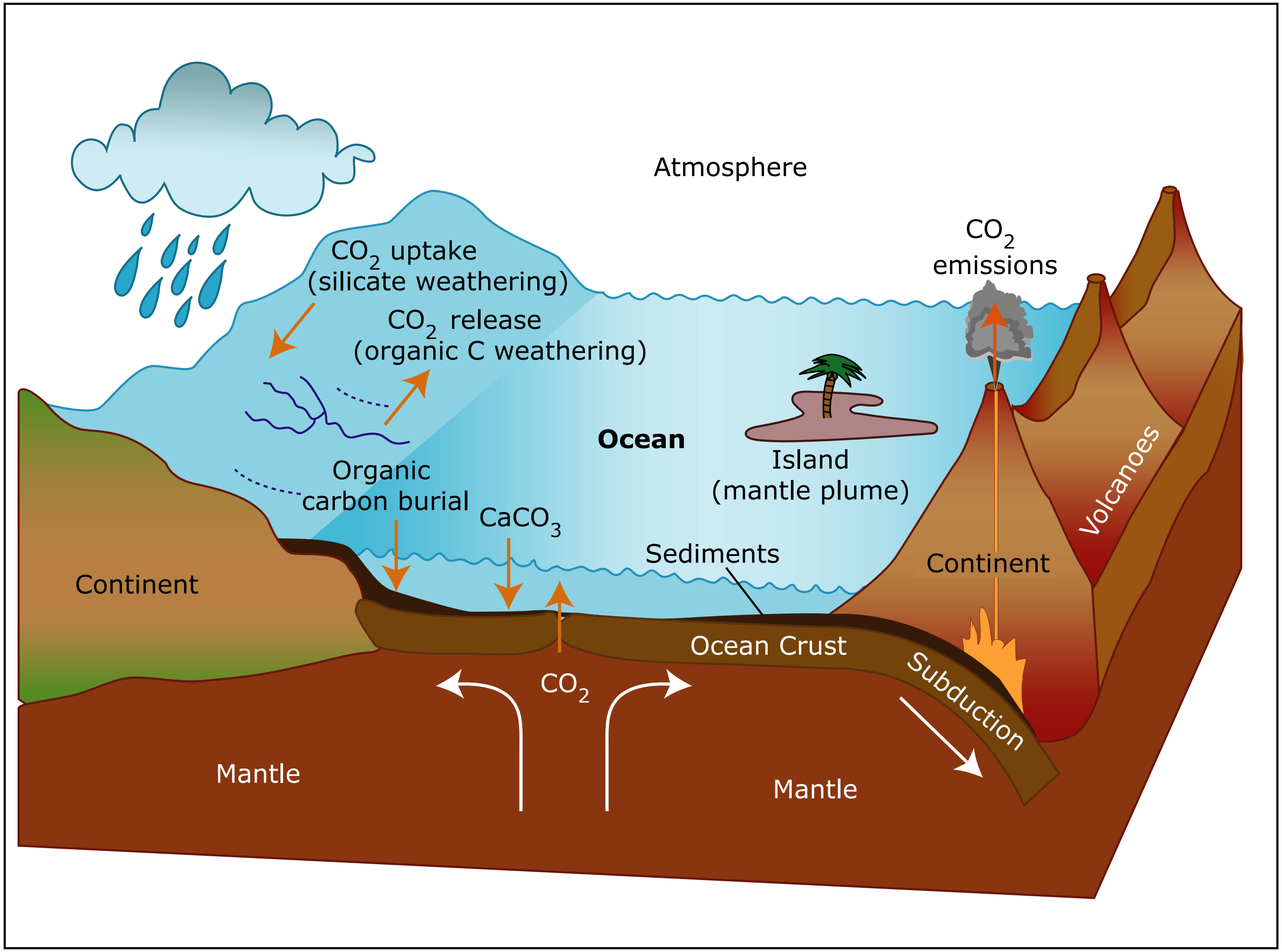
  Idealized as

  $$CaSiO_3 + CO_2 \text{ (in soils)} \longrightarrow$$

  $$\text{river transport of dissolved Ca, Si, } CO_2 \longrightarrow$$

  $$CaCO_3 + SiO_2 \text{ (in the ocean)}$$

Geologic timescales



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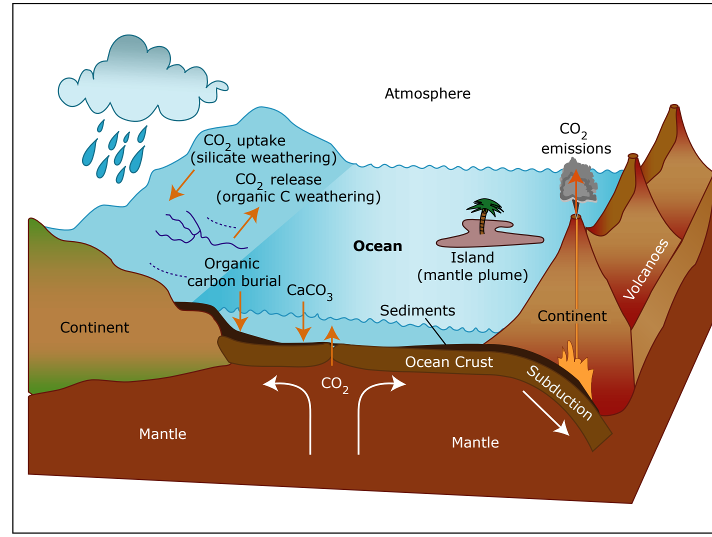
The global carbon cycle can be approximated as:

$$\frac{dM_{CO2}}{dt} = F_{volc} - F_{sil} - F_{org}$$



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<u>Where:</u>

M_{CO2}=Mass of CO_2 in the atmosphere

F_{volc}=Volcanic CO_2 emissions (~0.2 $GtCO_2$/yr)*

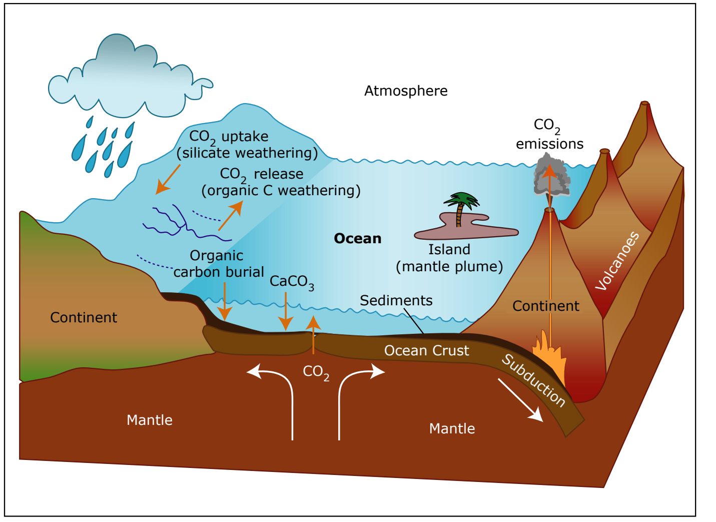
F_{sil}=Silicate weathering flux (~flux of Ca ~flux of $CaCO_3$)

F_{org}=Organic C burial flux (can be positive or negative)

*(note: $M_{CO2}=M_C*44/12$)

The silicate weathering CO_2 thermostat: An explanation for long-term climate stability

$$\frac{dM_{CO2}}{dt} = F_{volc} - F_{sil} - F_{org}$$



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IMPORTANT: Because the atmosphere contains so little carbon, these fluxes cannot be out of balance on Myr timescales.

F_{org} is generally ~3x smaller than F_{sil} and is not thought to be strongly sensitive to climate.

F_{sil} should increase with increasing atmospheric CO_2 and temperature.

Thus, on Myr timescales we can write:

$$F_{volc} = F_{sil} + F_{org} = k_{sil} M_{CO2} + F_{org}$$

where k_{sil} is the slope of the weathering-CO_2 relationship.

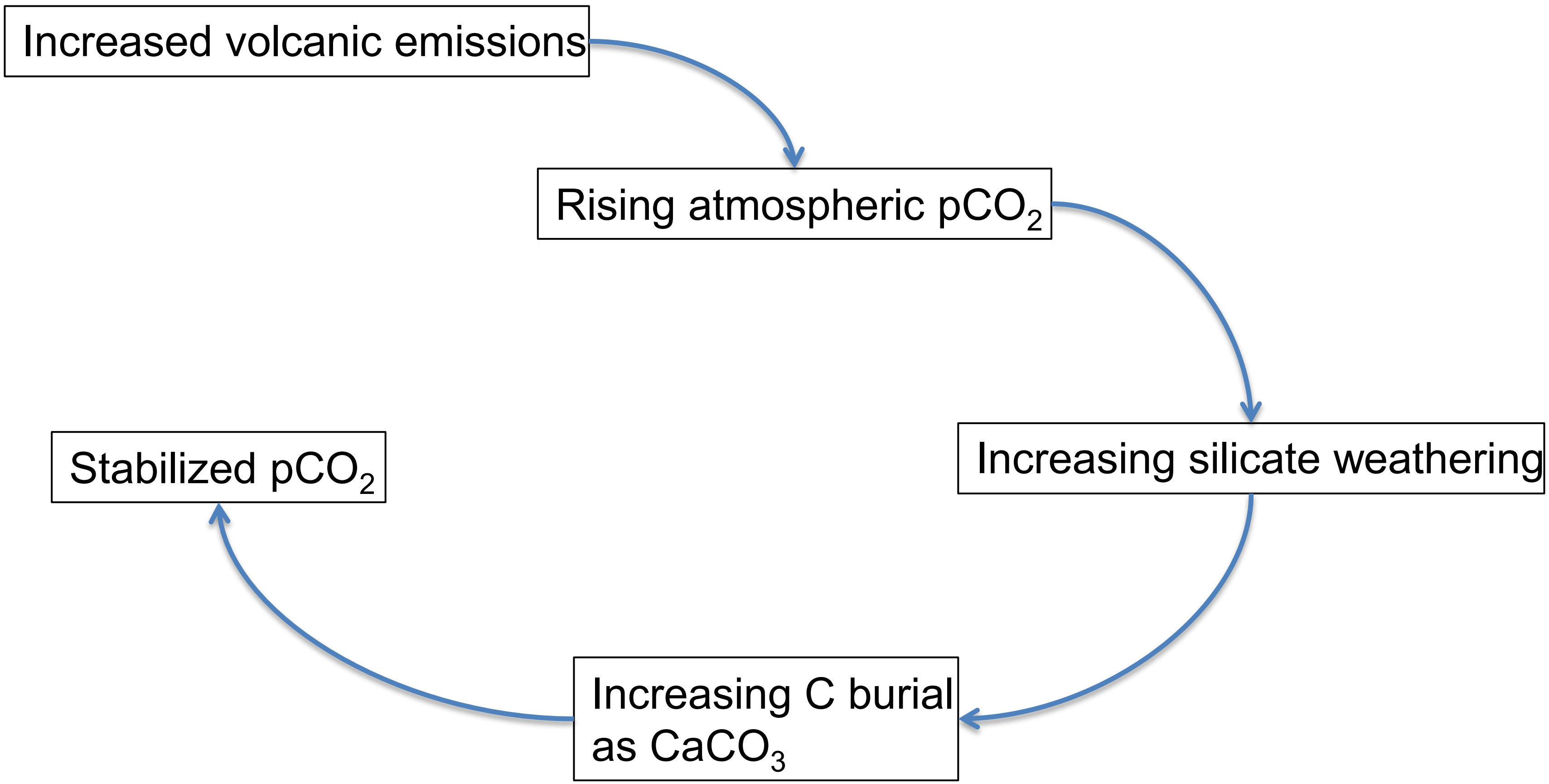
This image has been removed due to copyright restrictions. Please see: Figure 1. Beerling, D. J., D. L. Royer, et al. "Convergent Cenozoic CO2 history". *Nature Geoscience* 4, no. 7 (2011): 418–20. doi:10.1038/ngeo1186.

Long-term climate change can thus be interpreted in terms of

a) Changes in volcanic outgassing (e.g., due to changes in oceanic crust production at mid-ocean ridges)

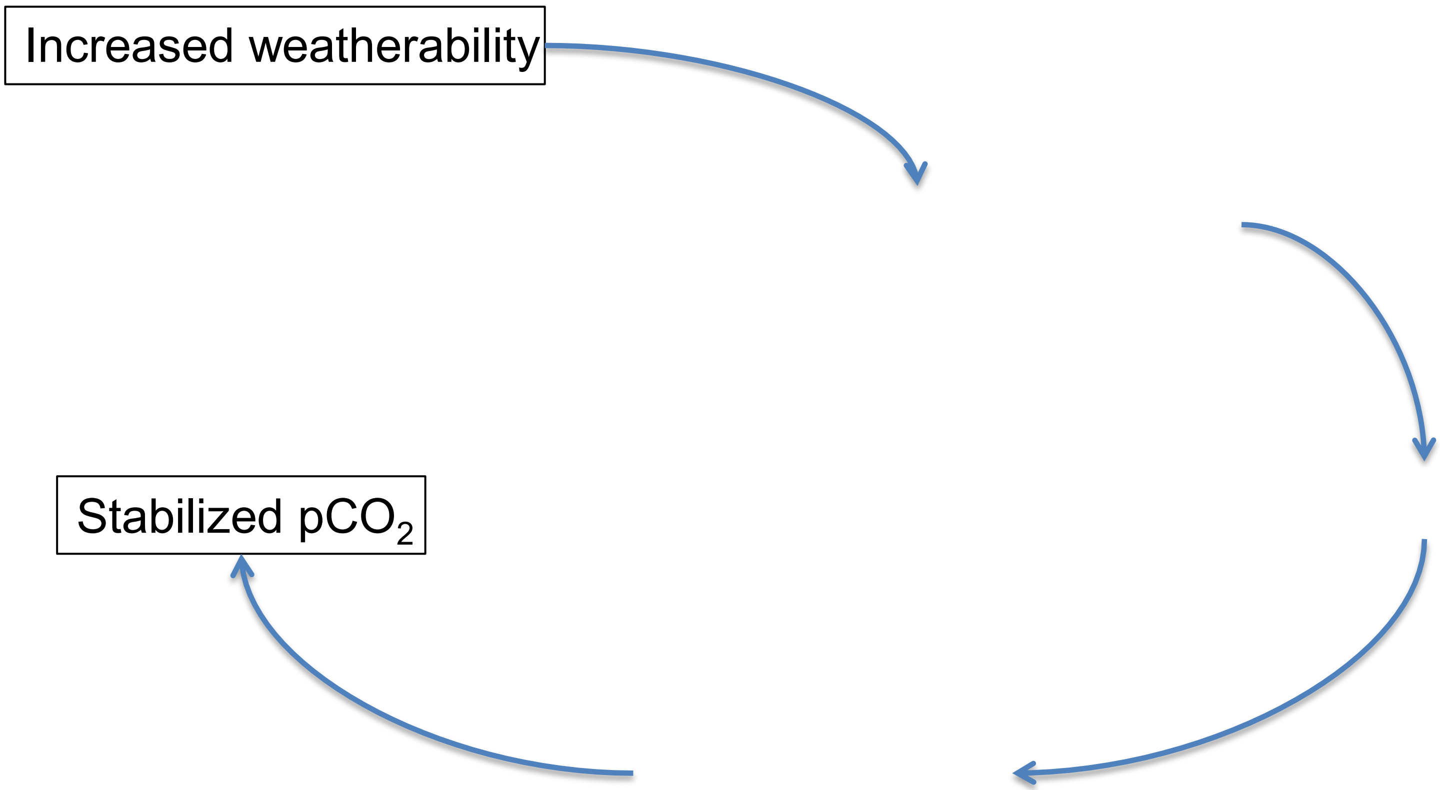
b) Changes in k_{sil} through changes in the “weatherability” of continents (e.g., due to mountain building, concentration of land masses near the equator, or volcanic activity producing large, highly-weatherable areas of Earth’s surface)

Silicate weathering CO_2 thermostat: examples

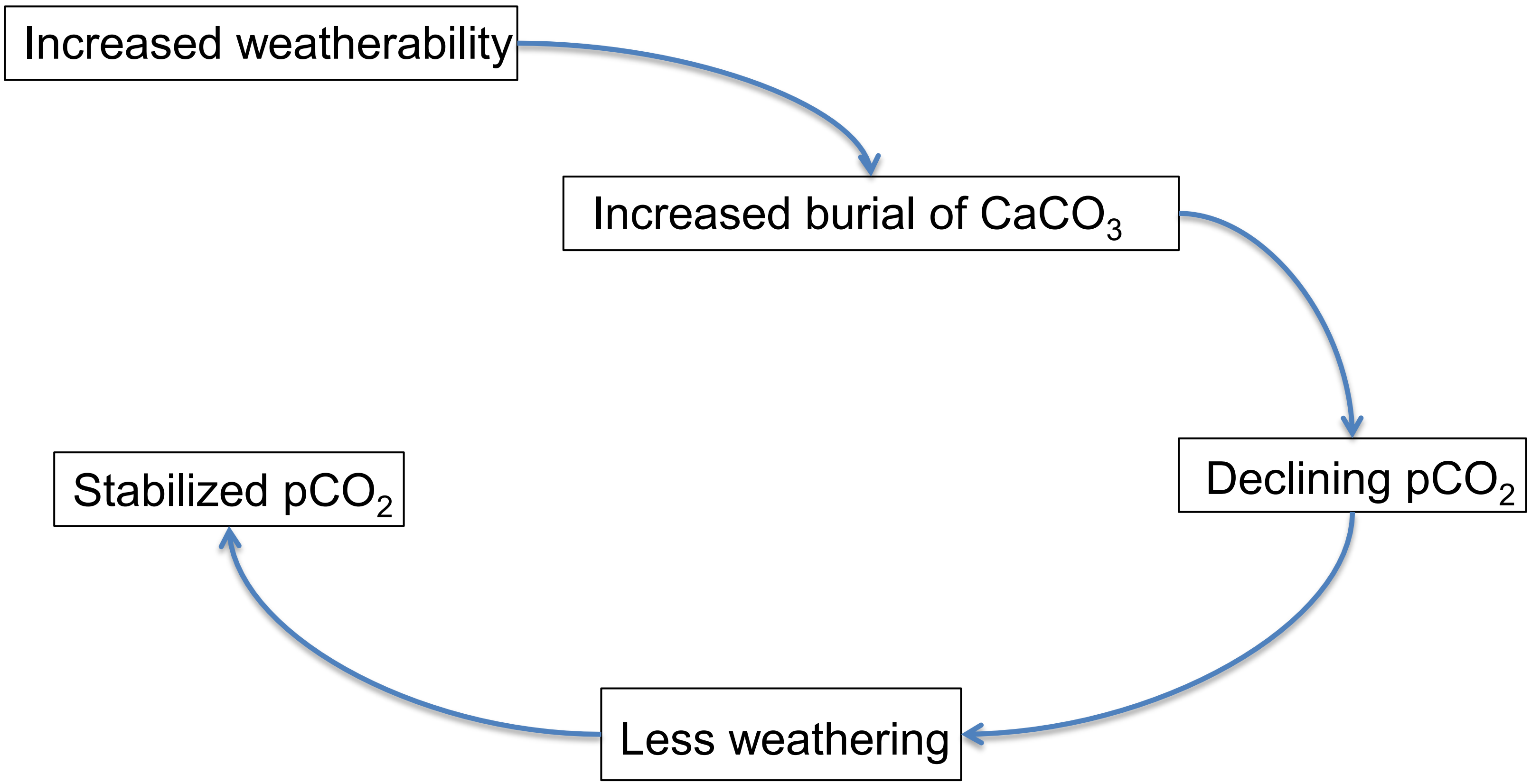


Atmospheric pCO_2 rises until weathering is sufficient to balance increased volcanic inputs, stabilizing atmospheric pCO_2.

Walker feedback: examples

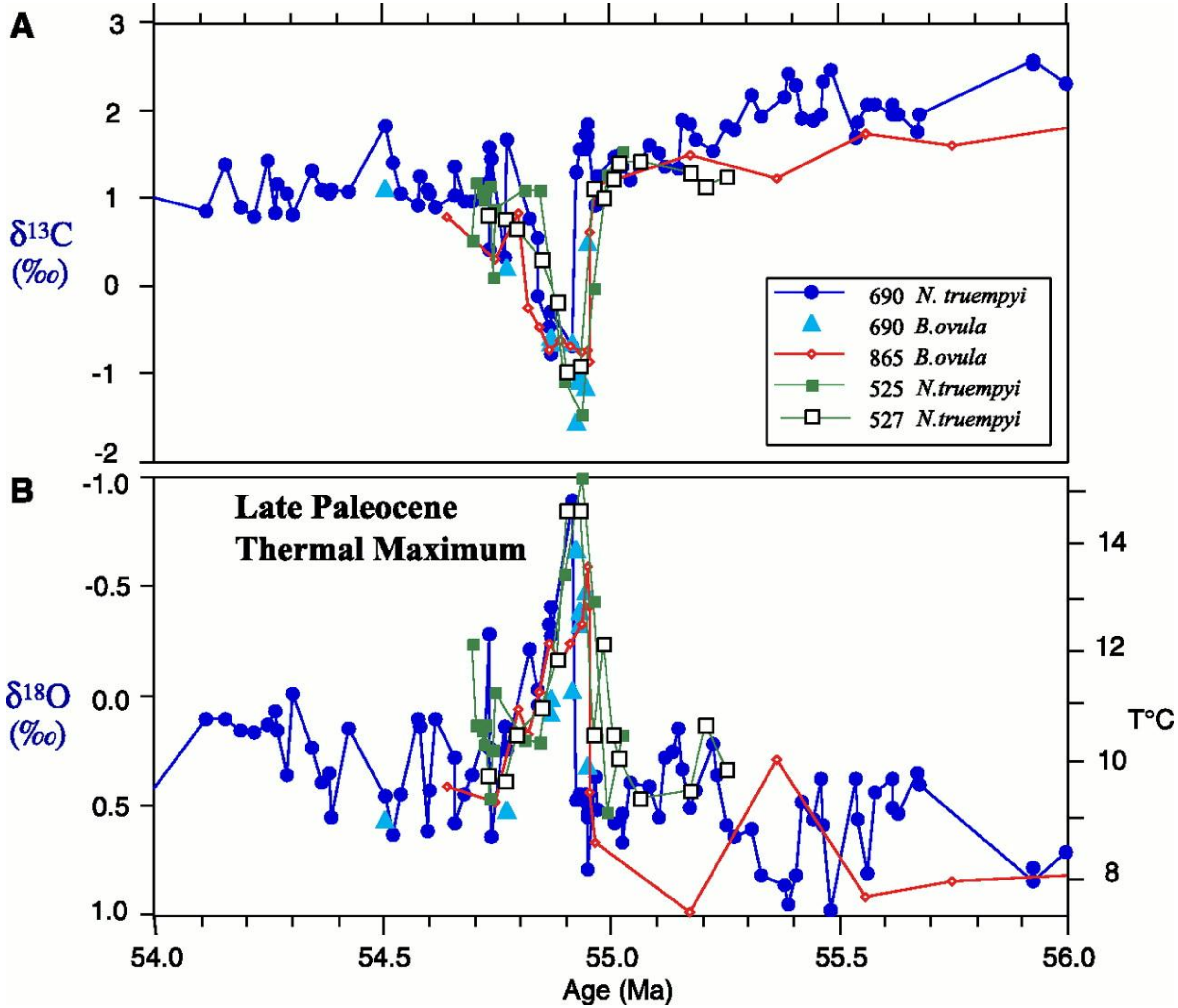


Walker feedback: examples



Atmospheric pCO_2 falls until weathering falls back into balance with volcanic inputs, stabilizing atmospheric pCO_2.

The Paleocene-Eocene Thermal Maximum (PETM), 55 Myr ago

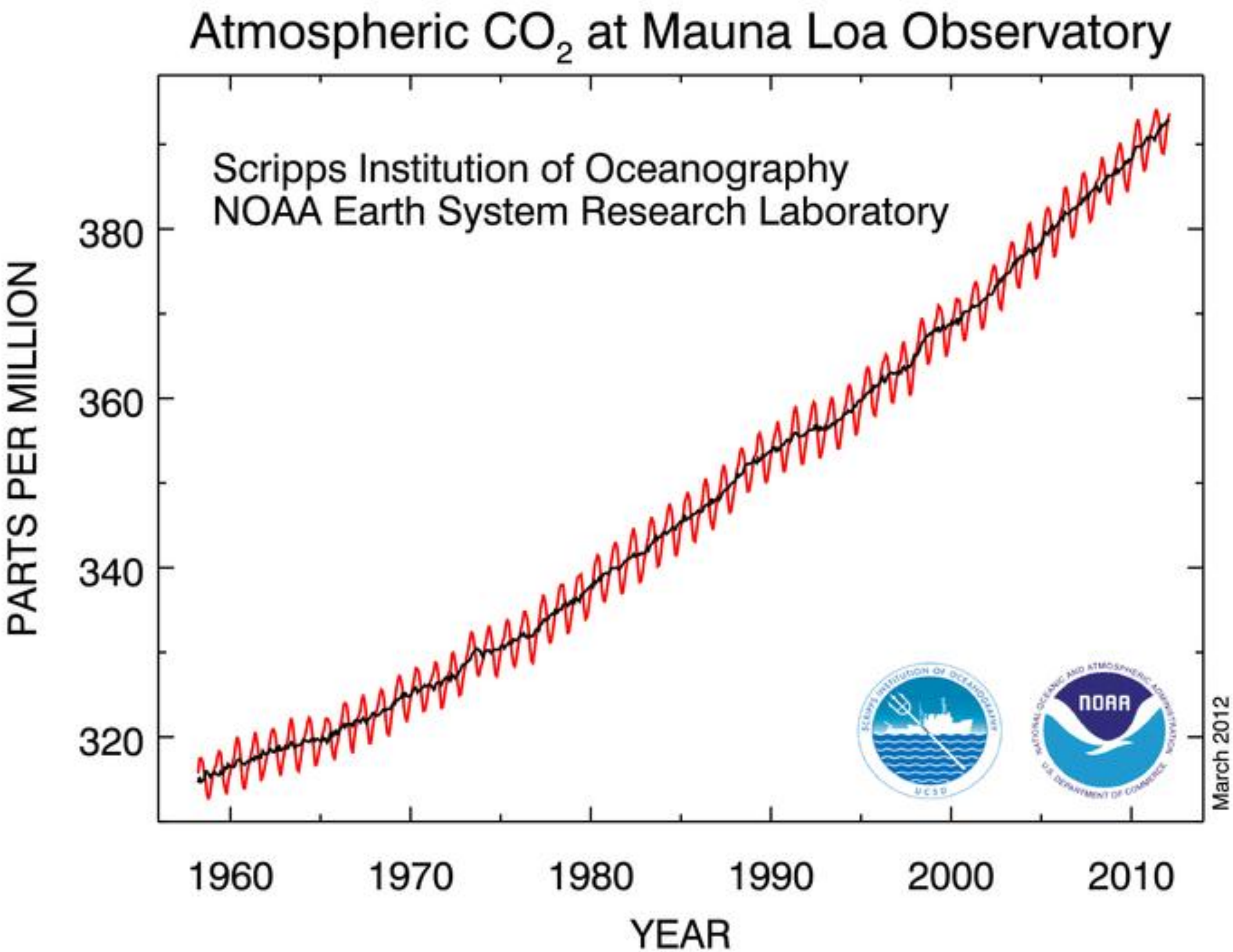


Addition of carbon to the atmosphere and ocean over ~10kyrs

Removal chiefly by silicate weathering feedback over ~200 kyrs

Short-term carbon fluxes

Sarmiento and Gruber, 2002



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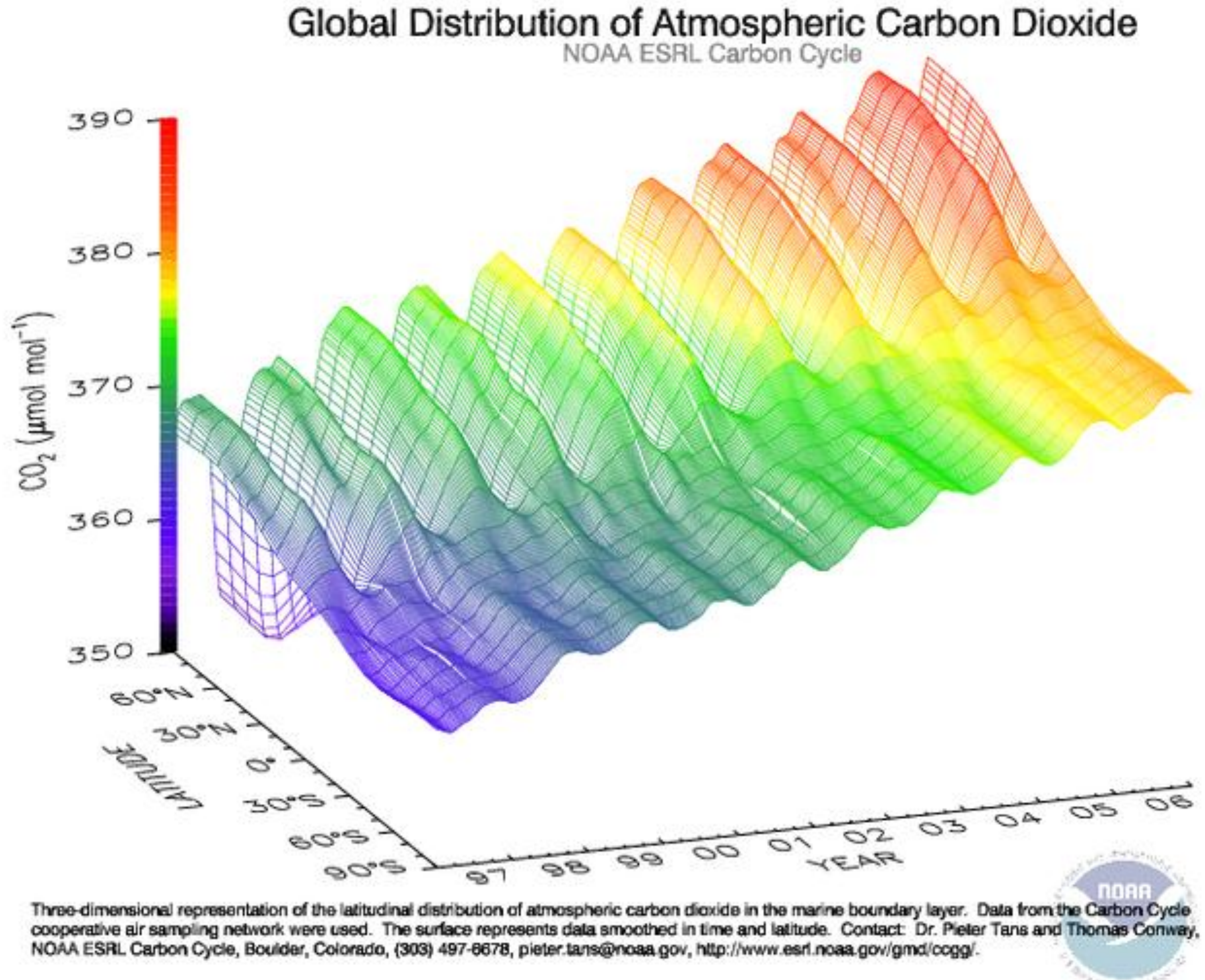

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Carbon emissions from fossil fuel use

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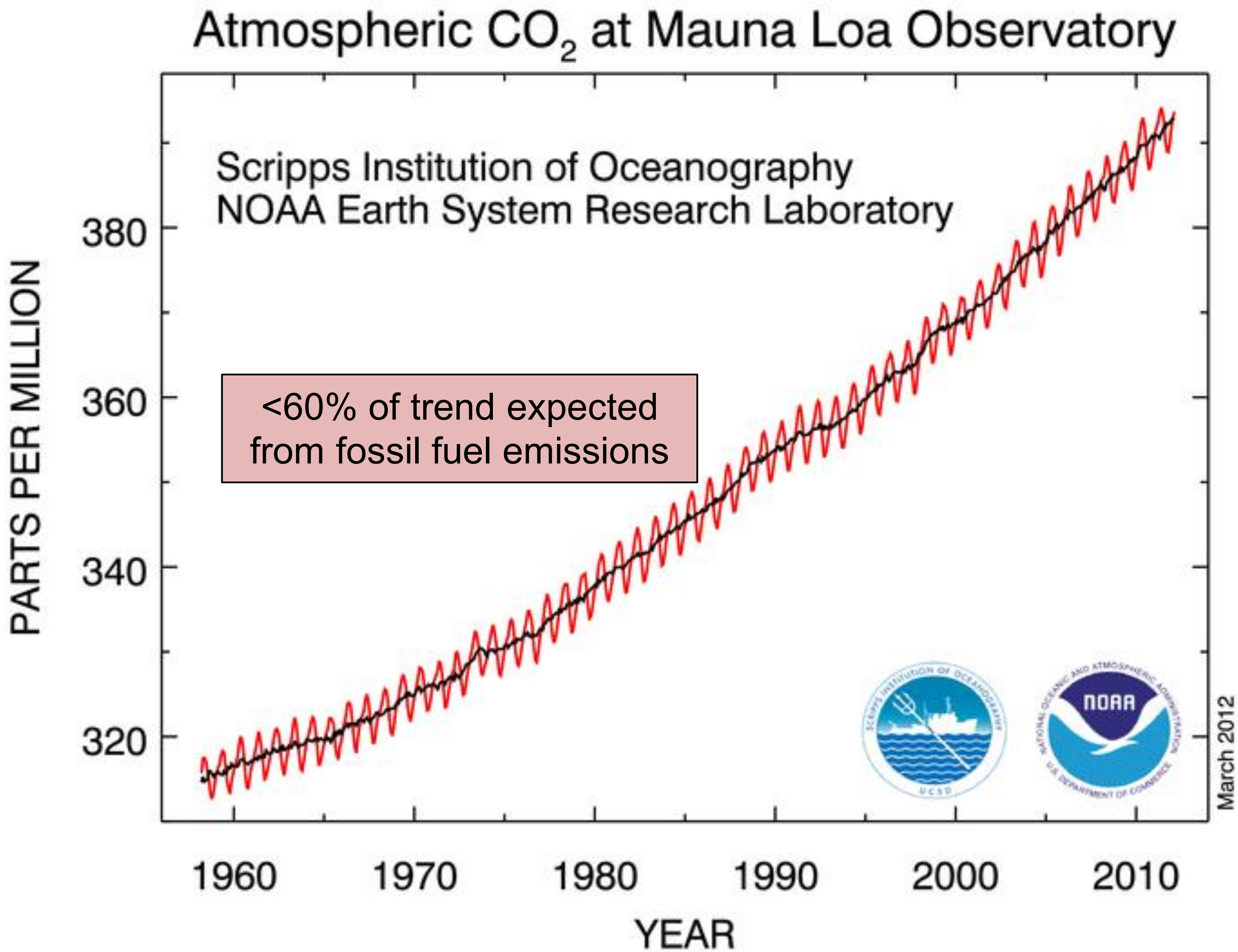

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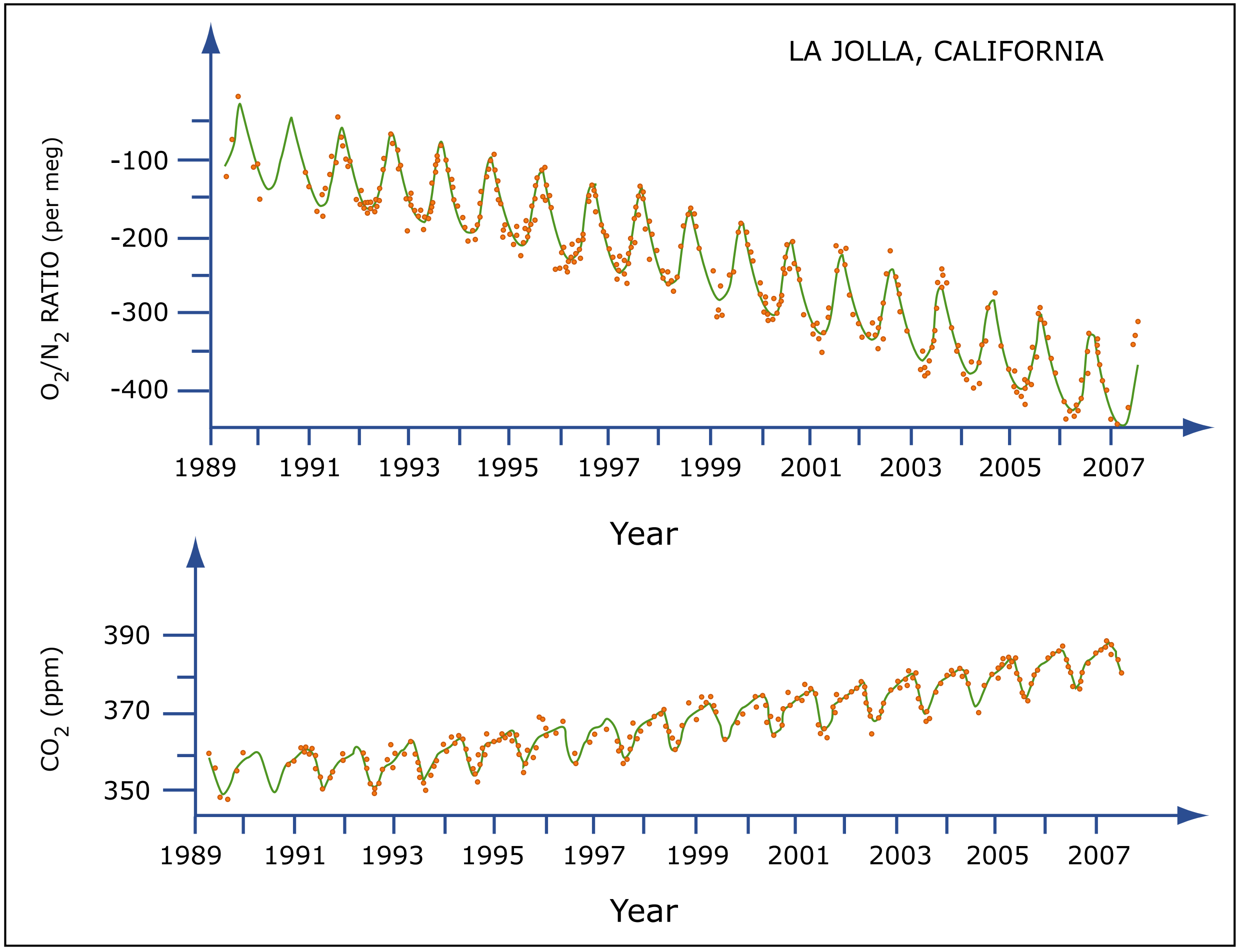
Where is the rest of the CO_2?

Important short-term CO_2 sinks

Terrestrial biosphere: Increase due to afforestation, CO_2 fertilization?

Ocean: Increase in CO_2 content of ocean waters?

One way of checking: measure changes in the O_2 content of the atmosphere



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Burning of fossil fuels leads to declining O_2, while increase in size of terrestrial biosphere causes rising O_2, and ocean uptake of CO_2 doesn't affect O_2.

Suggests net terrestrial sink is smaller than the marine sink

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Note large uncertainties in terrestrial source and sink!

Global Carbon Project 2010; Updated from Le Quéré et al. 2009, Nature Geoscience; Canadell et al. 2007, PNAS

Why is so much CO_2 going into the ocean?

Argon (similar mass to CO_2):

~40x more Ar in the atmosphere than in the ocean

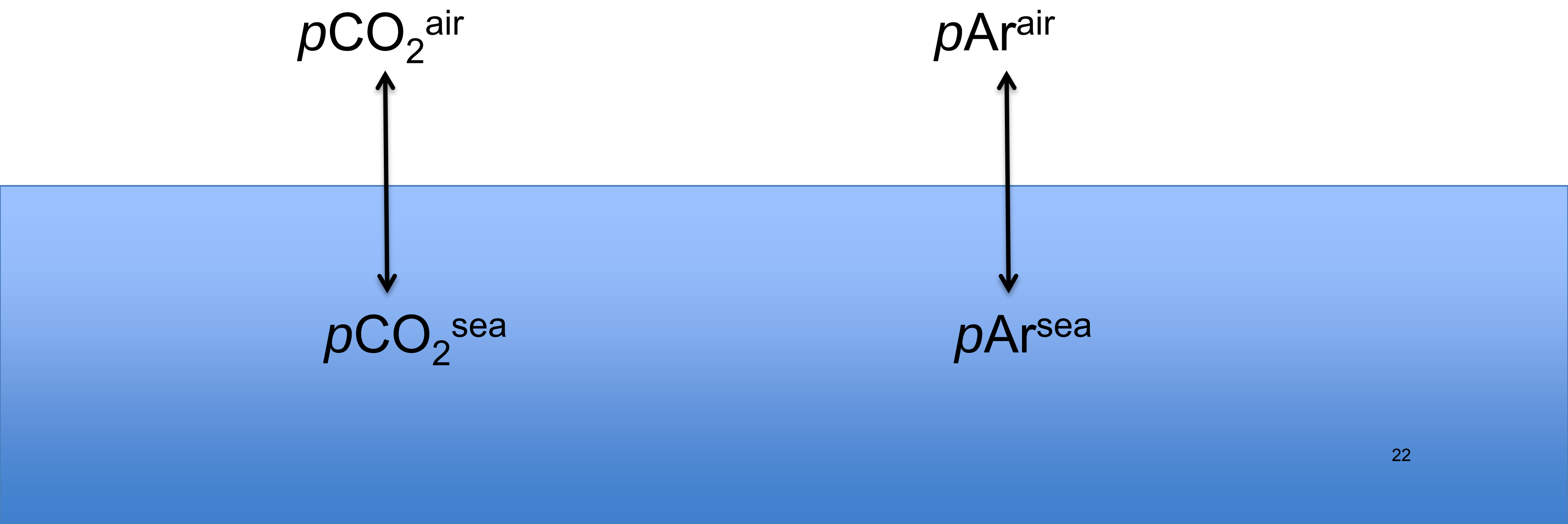
CO_2:

>60x more CO_2 in the ocean than in the atmosphere!

Why is so much CO_2 going into the ocean?

For both gases, air-sea fluxes are proportional to the difference in partial pressures between the atmosphere and surface ocean:

$$F_{air-sea}\alpha(p^{air}-p^{sea})$$



Why is so much CO_2 going into the ocean?

But while Ar stops there, CO_2 undergoes a number of transformations:

pCO_2^{air} $\updownarrow$ pCO_2^{sea}

pAr^{air} $\updownarrow$ pAr^{sea}

pCO_2^{sea}

$\updownarrow$

$H_2CO_3^*$ — Carbonic acid + aqueous CO_2

$\updownarrow$

HCO_3^- — Bicarbonate ion

$\updownarrow$

CO_3^{2-} — Carbonate ion

(note: full equations not shown for clarity)

The full equations:

$$CO_{2(gas)} + H_2O \leftrightarrow H_2CO_3^*$$

$$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$$

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

Dissolved inorganic carbon = DIC = TCO_2

$= H_2CO_3^* + HCO_3^- + CO_3^{2-}$

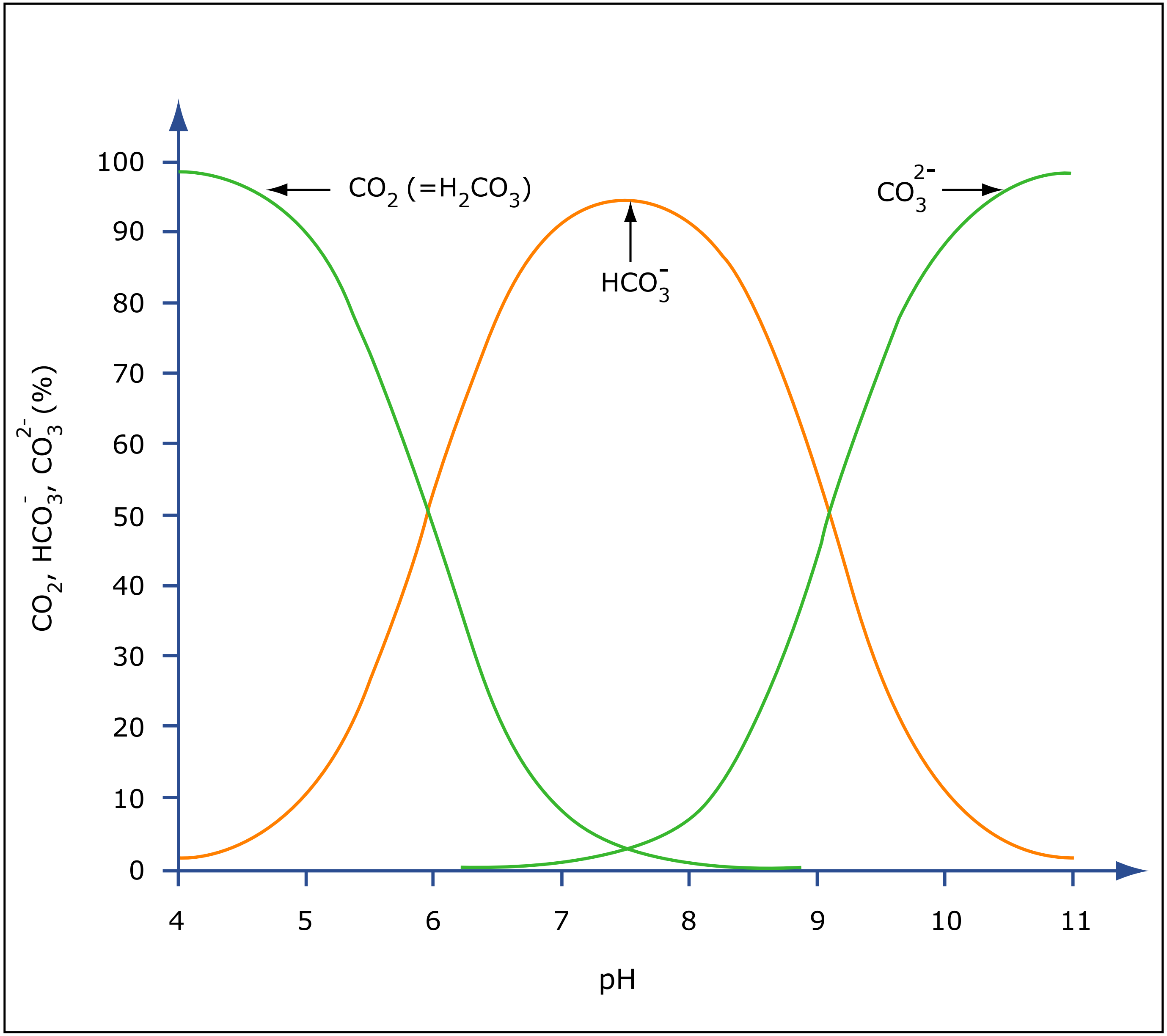
Where $H_2CO_3^*$ (sometimes shown simply as CO_2) denotes the combination of H_2CO_3 and $CO_{2(aq)}$, which are hard to distinguish analytically.

Note that adding CO_2 to the ocean acts to increase H^+ concentrations (i.e., reduce pH)

$$CO_{2(gas)} + H_2O \leftrightarrow H_2CO_3^*$$

$$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$$

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



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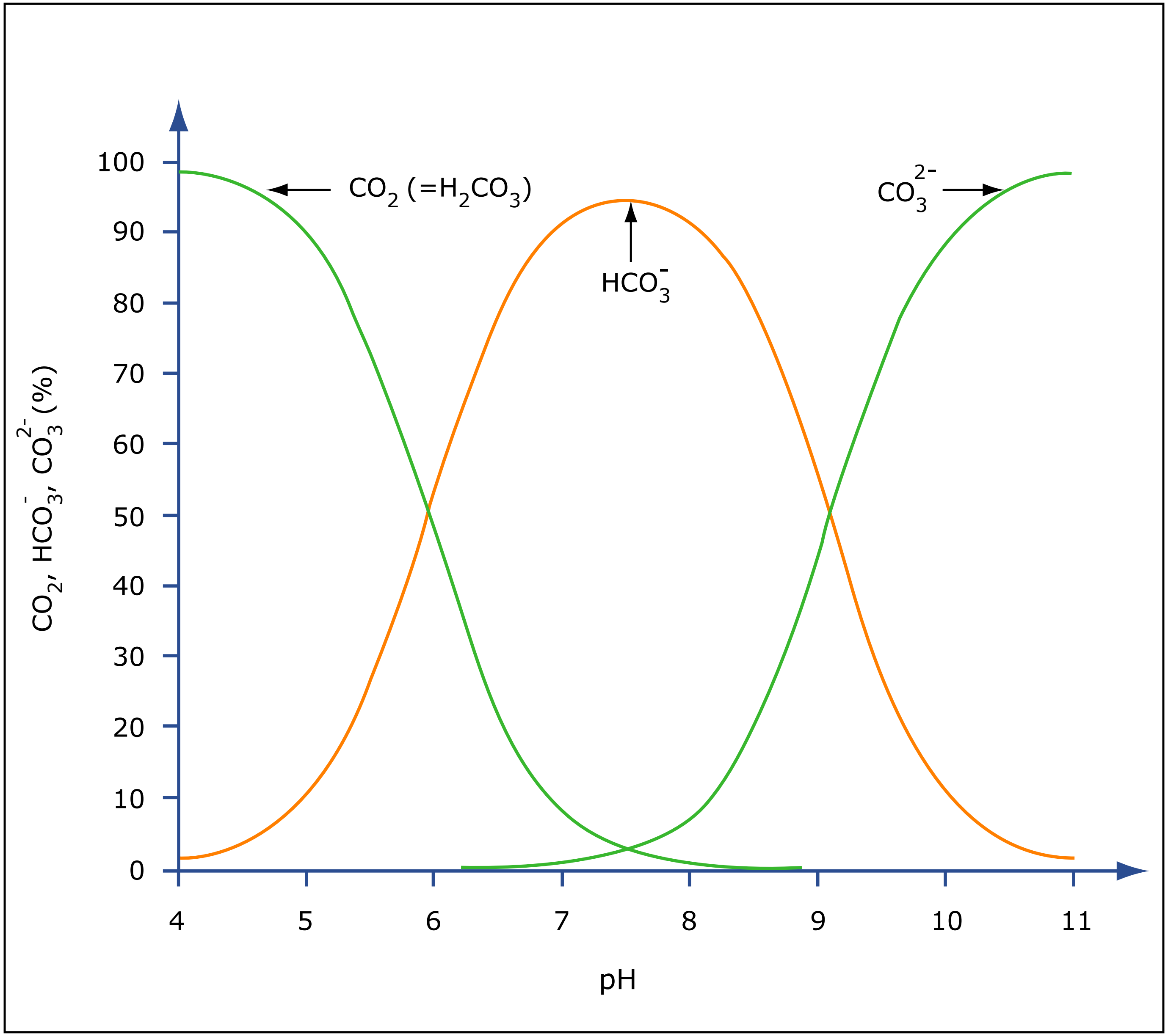
At the pH of seawater (~8.2), DIC is ~0.5% $H_2CO_3^*$, 88.5% HCO_3^-, and 11% CO_3^{2-}



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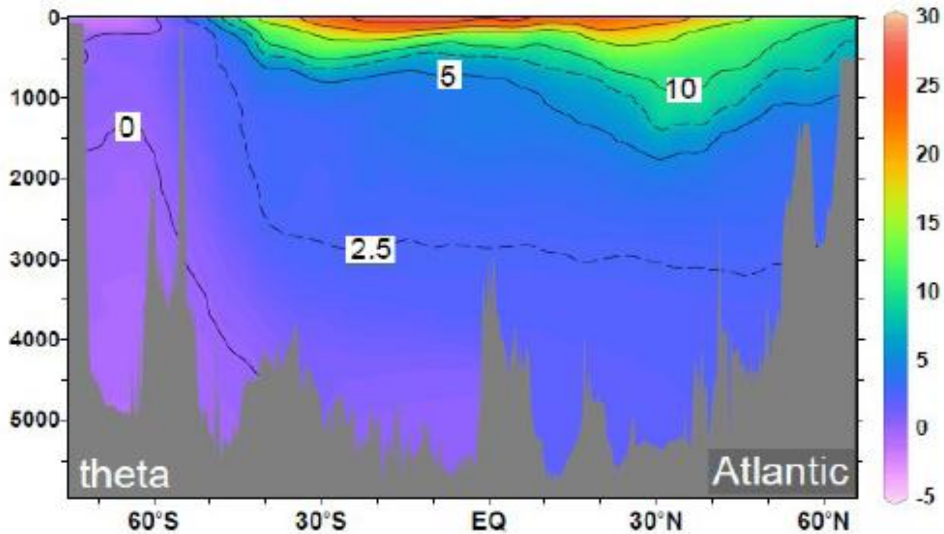
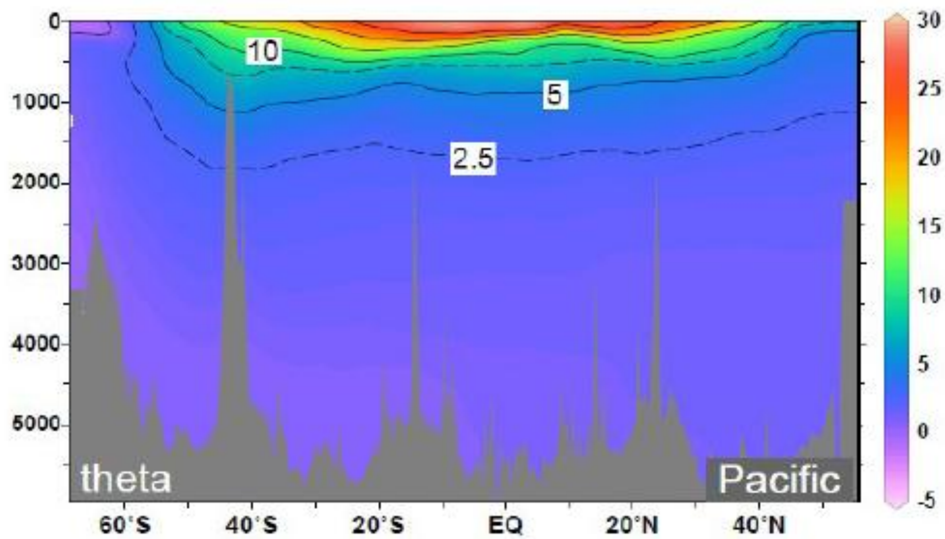
As pH falls, carbonate ion concentrations go down and $H_2CO_3^*$ concentrations go up, reducing the ocean's ability to take up more CO_2.

"Pumps" and vertical DIC gradients





Potential temperature θ (°C)

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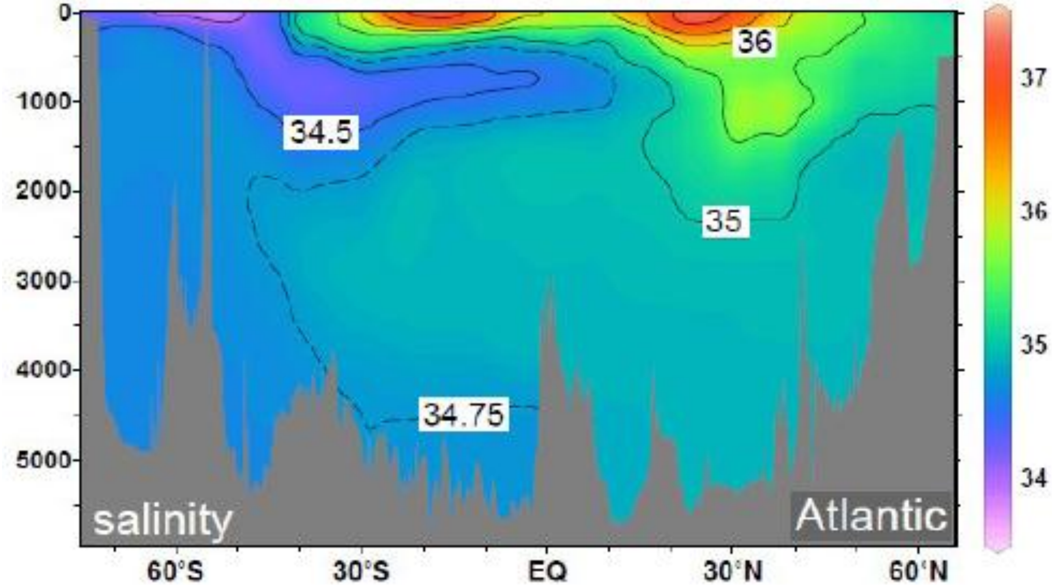
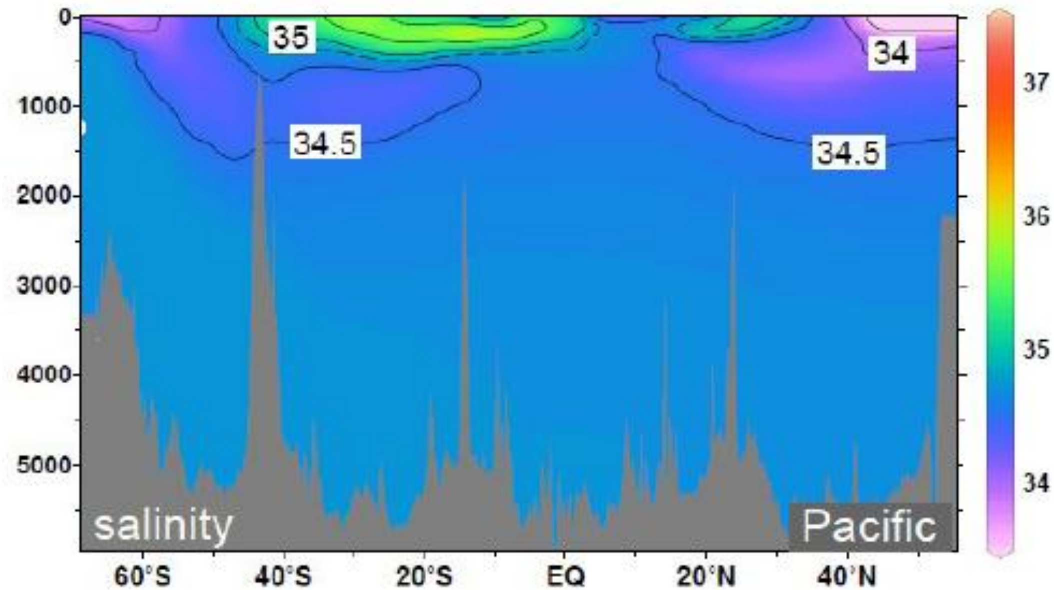


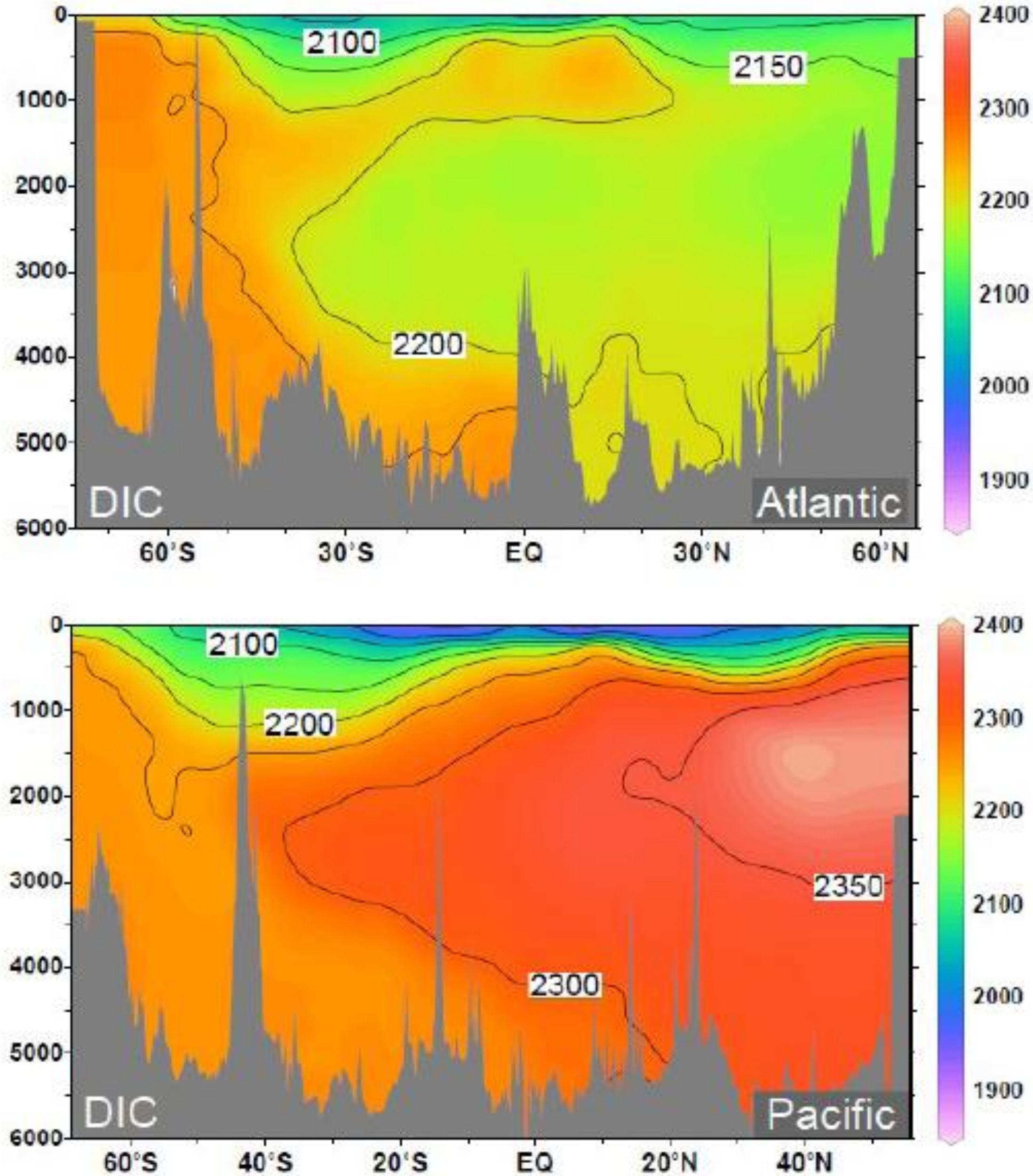


Salinity S (psu)

- Renewal of deep and bottom waters takes on the order of 1000 yrs

Dissolved Inorganic Carbon

DIC (μmol kg^{-1})



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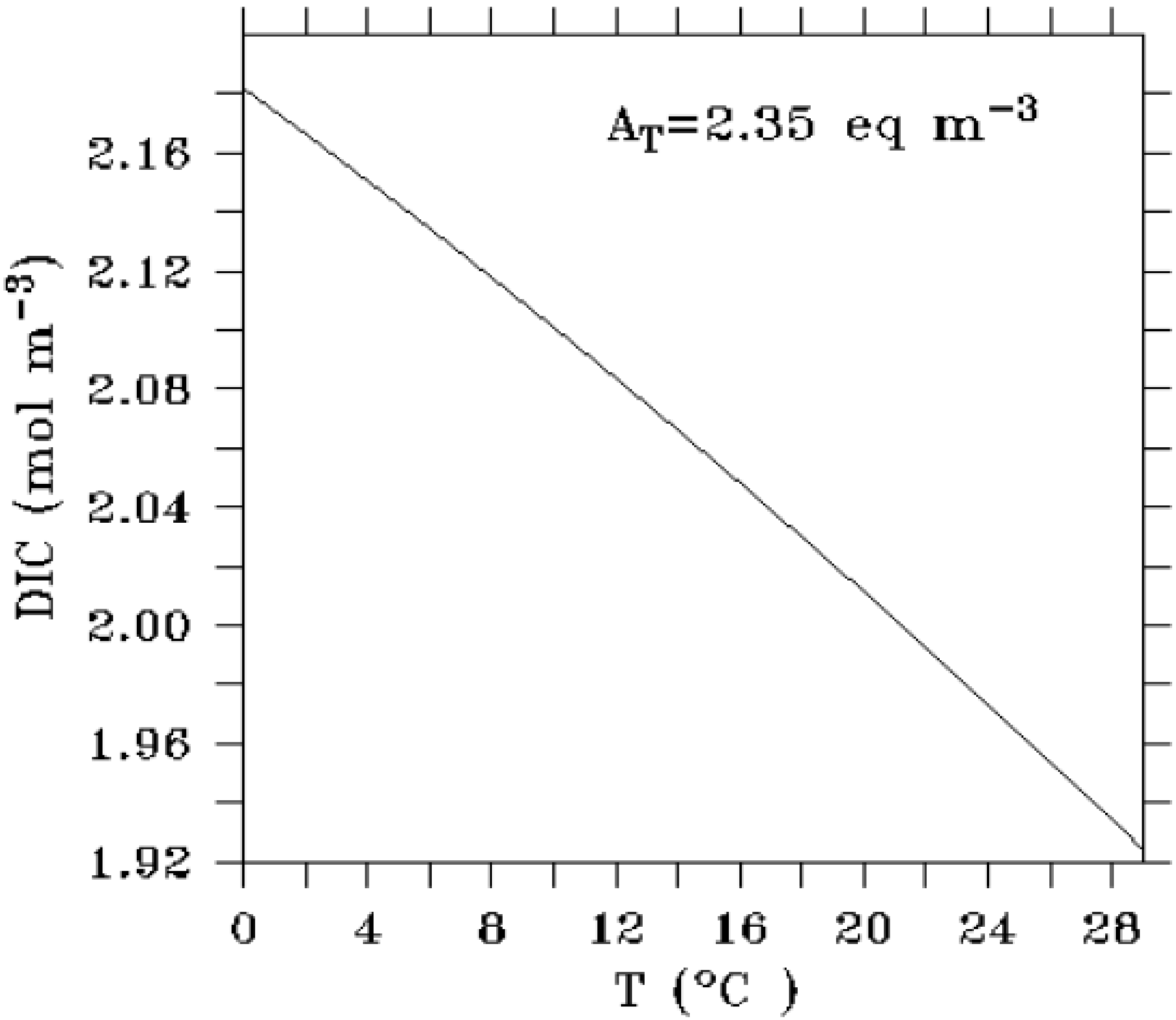
- Why does DIC increase with depth?
- What causes the gradients in deep Pacific?

Equilibrium DIC higher at lower T



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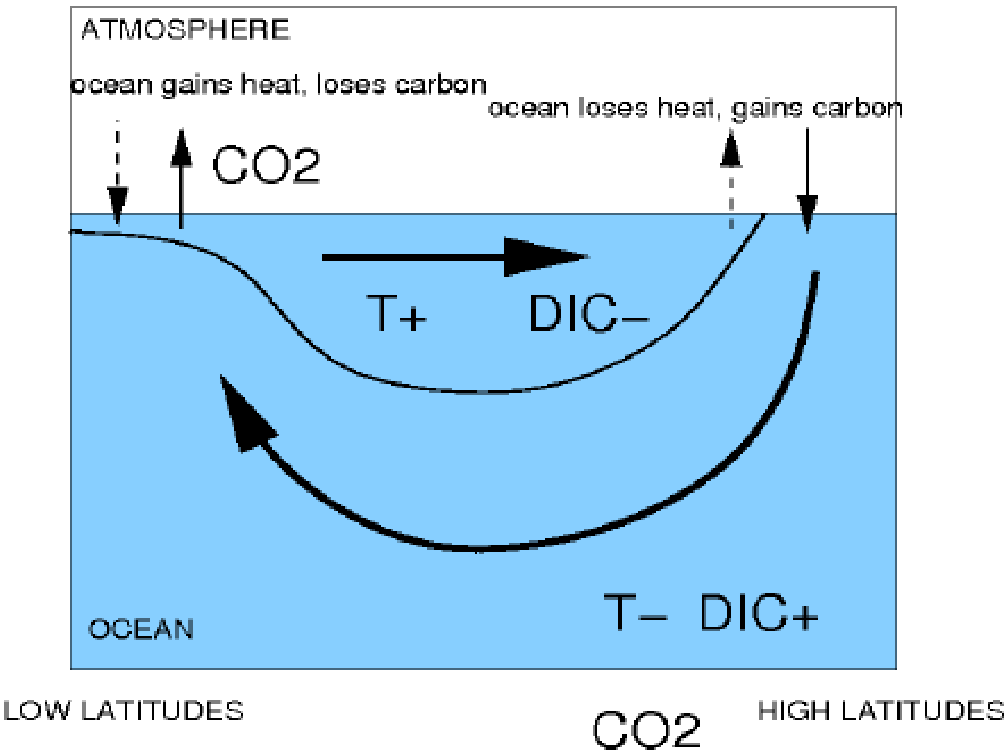
"Solubility Pump" of carbon



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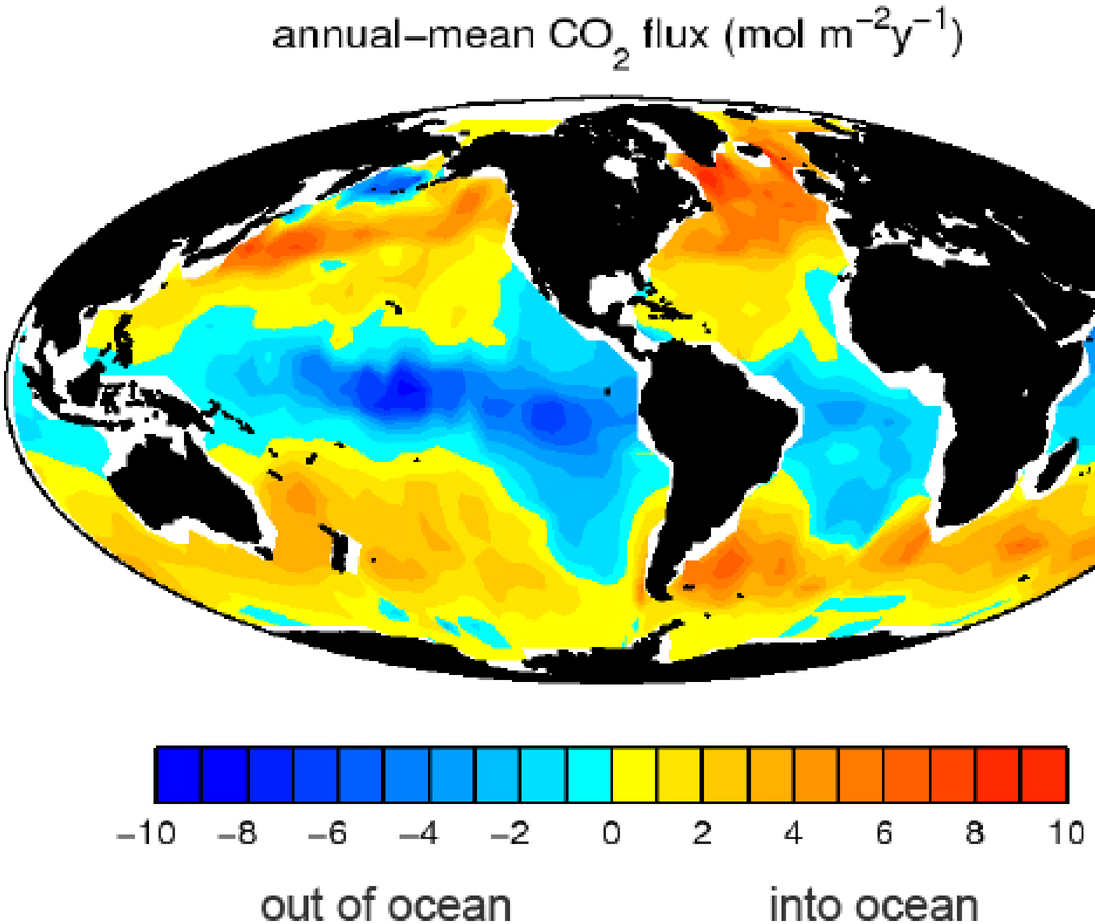
- Cooling of high latitude surface waters increases solubility of CO2 and saturation DIC
- Induces uptake of CO2 from atmosphere and increase of DIC
- Cooler waters are denser and form oceans deep waters, sliding under warmer surface layer
- Cool, DIC rich waters underneath warm, DIC-depleted waters
- Sequesters carbon as DIC in deep ocean, away from atmosphere

Air-Sea Flux of CO2



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Data from Takahashi et al (2002)

Marine food web and carbon cycle

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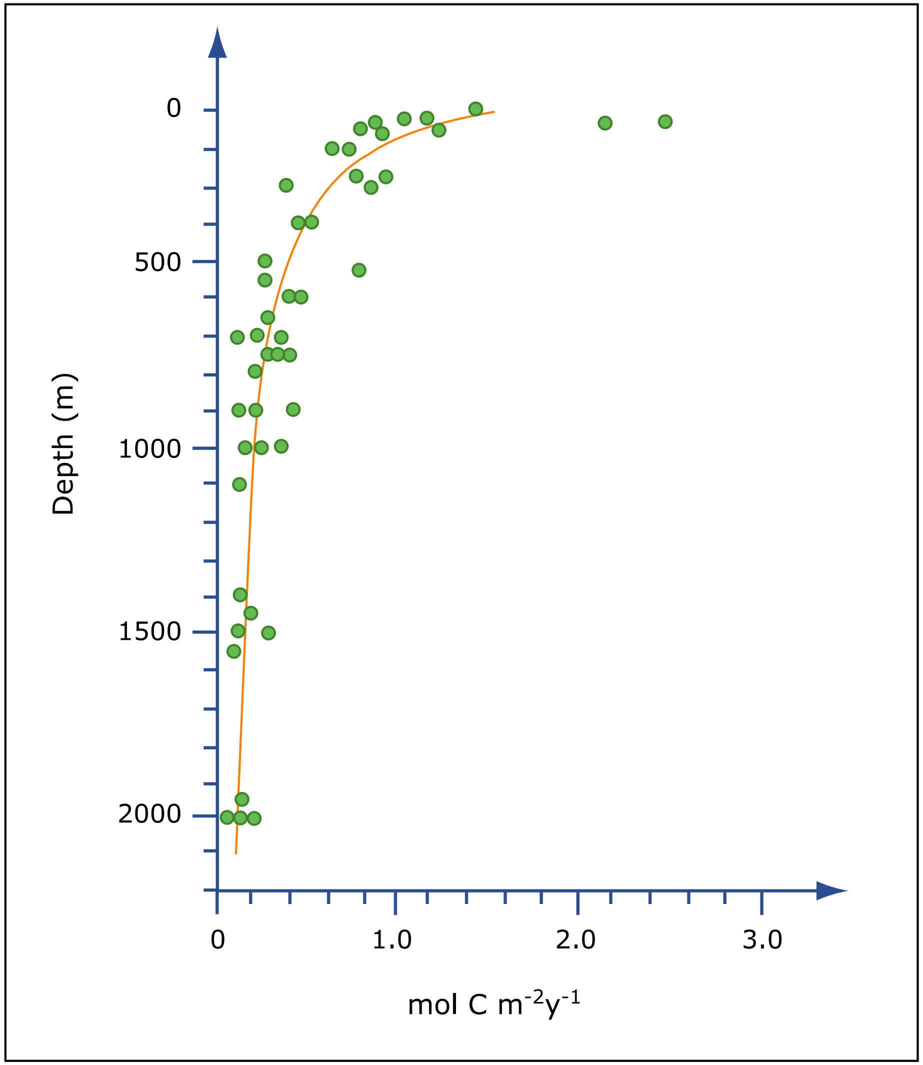
Sallie Chisholm

Organic particles sink from surface to be respired at depth



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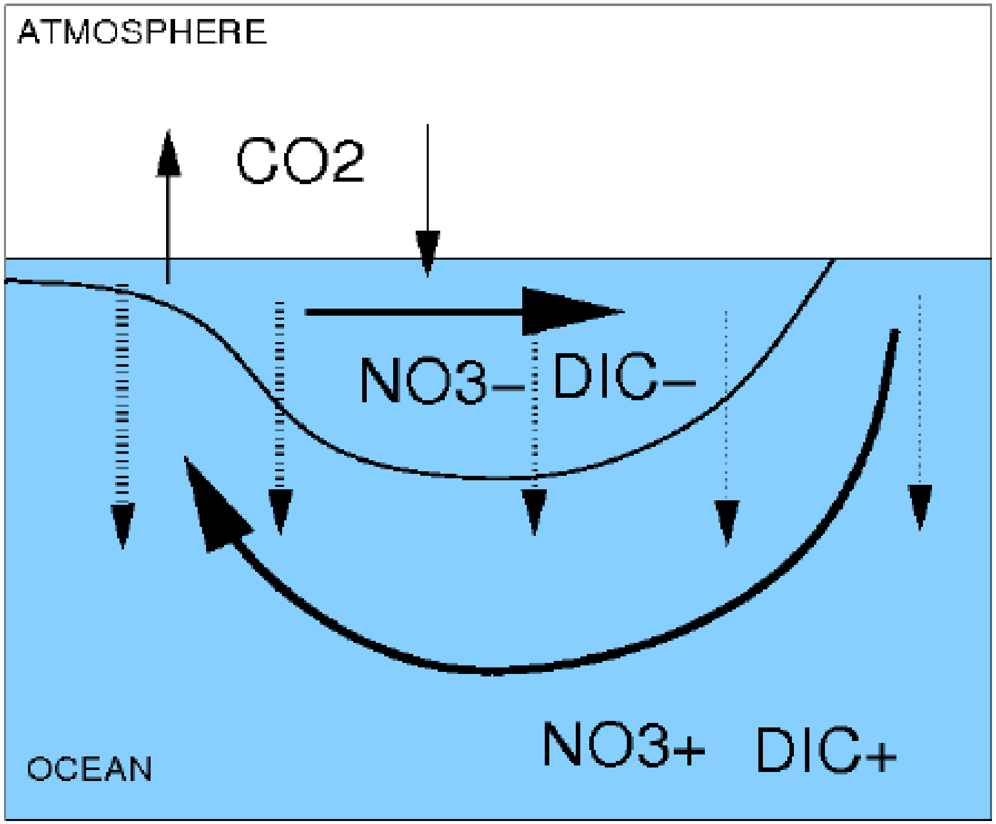
- Less than 1% reaches sea floor in deep ocean
- Carbon, nitrogen, phosphorus, iron, etc. returned to inorganic form in the deep waters

"Biological Pump" of carbon (soft tissue pump)



UPWELLING DOWNWELLING

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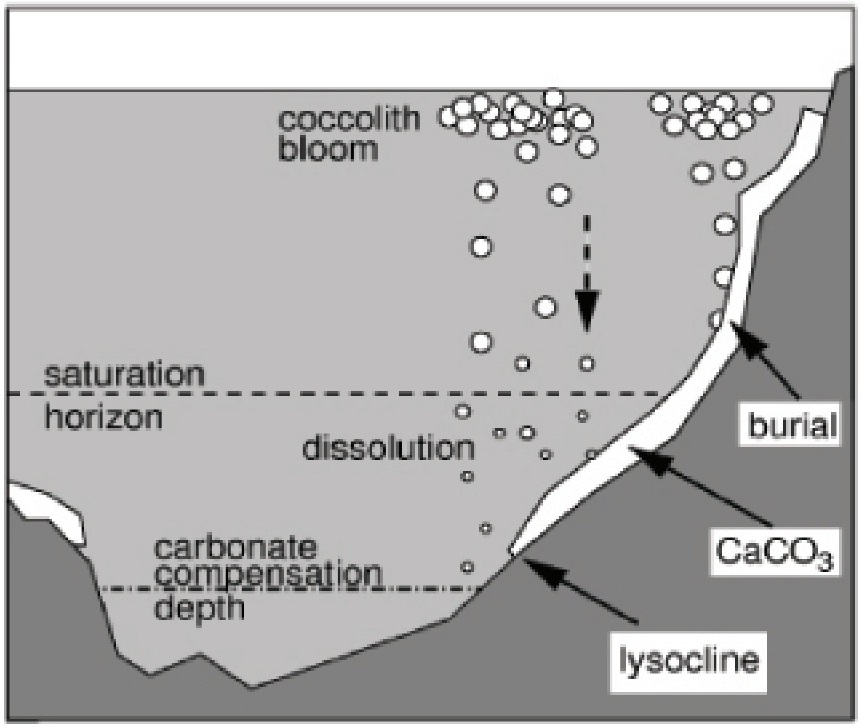
- Production of organic matter consumes nitrate, DIC in surface waters
- Reduces surface ocean CO_2, induces uptake from atmosphere
- Organic particles sink, respired at depth
- Increase deep ocean DIC and reduce atmospheric pCO_2

"Biological Pump" of carbon (carbonate pump)



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- Some phytoplankton create mineral calcium carbonate structures
  - $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$
- Sinks and dissolves in deep waters where undersaturated

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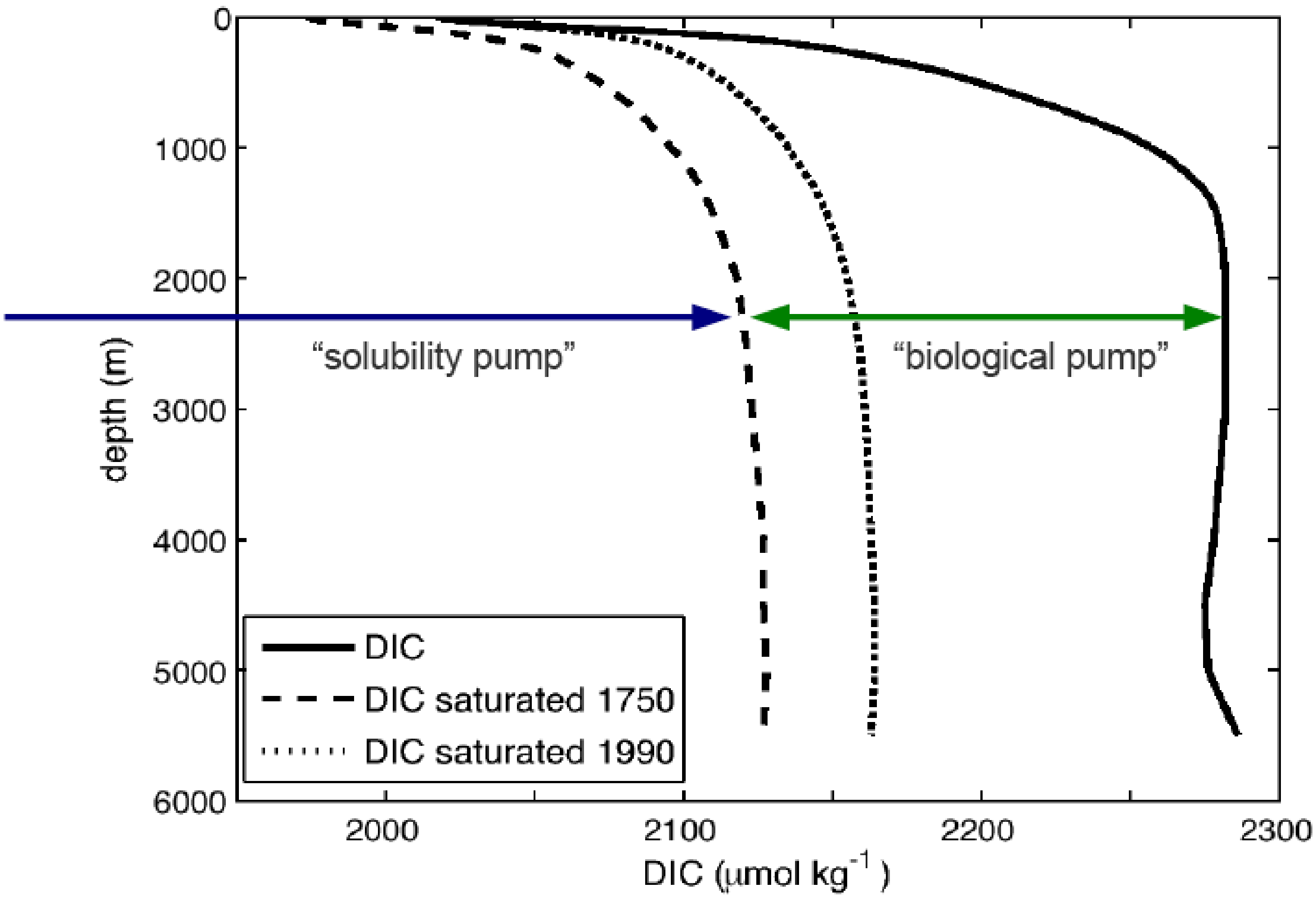
Vertical profile of DIC in global ocean



Killing biological pump would lead to increase in atmos CO2 of ~200ppmv

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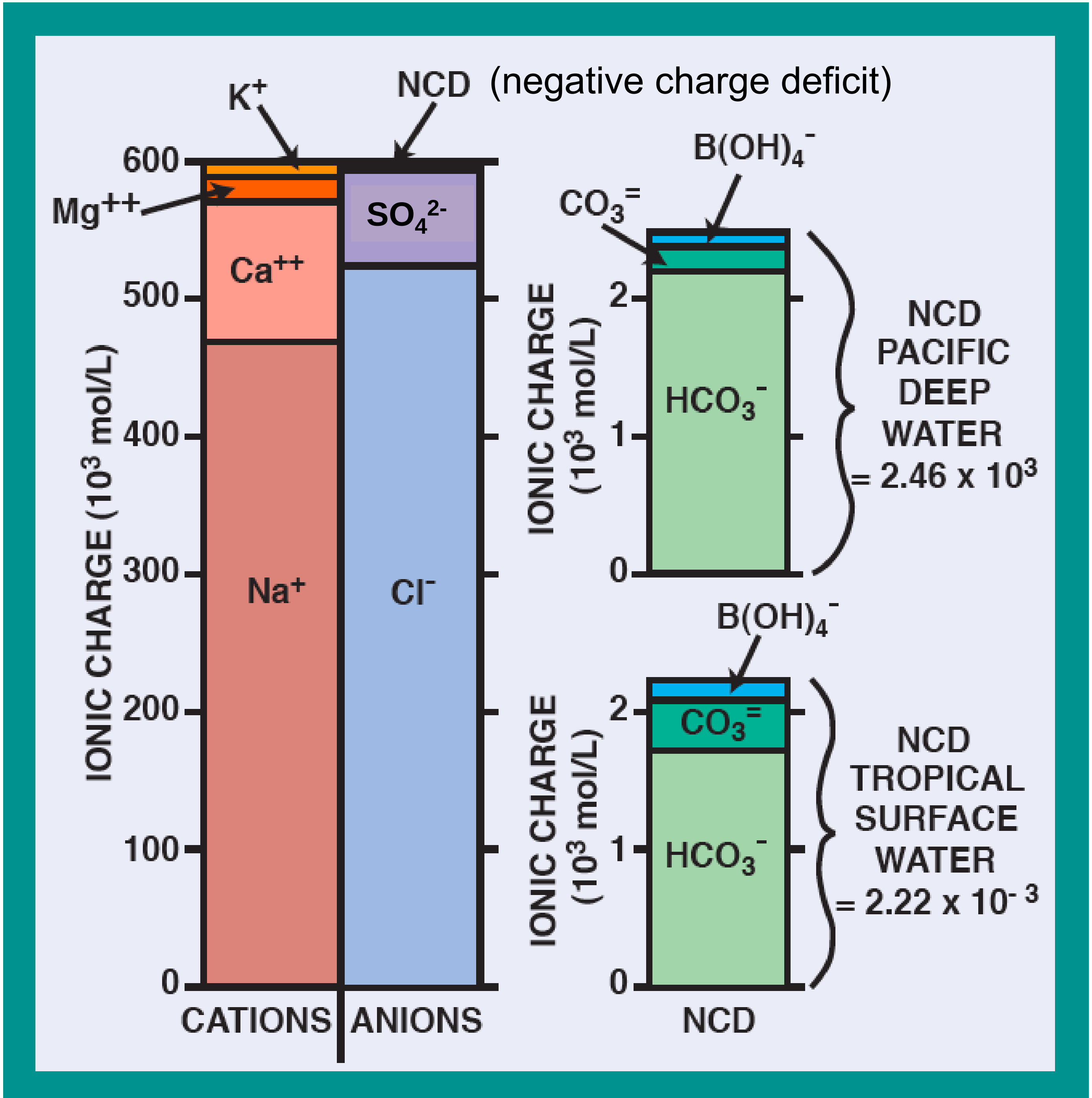
Alkalinity

The ocean's acid-buffering capability.

Equivalent to the charge imbalance between strong (i.e., unchanging) positive and strong negative ions. Silicate weathering increases alkalinity by preferentially adding ions like Ca^{2+}, Mg^{2+}, etc.

The charge imbalance between strong cations and strong anions is largely balanced by carbonate and bicarbonate ions, meaning that the higher the imbalance and the lower the DIC, the more DIC must exist as carbonate ion (-2 charge).

Rule of thumb: Alk-DIC ~ $[CO_3^{2-}]$.



NCD (negative charge deficit)
K+
Mg++
Ca++
Na+
SO4 2-
Cl-
600
500
400
300
200
100
0
IONIC CHARGE (10^3 mol/L)
CATIONS
ANIONS
B(OH)4-
CO3=
HCO3-
IONIC CHARGE (10^3 mol/L)
2
1
0
NCD
PACIFIC
DEEP
WATER
= 2.46 x 10^3
B(OH)4-
CO3=
HCO3-
IONIC CHARGE (10^3 mol/L)
2
1
0
NCD
TROPICAL
SURFACE
WATER
= 2.22 x 10- 3
NCD

Right now anthropogenic CO_2 is causing DIC in the oceans to increase while alkalinity stays roughly constant. What do you predict is happening to carbonate ion concentrations?

The "long tail" of anthropogenic CO_2

Uptake of 1000 Pg C pulse

Different experiments reflect model runs with varying feedbacks included; the dotted lines include the most feedbacks (climate, sediments, weathering, vegetation)

The "long tail" of anthropogenic CO_2

CONCLUSIONS

The models presented here give a broadly coherent picture of the fate of fossil fuel CO_2 released into the atmosphere. Equilibration with the ocean will absorb most of it on a timescale of 2 to 20 centuries. Even if this equilibration were allowed to run to completion, a substantial fraction of the CO_2, 20–40%, would remain in the atmosphere awaiting slower chemical reactions with $CaCO_3$ and igneous rocks. The remaining CO_2 is abundant enough to continue to have a substantial impact on climate for thousands of years. The changes in climate amplify themselves somewhat by driving CO_2 out of the warmer ocean. The CO_2 invasion has acidified the ocean, the pH of which is largely restored by excess dissolution of $CaCO_3$ from the sea floor and on land and, ultimately, by silicate weathering on land. The recovery of ocean pH restores the ocean's buffer capacity to absorb CO_2, tending to pull CO_2 toward lower concentrations over the next 10,000 years. The land biosphere has its greatest impact within the first few centuries, which is when CO_2 peaks. Nowhere in these model results or in the published literature is there any reason to conclude that the effects of CO_2 release will be substantially confined to just a few centuries. In contrast, generally accepted modern understanding of the global carbon cycle indicates that climate effects of CO_2 releases to the atmosphere will persist for tens, if not hundreds, of thousands of years into the future.

Archer et al., Annual Reviews of Earth and Planetary Science 2009 (a nice paper)