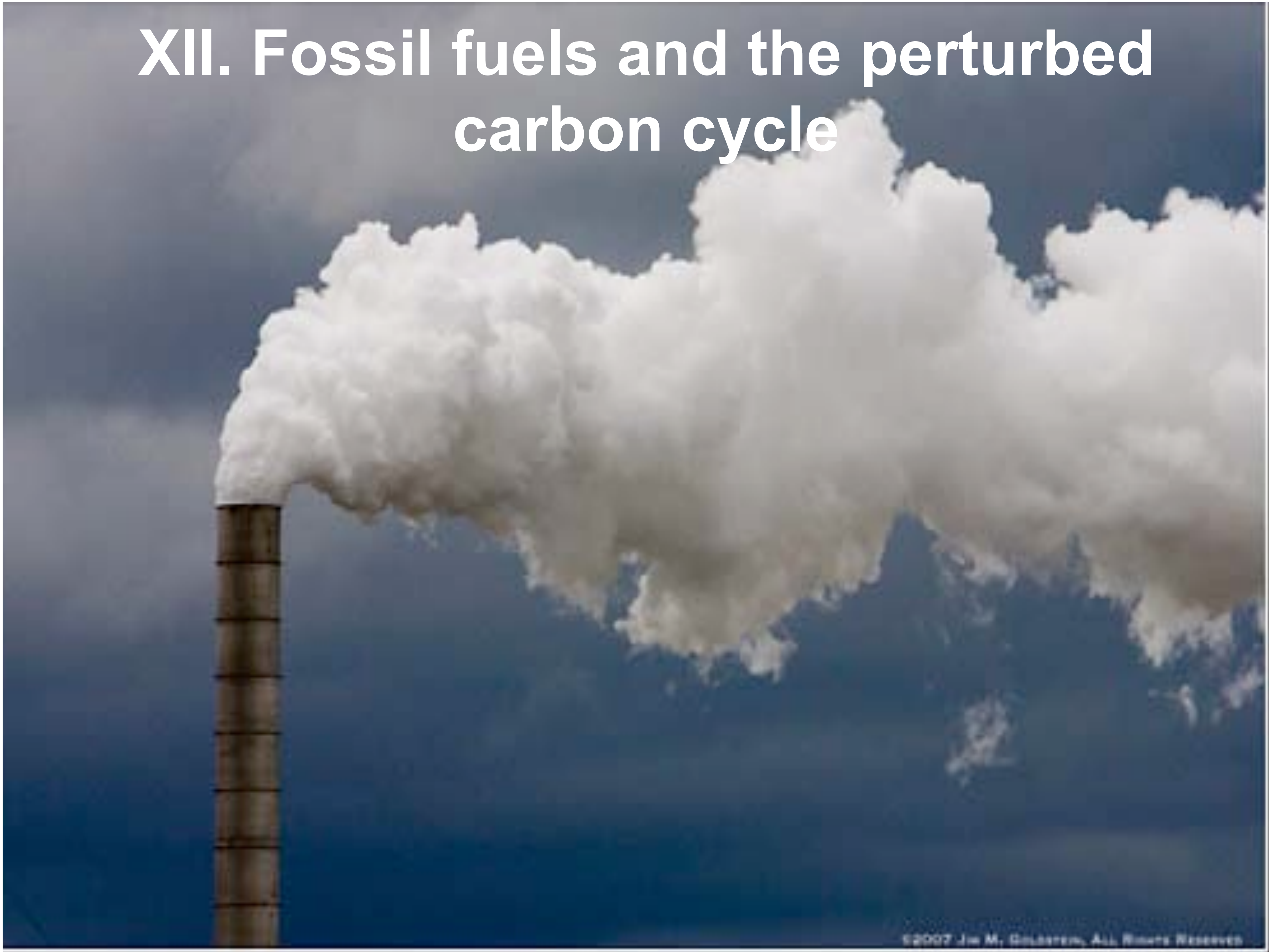
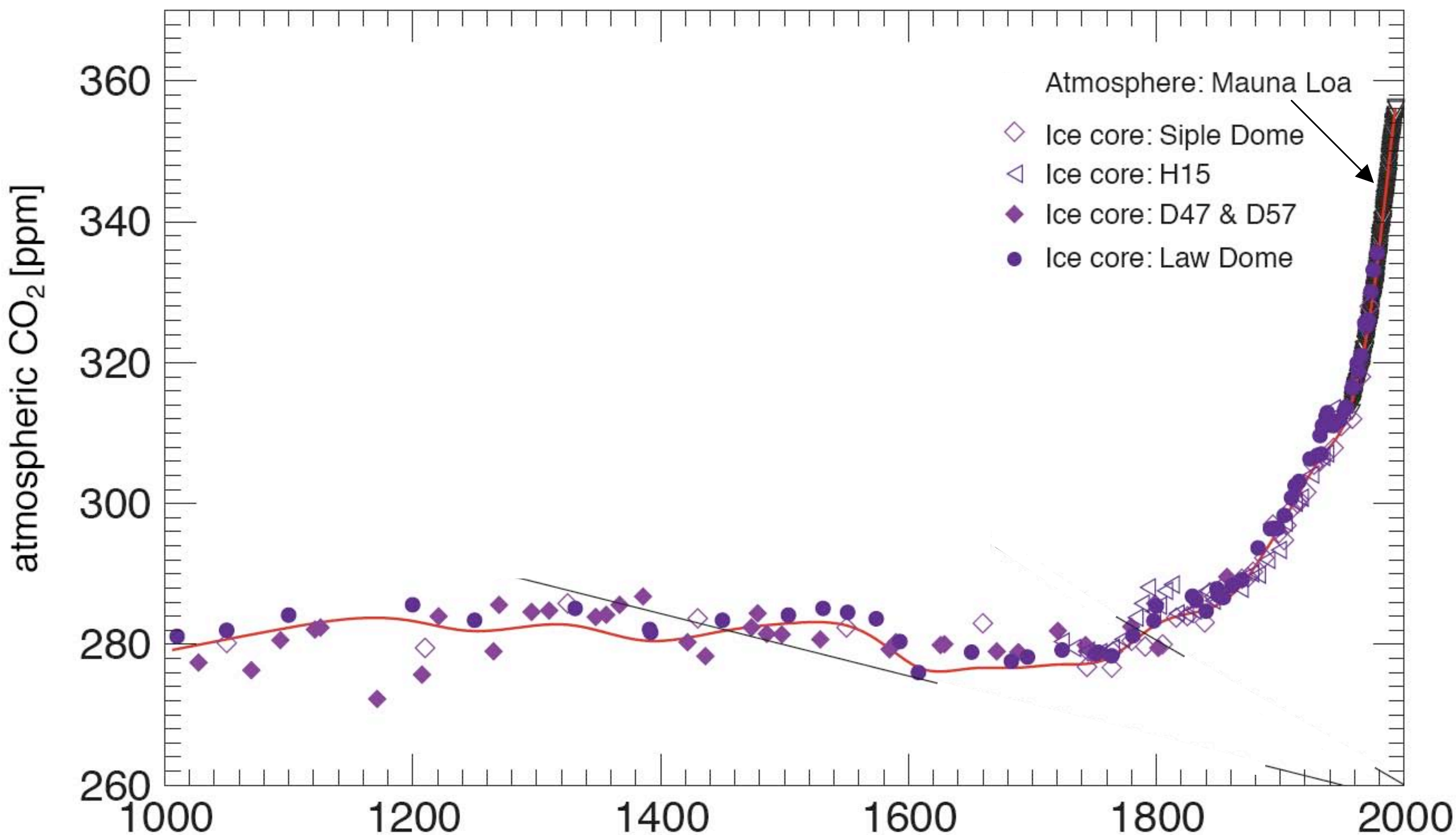
# XII. Fossil fuels and the perturbed carbon cycle



# review

- carbon cycle includes the atmosphere, ocean, terrestrial biosphere and rock reservoirs
- *natural exchanges between reservoirs are balanced*
- each of the reservoirs influences the atmosphere on different time scales, depending on *size of exchange* and *size of reservoir*
- the terrestrial biosphere is responsible for seasonal variations in $CO_2$
- other reservoirs must be responsible for longer time scale changes in $CO_2$
- *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*

# atmospheric $CO_2$ variations since 1000AD




initial increase ~1750 predates sign. fossil fuel use- this is land clearing and deforestation ("pioneer effect")

exponential increase after 1850 is primarily from fossil fuel use

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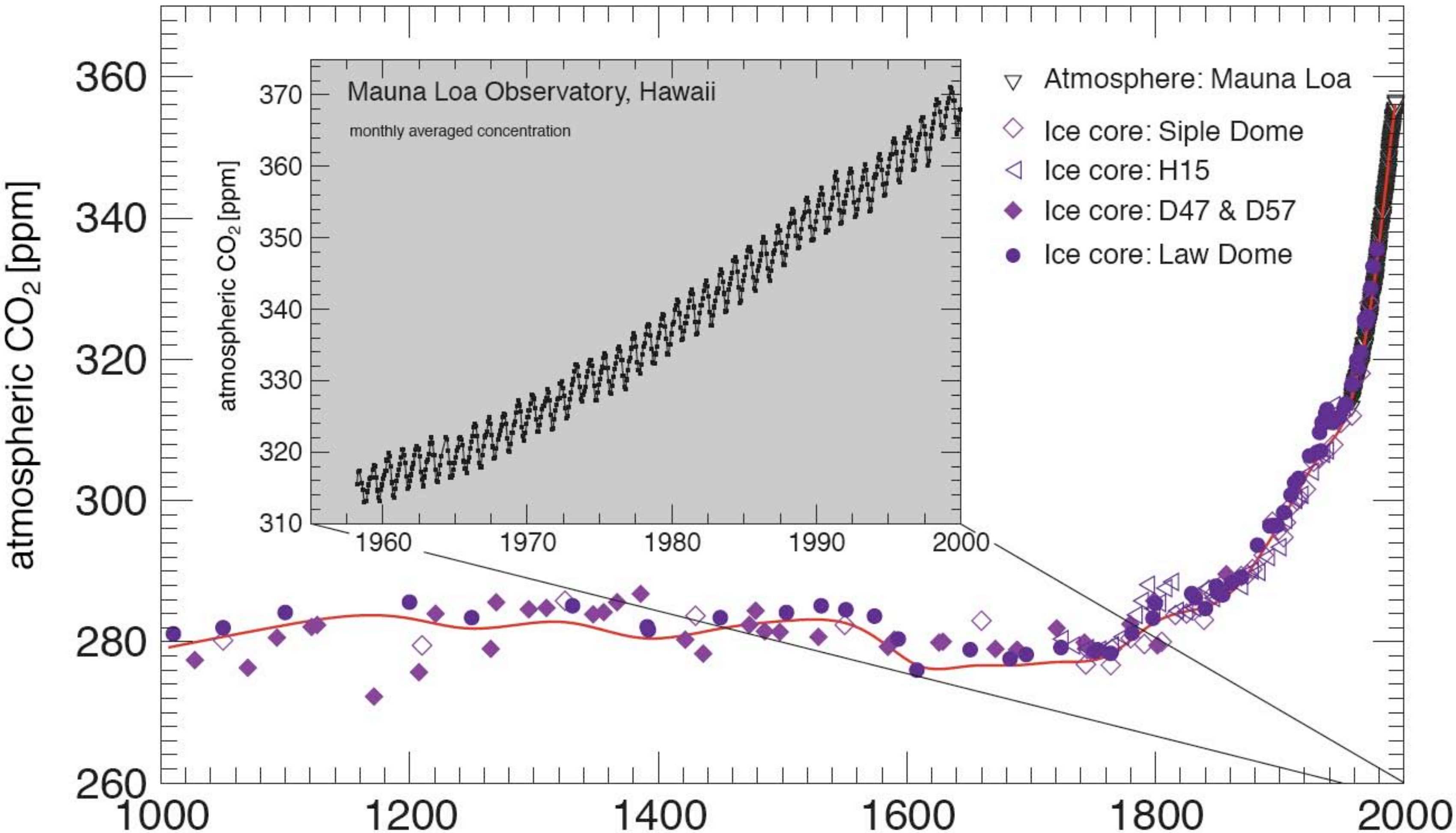
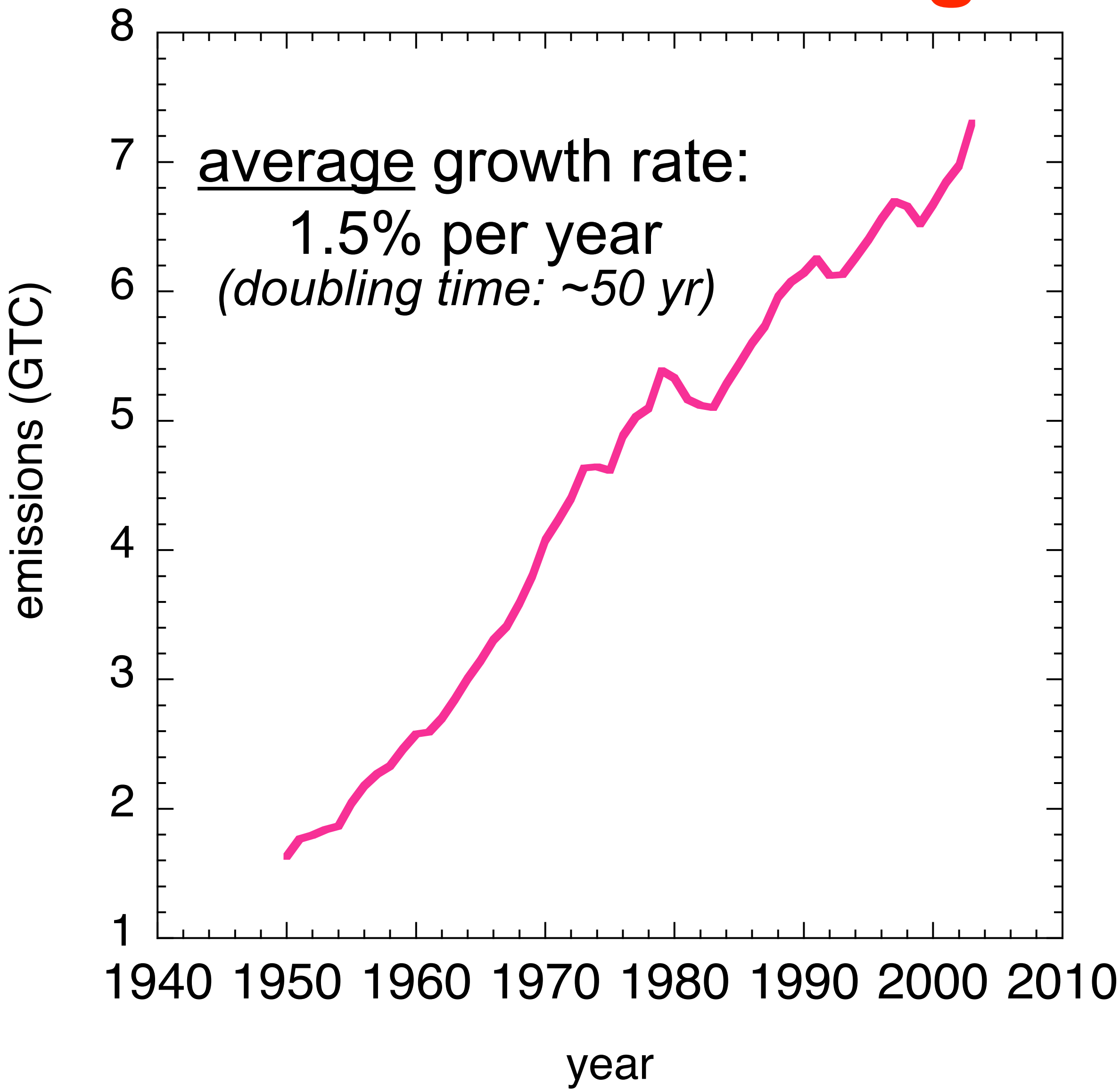
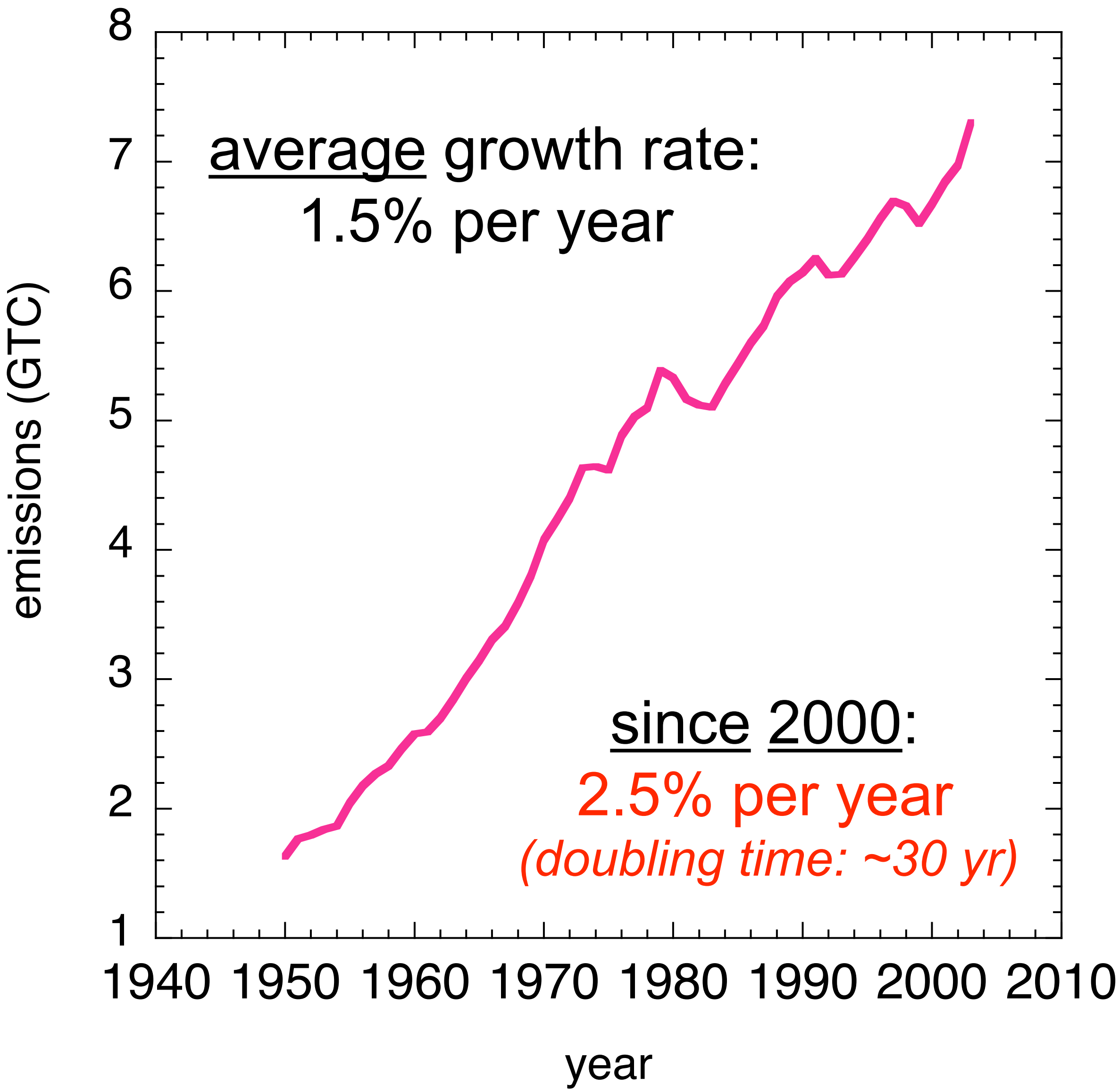


# fossil fuel burning



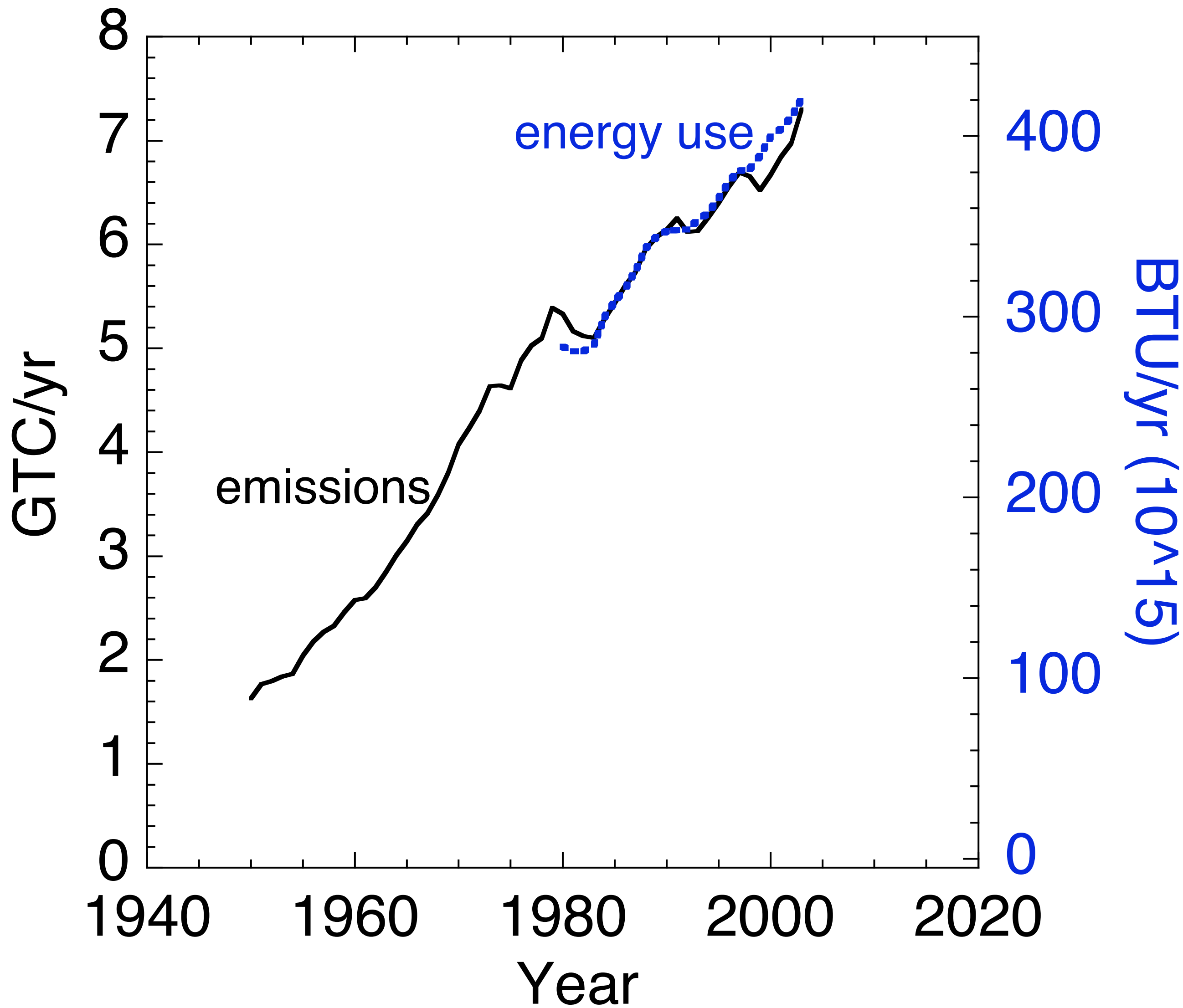

from all fossil fuel sources and cement production

# fossil fuel burning




the rate of growth is increasing

# global emissions and energy use




global fossil fuel emissions and the global energy use are closely related

# fate of fossil fuel $CO_2$

from our understanding of the natural carbon cycle, we might expect to look at

- atmosphere
- land biosphere
- oceans
- rocks (negligible change on this timescale)

# fate of fossil fuel $CO_2$

*observational constraints:*

- **fossil fuel use (emissions)**
  intntl' economic reporting — ***strong***
- **atmospheric burden**
  precise global measurements — ***strong***
- **ocean burden**
  global measurements w/ sign. interpolation — ***mod.***
- **land burden**
  ecological inventories and models — ***poor***

***quality of constraint***

# emissions reporting

**Energy Information Administration**
*Official Energy Statistics from the U.S. Government*

Home > Environment

**Environment** energy-related emissions data & environmental analyses

## U. S. Emissions Data

**Greenhouse Gas Emissions**
- Carbon Dioxide ($CO_2$)
- $CO_2$ from Manufacturing
- Methane ($CH_4$)
- Nitrous Oxide ($N_2O$)
- Other Gases

**Electric Power Plant Emissions**
- $CO_2$, $SO_2$, $NO_x$

**Environmental Equipment**
- Number of Generators & Capacity
- Average FGD (Scrubber) Costs

**Carbon Emission Factors**
- Gallons & Barrels
- Quadrillion ($10^{15}$) BTU

**State Carbon Dioxide Emissions**
- By Fuel
- By Energy Sectors
- Summary
- State Methodology

## International Emissions Data

**Energy-Related Carbon Emissions**
- Total Emissions
- Per capita Emissions
- Emissions from Petroleum Consumption
- Emissions from Natural Gas Consumption
- Emissions from Coal Consumption

**Carbon Intensity**
- Energy Related Carbon Intensity

## Greenhouse Gas Reporting

Revised reporting Form and Instructions
Voluntary Reporting of Greenhouse Gases complete program information
Emissions Inventory Report

## Environmental Analyses

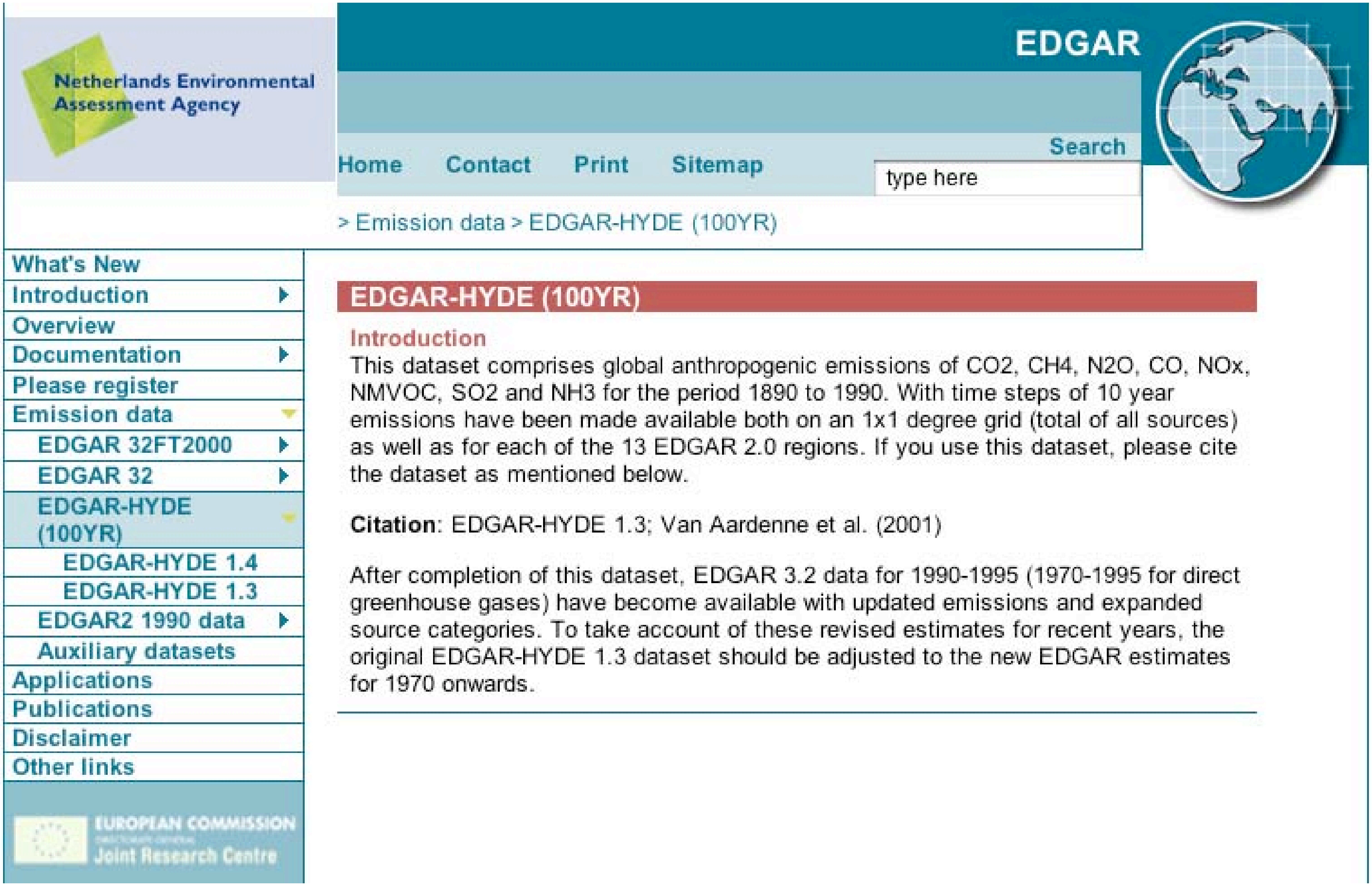
Climate Change, Kyoto, Greenhouse Gases
Electric Power Emissions
Refinery
Transportation

## Emissions Forecasts

Annual Energy Outlook Emissions Projections US projections to 2030 2/14/06
International Energy Outlook Emissions Projections International projections to 2030 6/20/06

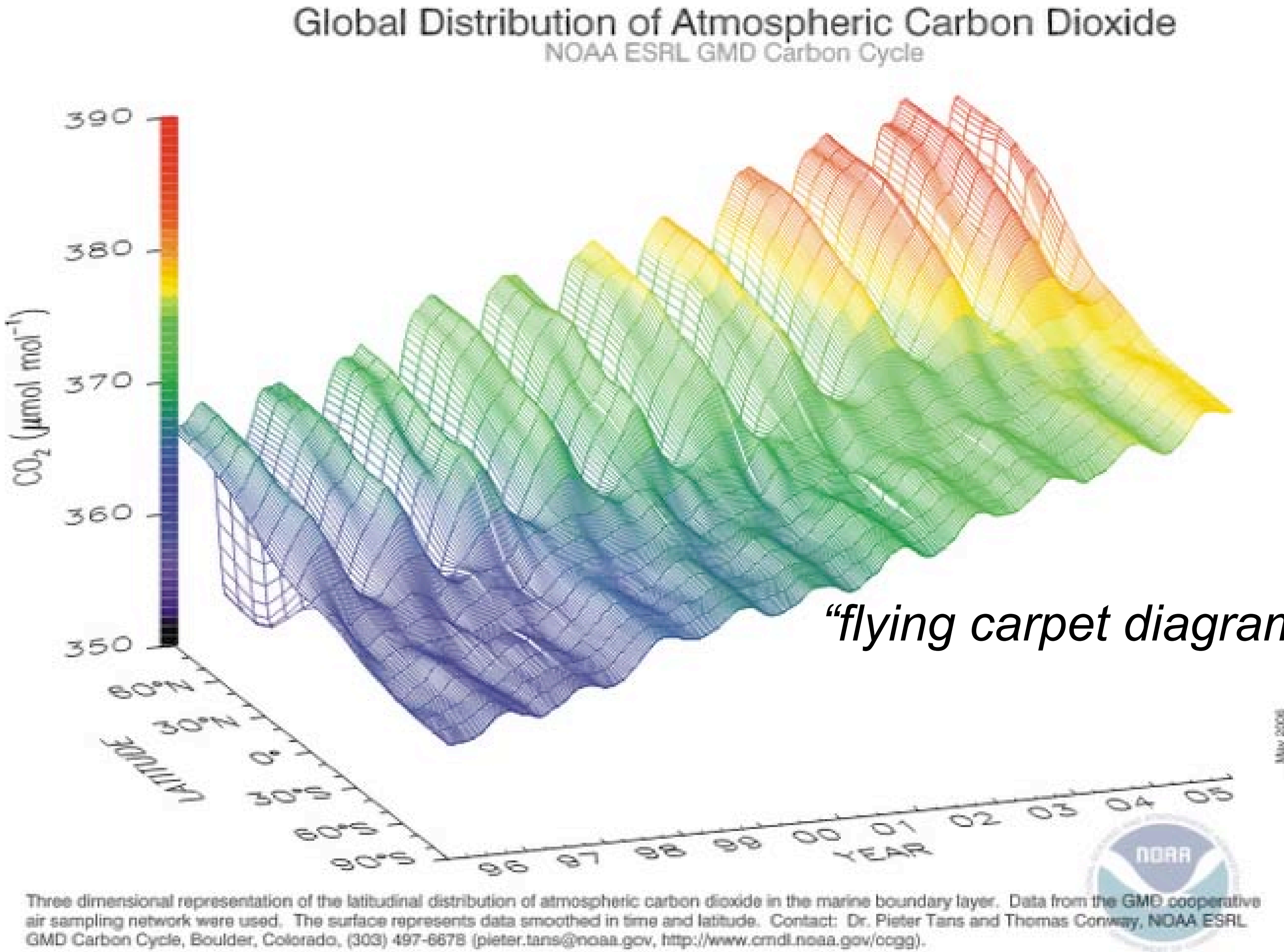
http://www.eia.doe.gov/environment.html

# emissions reporting




http://www.mnp.nl/edgar/model/100_year_emissions/

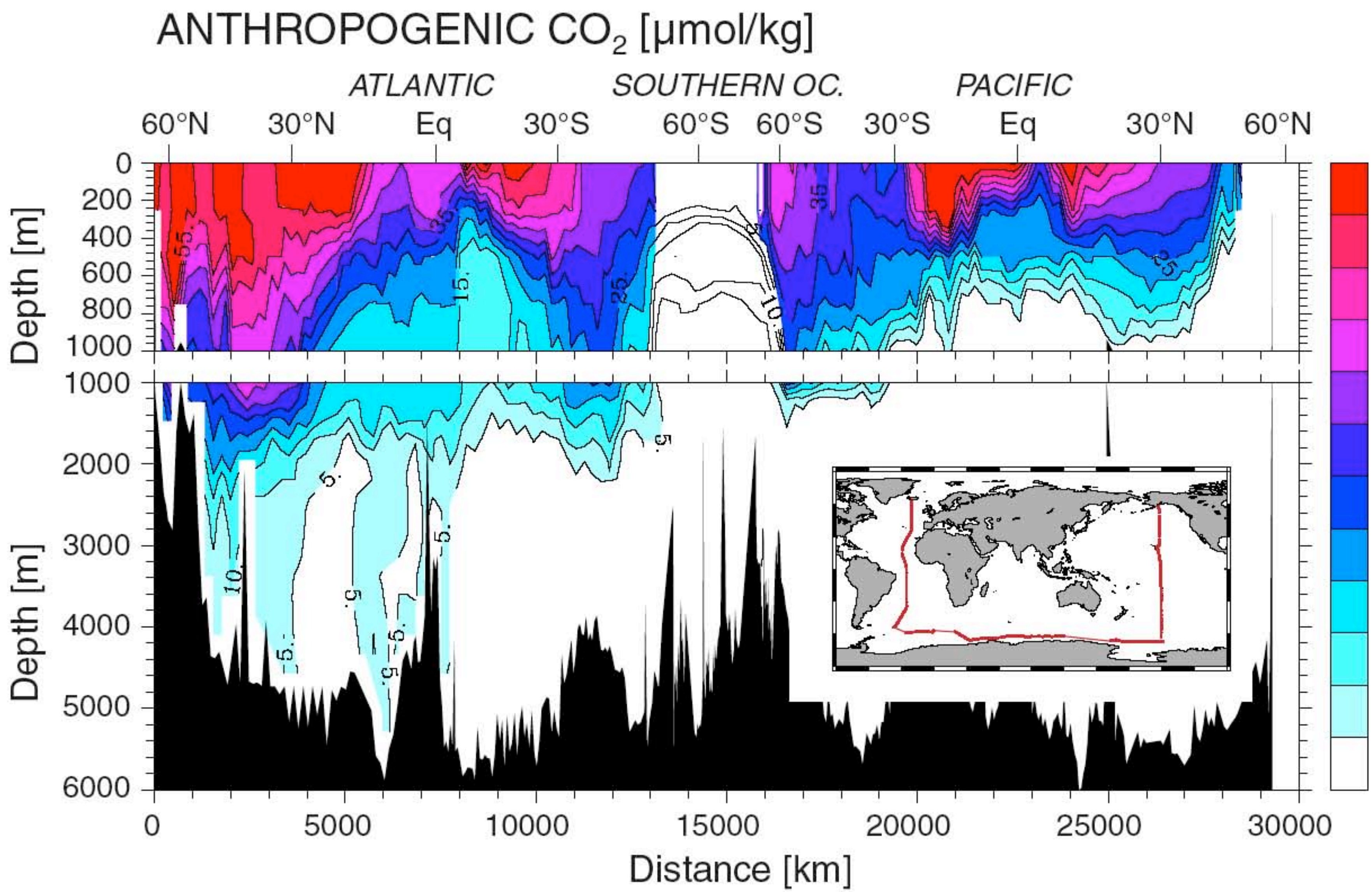
# atmospheric observations




*"flying carpet diagram"*

http://www.esrl.noaa.gov/gmd/ccgg/index.html

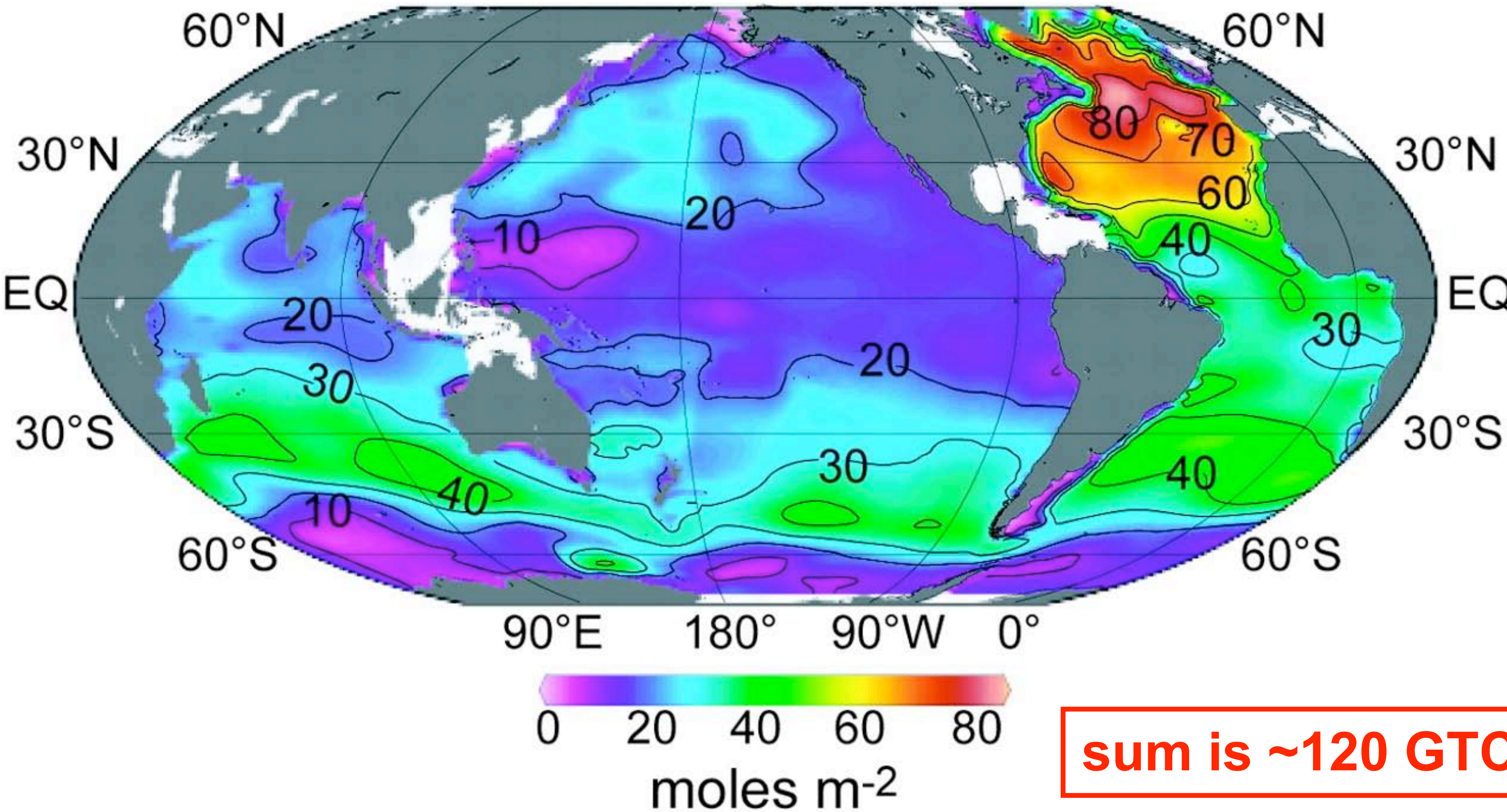
# ocean observations




concentration in micromoles/kg vs. depth

from Gruber

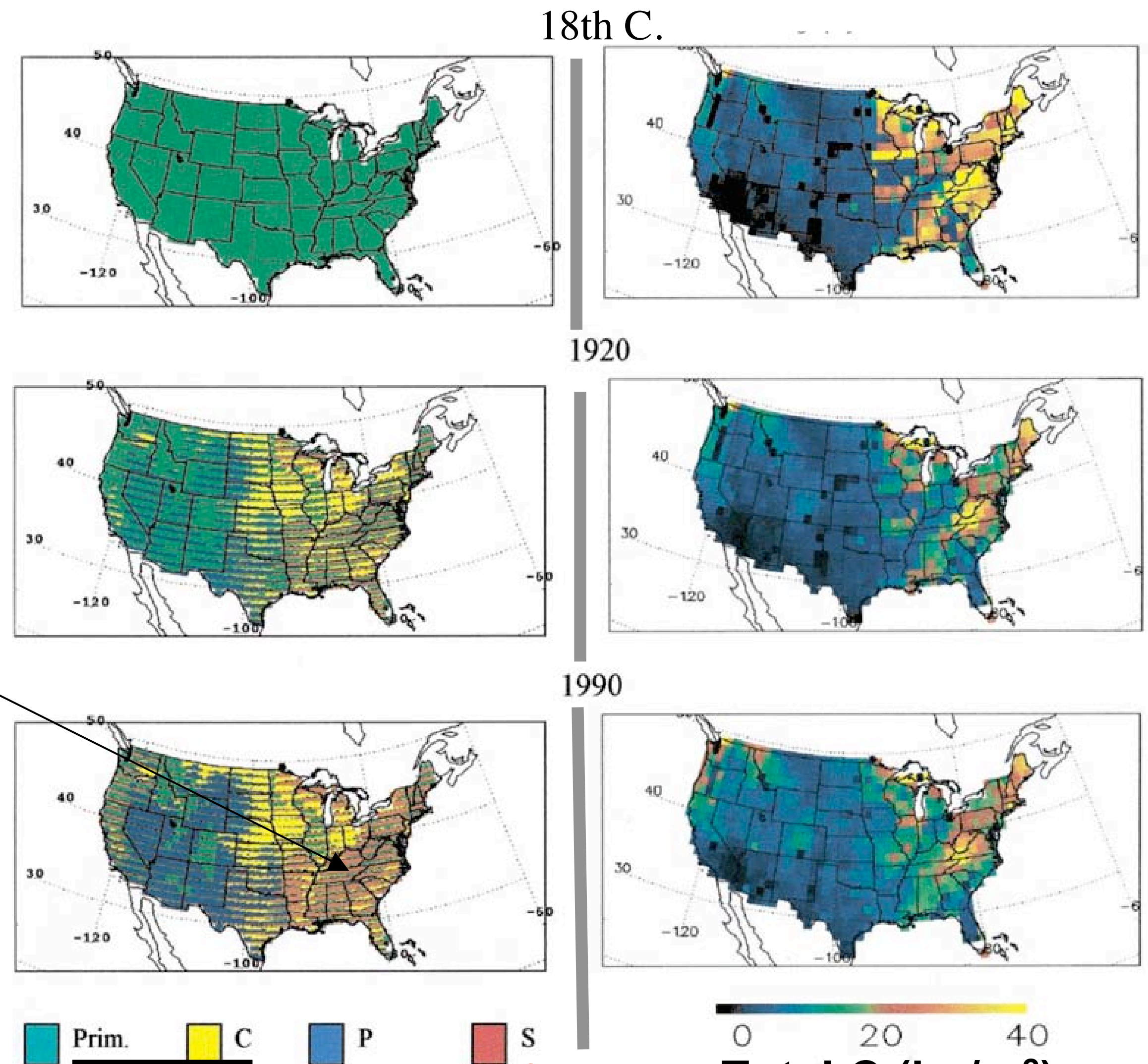
# ocean observations




sum is ~120 GTC

column inventories of anthropogenic C in moles ($6.02 \times 10^{23}$ atoms) compiled from shipboard measurements by Sabine et al. '04

# est. US land use and C change




orange denotes conversion of primary to secondary forest, i.e. logging

primary forest, cropland pasture, sec. forest

**Total C (kg/m$^2$)**

*"eastern US carbon stocks decimated by 1920......., now largely recovered "*

from Sarmiento & Gruber

## *“eastern US carbon stocks decimated by 1920......., now largely recovered ”*

Carbon release from landscape to atmosphere can be significant when forests are cut and converted to pasture etc. This is what occurred during early settlement of Europe and North America (i.e. the “pioneer effect”)

As forests are re-established (as between 1920 and 1990 in previous figure) they may take up carbon from the atmosphere.

*Problem: Re-growth of forests following cutting during early settlement is nearly complete. This reduces the capacity of the land to take up more carbon (and emissions from other sources are rising)*

# fossil fuel $CO_2$ budget

| | *1800 - 1994* |
|---|---|
| 1) fossil fuel emissions | 244 ± 20 GTC |
| 2) atmospheric increase | -165 ± 4 GTC |

***only about half of emitted fossil fuel C has remained in the atmosphere during this period (this is good) implying that other reservoirs have acted as C sinks***

# fossil fuel $CO_2$ budget

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Sabine et al., ‘04

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| 4) net land balance [=-1) - 2) -3)] | 39 ± 28 GTC |

***closing the budget implies that the terrestrial biosphere was a <u>source</u> of C to the atmosphere during this period- due to human land use (deforestation etc.)....***

**Sabine et al., '04**

# fossil fuel $CO_2$ budget

| | *1800 - 1994* |
|---|---|
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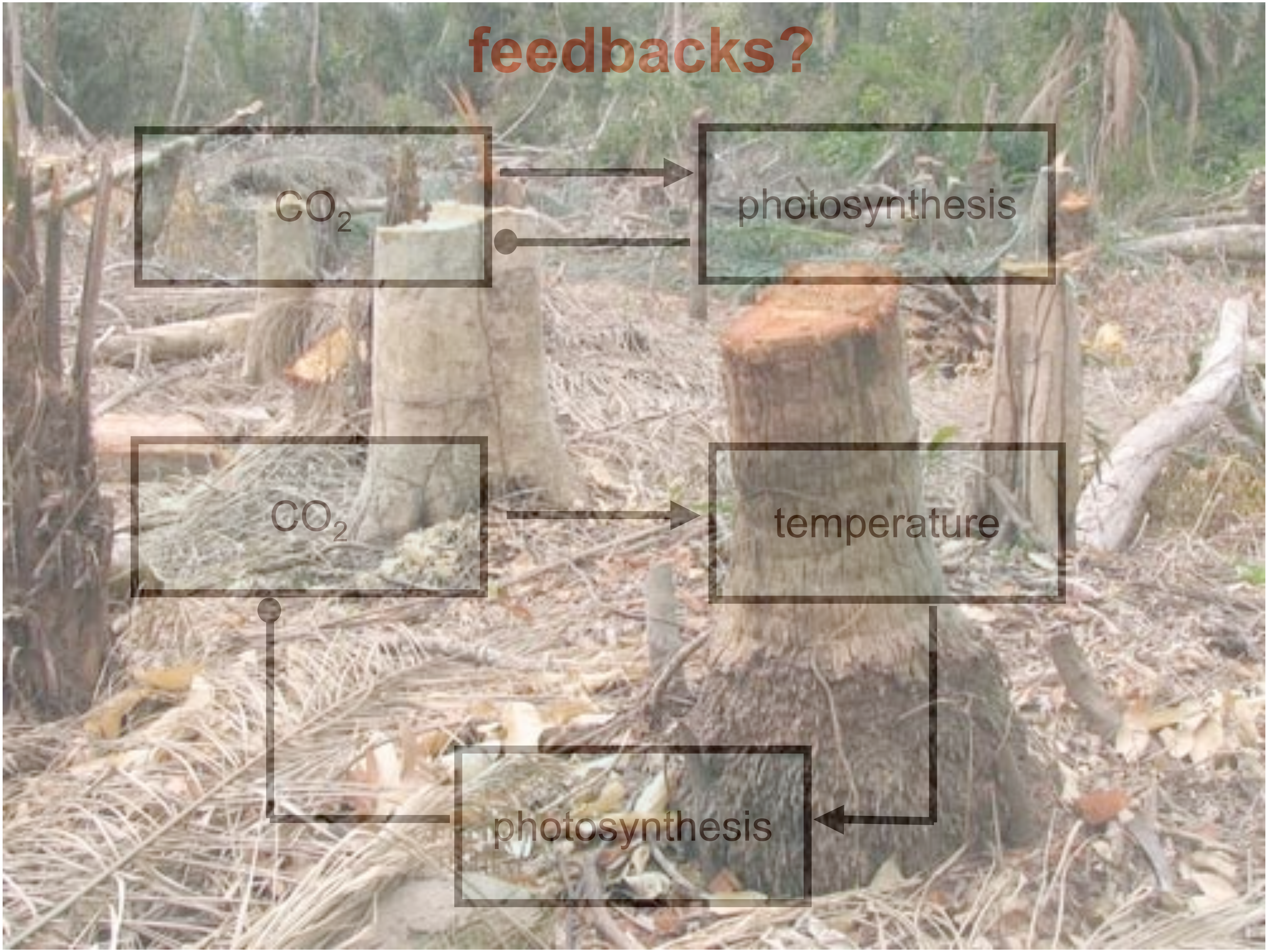
| 2) atmospheric increase | -165 ± 4 GTC |
| 3) ocean uptake | -118 ± 19 GTC |
| 4) net land balance [=-1) - 2) -3)] | 39 ± 28 GTC |
| 5) estimated emissions from land use change | 100 to 180 GTC |
| 6) terrestrial biosphere "sink" [=-1) - 2) -3) -4) -5)] | -61 to -141 GTC |

**Sabine et al., '04**

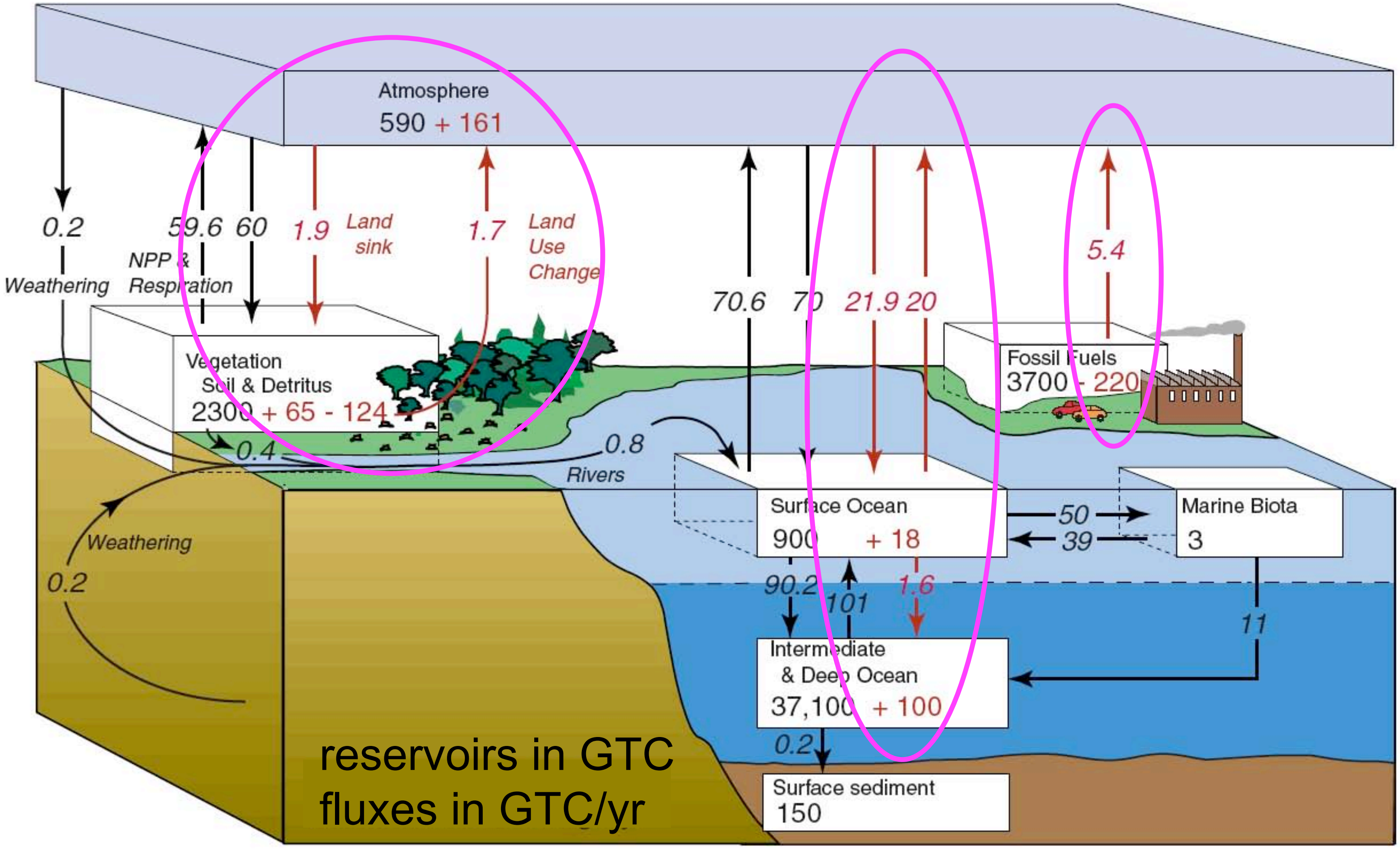

feedbacks?
$CO_2$
photosynthesis
$CO_2$
temperature
photosynthesis

# take home points (so far)

- about half of emitted C remains in the atmosphere
- the remainder is taken up by other surface reservoirs
- to date, the ocean has accounted for most of the uptake
- uptake of C by the terrestrial biosphere (arising from excess of $CO_2$ in the atmosphere) appears to have been offset by emissions due to land use changes
- in other words, we are cutting down and burning forests more quickly than they (and other plants) are expanding

# natural & perturbed carbon cycles

(estimates for 1980s)




perturbation fluxes and stocks for 1980's in red (natural in black)

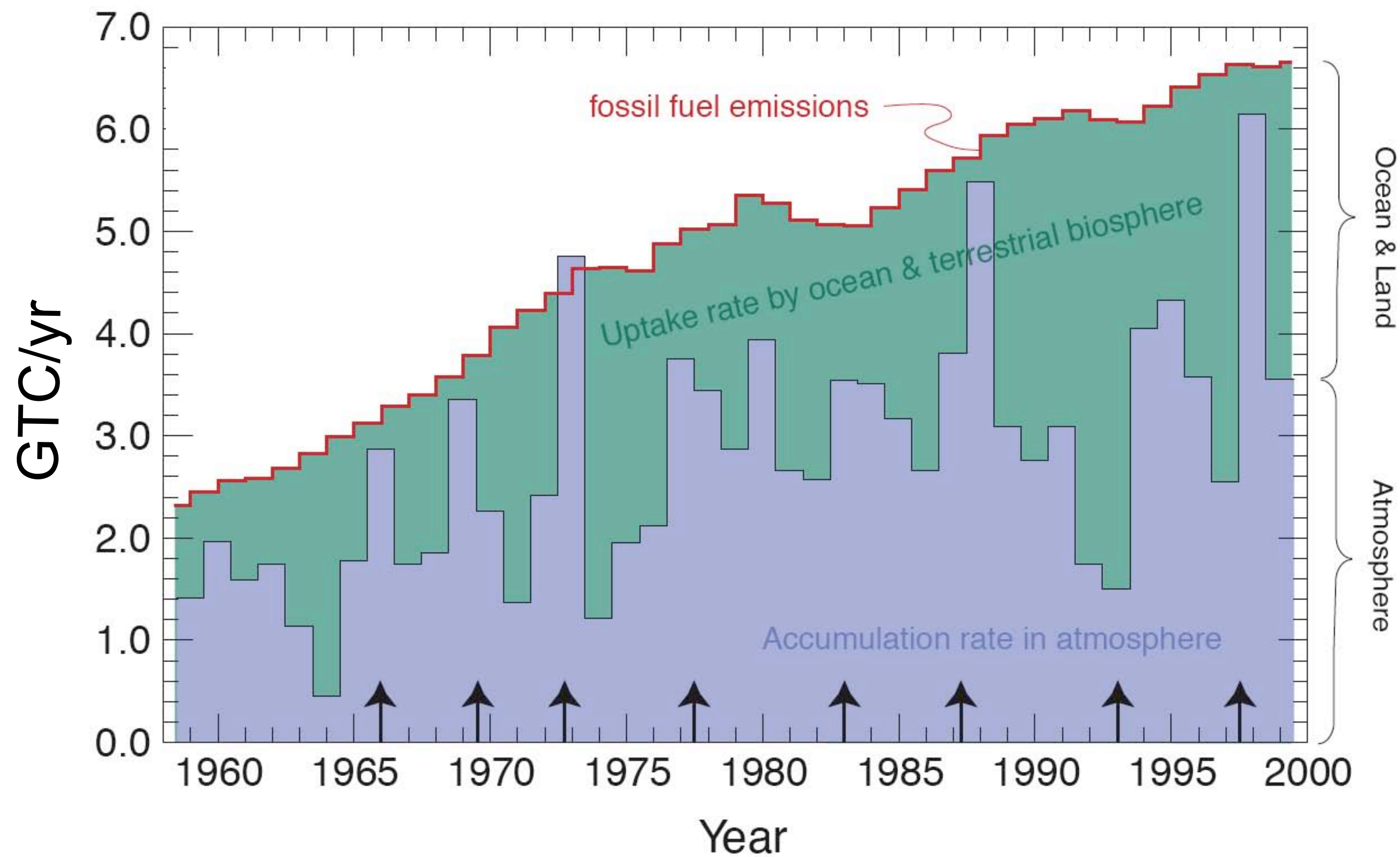
(by 2006 305 GTC fossil fuels burned since ~1850)

# perturbations

- cycling of C between the atmosphere and terrestrial biosphere has increased due to land use change (forest cutting and re-growth etc.) and the “fertilization effect”
- the cycling of $CO_2$ between the atmosphere and surface ocean has increased significantly due to rising atmospheric $CO_2$ (i.e more C exchange for the same rate of air-sea gas exchange)
- in addition, the biological pump has assisted  an ocean uptake of about ~2 GTC/yr
- the carbon stocks in all reservoirs are increasing

# annual changes in uptake

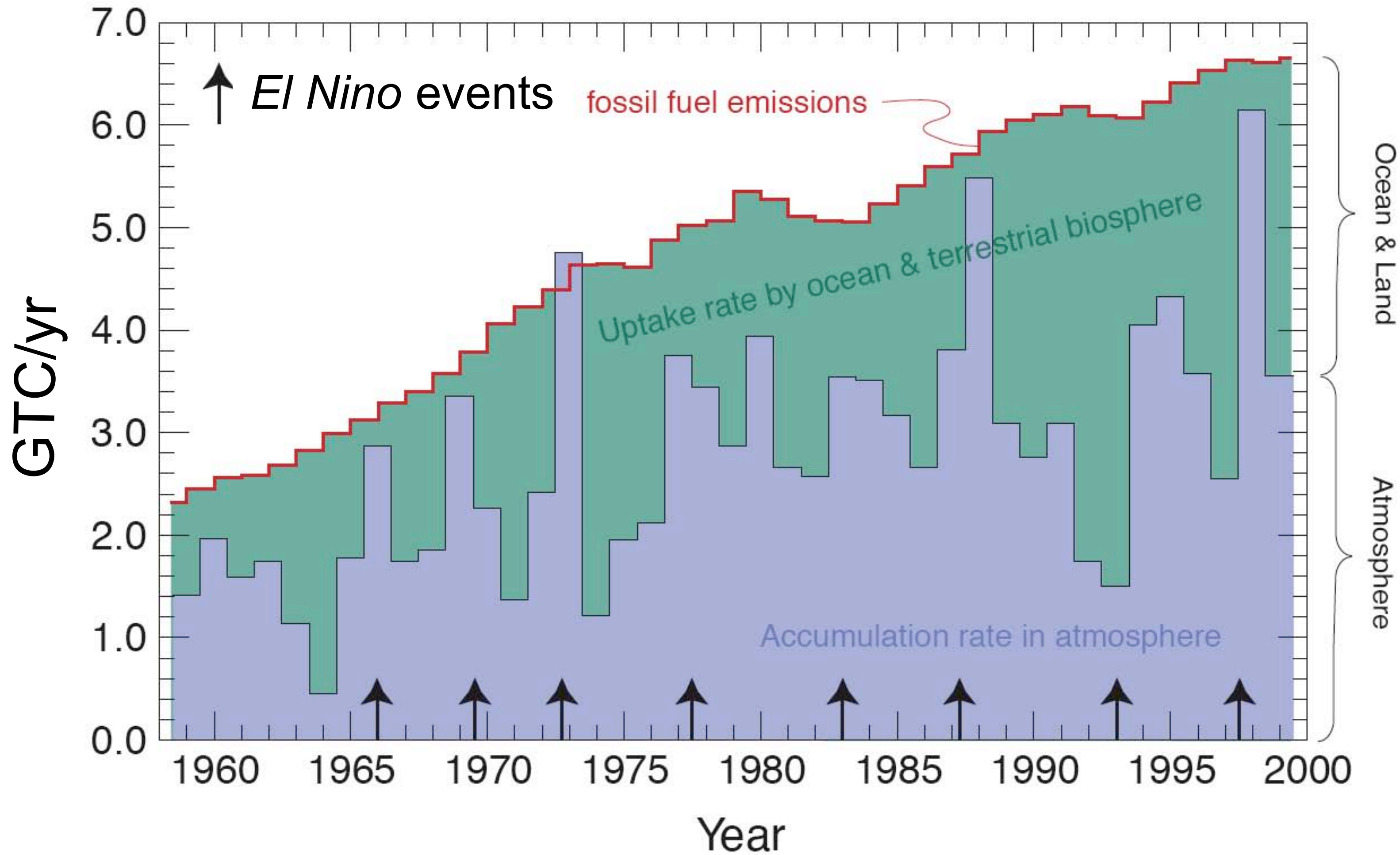
(*well constrained by atm. measurements and economic statistics*)




partitioning of emissions between atmosphere and ocean+land
highly variable but......,
every year the atmospheric burden increases

# annual changes in uptake

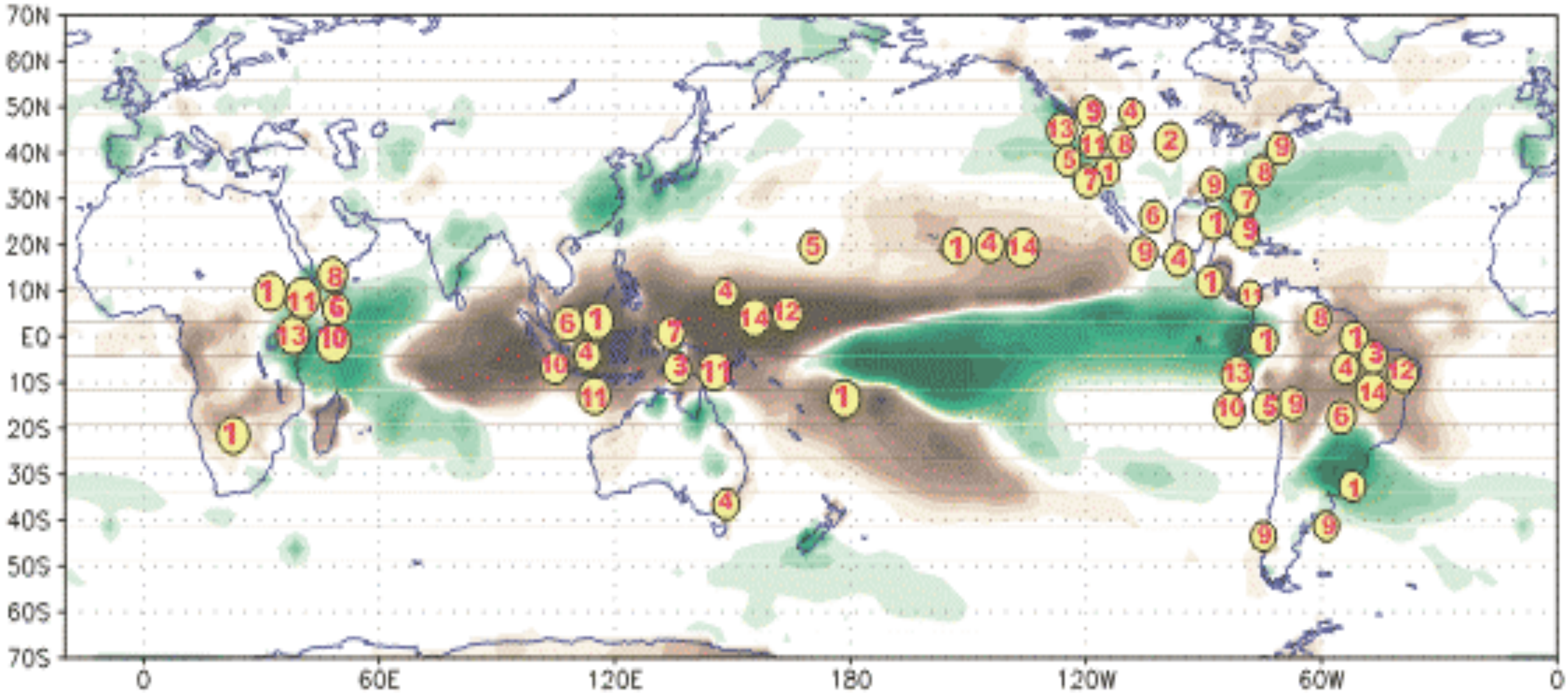
(*well constrained by atm. measurements and economic statistics*)




C uptake appears to decrease during most *El Nino* years due to enhanced respiration and forest burning

*partitioning of C is sensitive to climate!*

# recall (1997/8) El Niño




Wet

Dry

drought (brown) and rainforest burning (Amazon, Indonesia)

# carbon uptake

- varies year to year
- difficult but important to quantify since, for any given emissions scenario, amount of uptake will determine atmospheric concentration of $CO_2$
- signs are that uptake by land is diminishing
- the ocean does the heavy lifting

## ***the ocean does the heavy lifting .....***

- we have seen that the ocean is responsible for most uptake of anthropogenic $CO_2$

- this helps to reduce the rate of atmospheric $CO_2$ growth (this is good)

- but for how long and at what cost?

- *is there such a thing as a “free lunch”?*

# how $CO_2$ is dissolved into sea water:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{=} + 2H^+$$

| | | | |
|---|---|---|---|
| carbon dioxide | carbonic acid | bicarbonate ion | carbonate ion |

*dissolved inorganic carbon ("DIC")*

reactions are not sequential but occur together
(in chemical equilibrium)

# charge balance

in order to maintain electrical neutrality (or *charge balance*) of sea water, the net reaction will be:

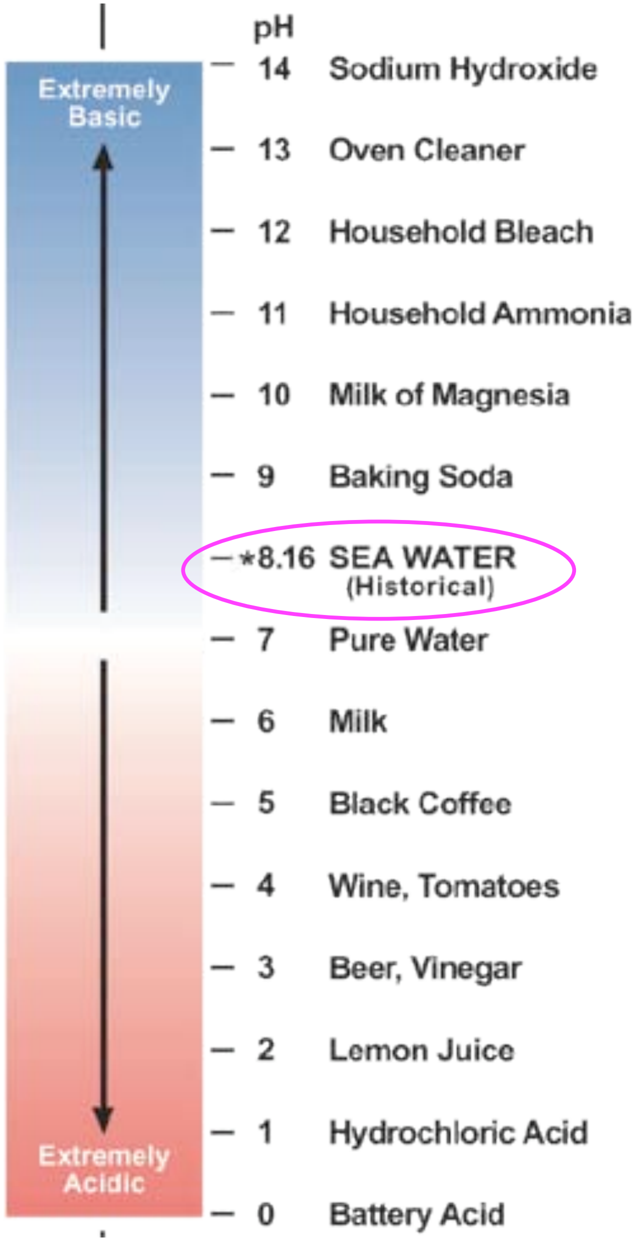
$$CO_2 + H_2O + CO_3^{=} \Longleftrightarrow 2\ HCO_3^-$$

this reaction can remove $CO_2$ from the atmosphere with no change in the amount of $H^+$ (*i.e.*, no change in pH)

*however, if too much $CO_2$ is added too quickly, the reactions are not balanced, and $H^+$ can build up (i.e., some change in pH)*

***this is the case for the rapid rise in excess $CO_2$ from combustion of fossil fuel***

# ocean acidification

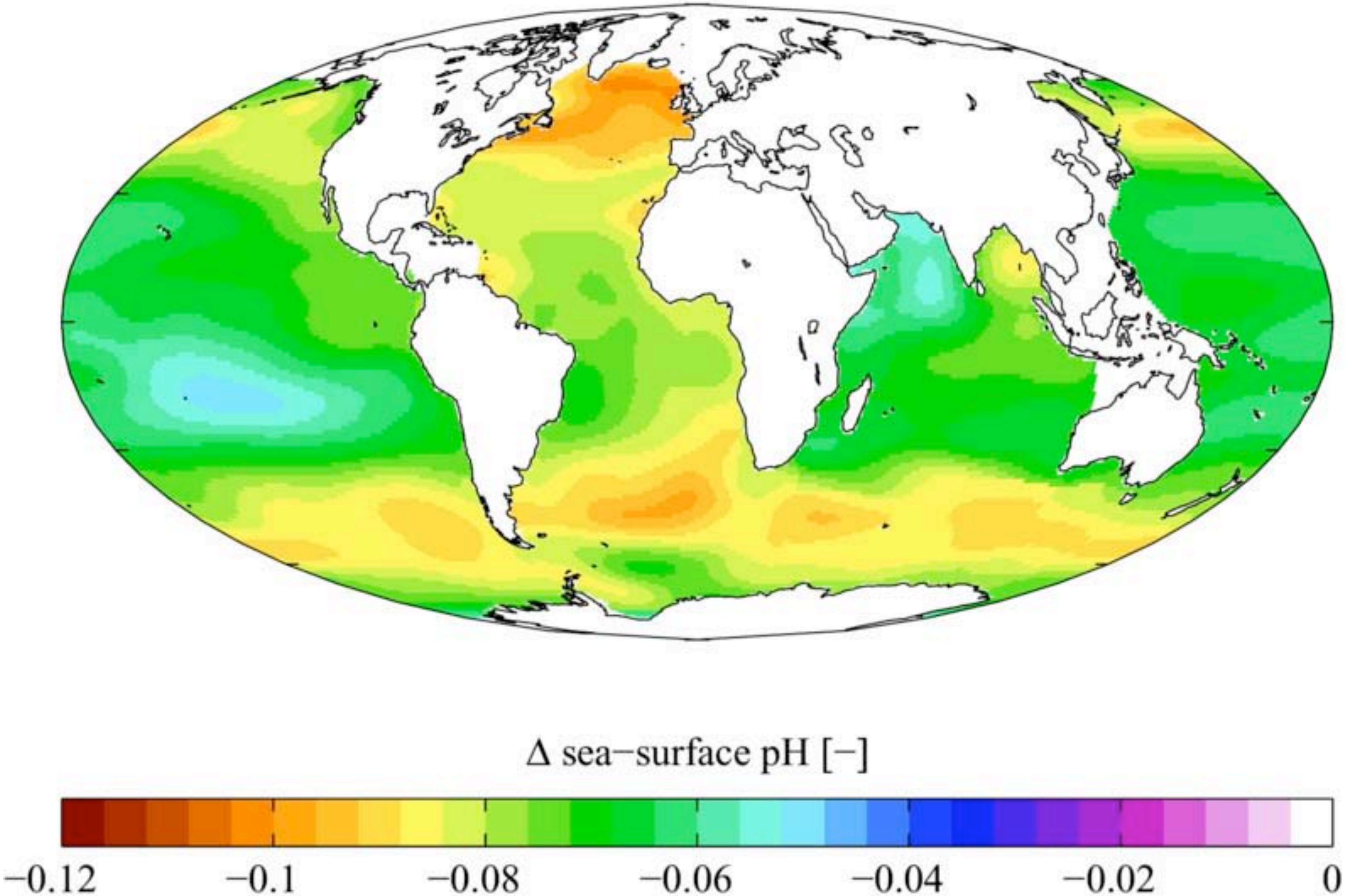



$$pH = -\log_{10} [H+]$$

*(scale is inversely related to log concentration of H+)*

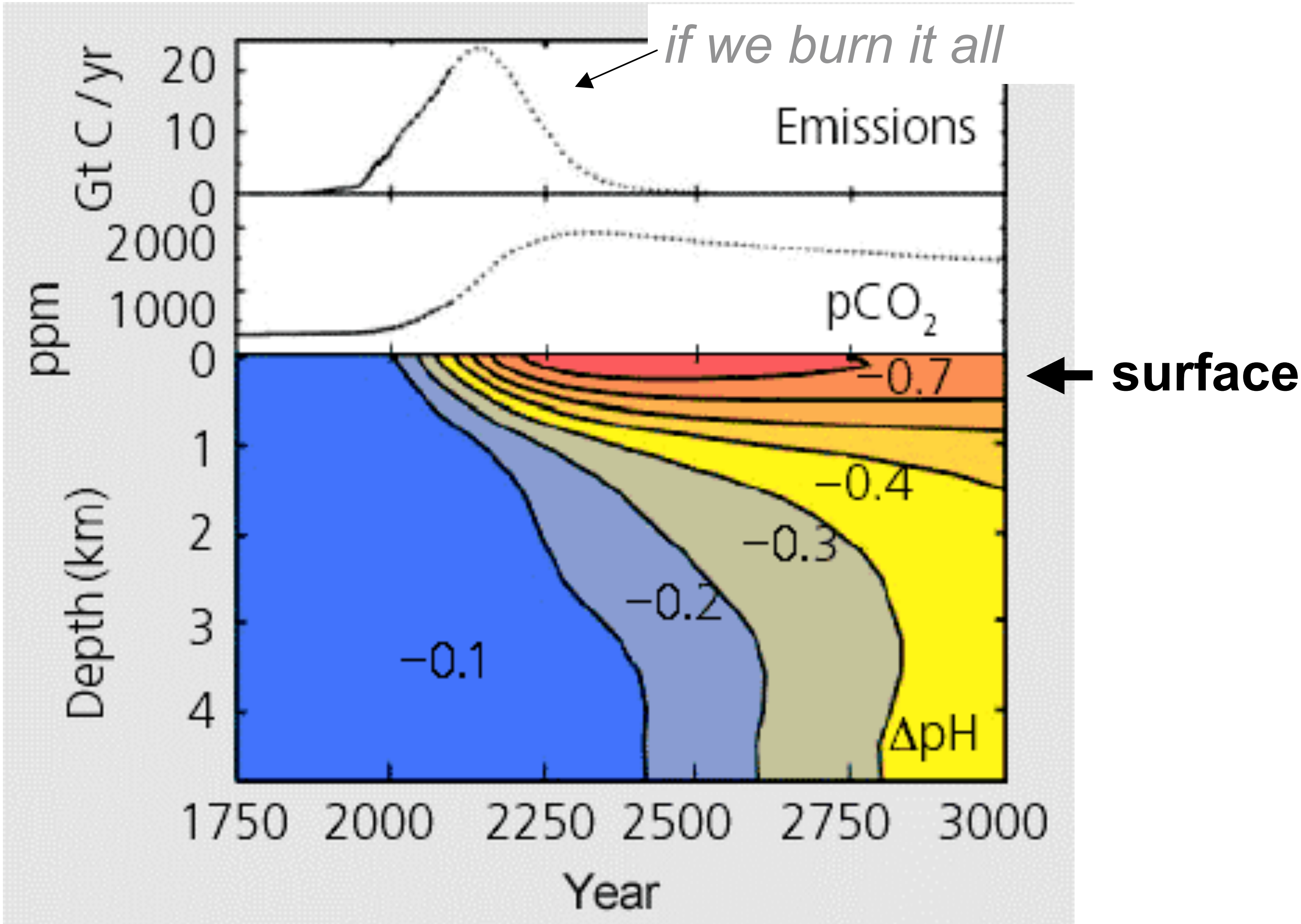
more H+ ions = greater acidity

# ocean acidification




observed decrease in ocean pH due to uptake of anthropogenic $CO_2$

# ocean acidification




ocean pH forecast based on proven chemistry
(and ocean mixing)

# $CO_2$ and calcite

in order to maintain electrical neutrality (or *charge balance*) of sea water, the net reaction will be:

$$CO_2 + H_2O + CO_3^{=} \Longleftrightarrow 2\ HCO_3^{-}$$

and calcite formation and dissolution follows:

$$CaCO_3^{=} \underset{saturated}{\overset{undersat.}{\rightleftarrows}} Ca^{2+} + CO_3^{=}$$

# $CO_2$ and calcite

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and calcite formation and dissolution follows:

$$CaCO_3^{=} \underset{\text{saturated}}{\overset{\text{undersat.}}{\rightleftarrows}} Ca^{2+} + \cancel{CO_3}^{=}$$

and the summary equation is then:

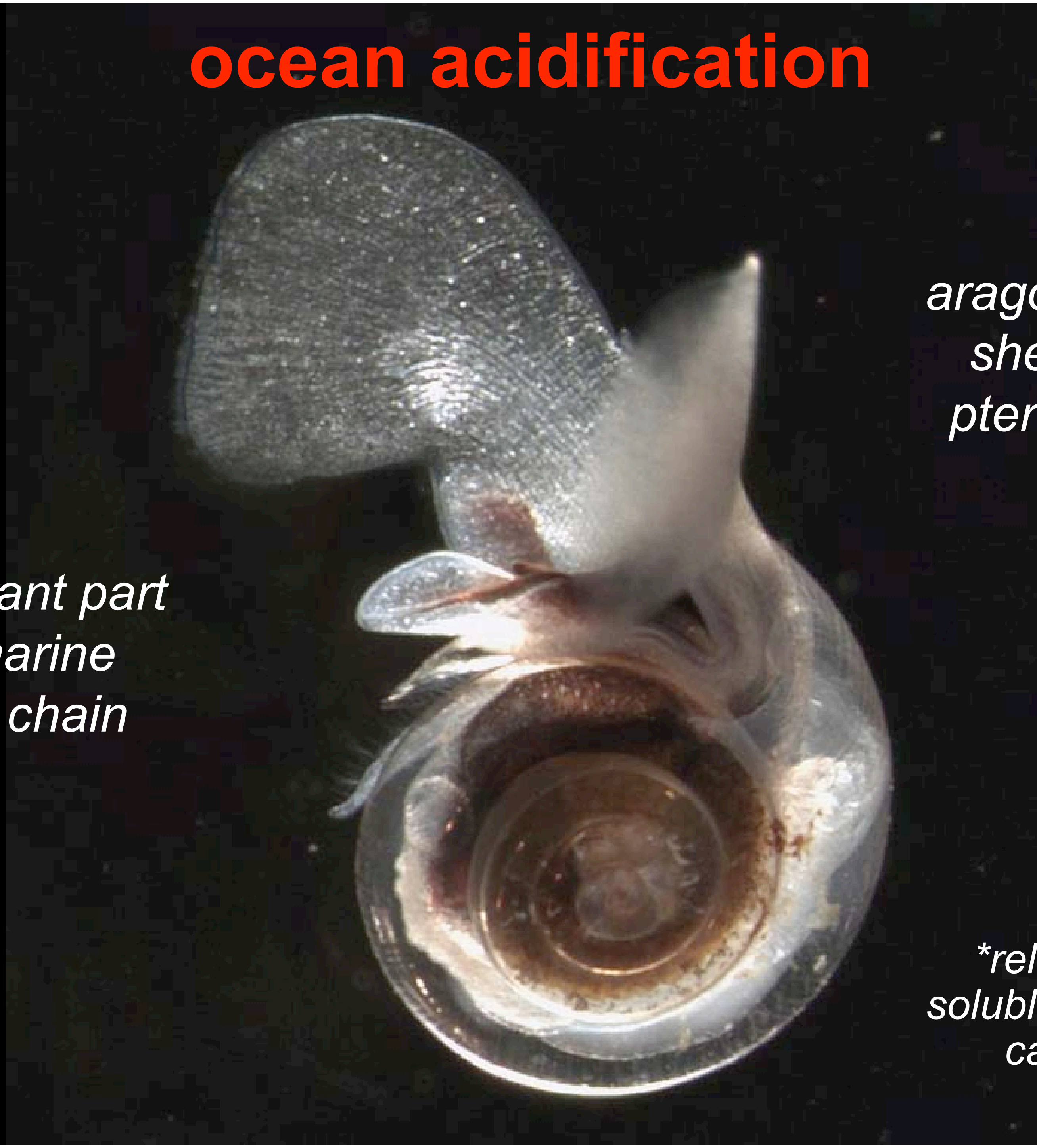
$$CO_2 + H_2O + CaCO_3 \Longleftrightarrow 2\ HCO_3^- + Ca^{2+}$$

# $CO_2$ and calcite

$$\uparrow CO_2 + H_2O + CaCO_3 \longrightarrow 2\,HCO_3^- + Ca^{2+}$$

*in the presence of excess $CO_2$ from fossil fuel combustion, the reaction is driven to the right, dissolving $CaCO_3$ (i.e. excess acidity dissolves $CaCO_3$ by reducing the saturation state of calcite)*

# ocean acidification

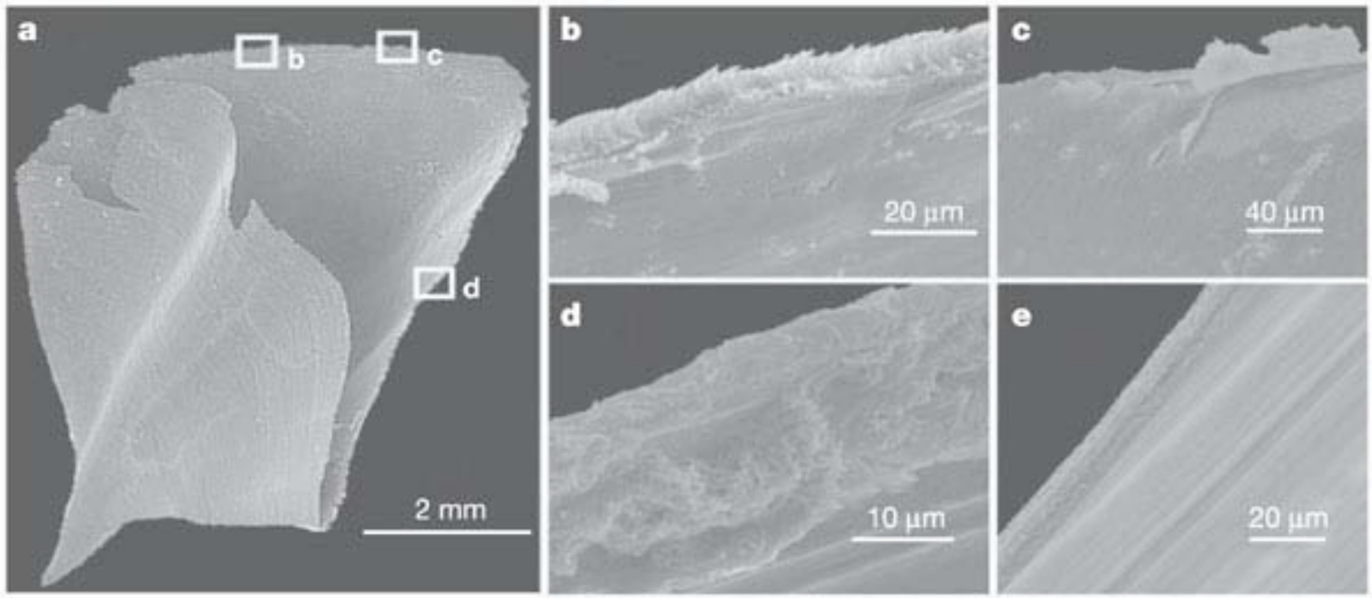


*aragonite*-shelled pteropod*

*important part of marine food chain*

**relatively soluble form of calcite*

# ocean acidification

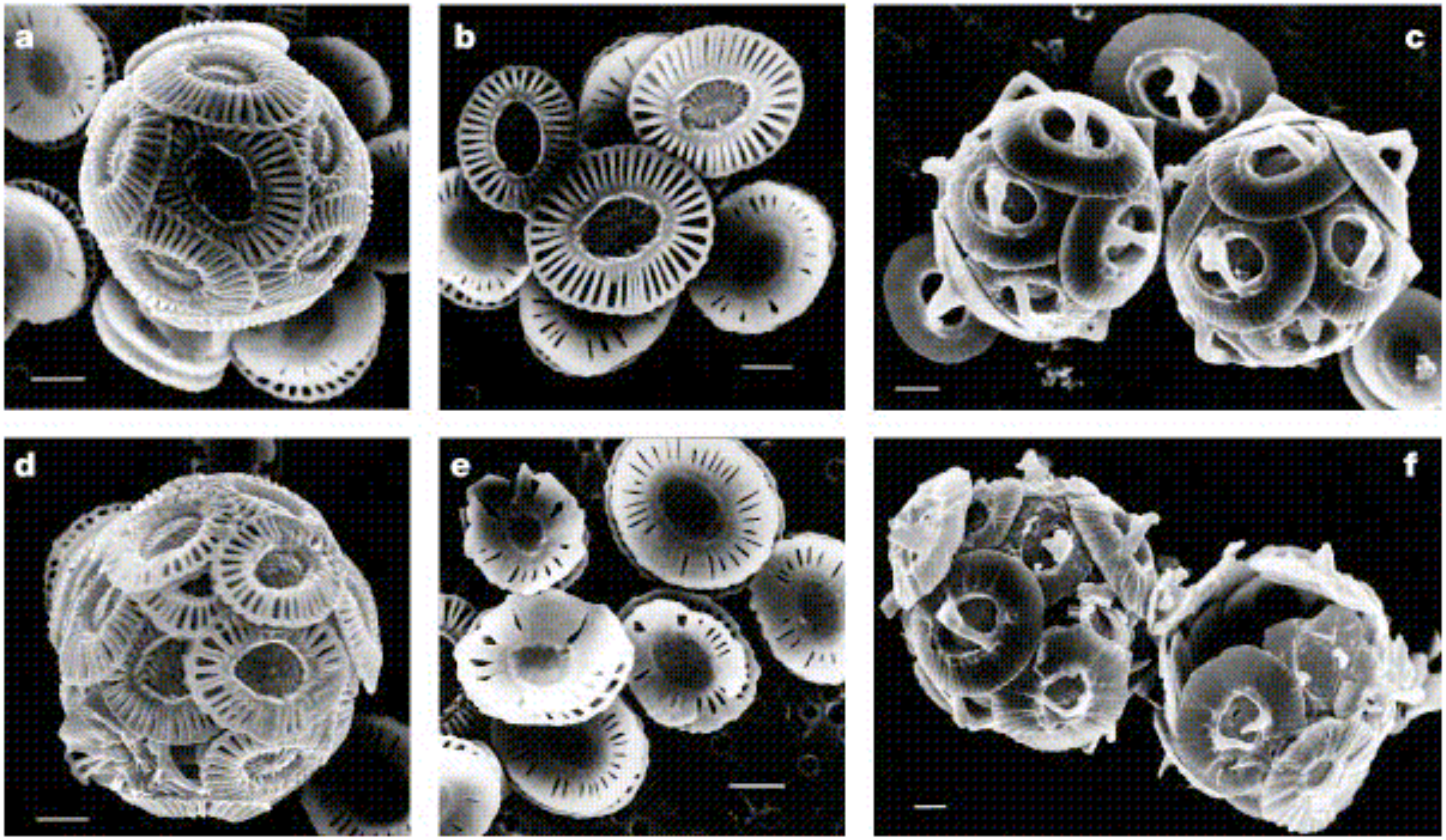



chemical destruction of pteropod shell exposed live for 48 hrs to undersaturated waters of the N. Pacific (images a - d)

image e) is from typical unexposed specimen

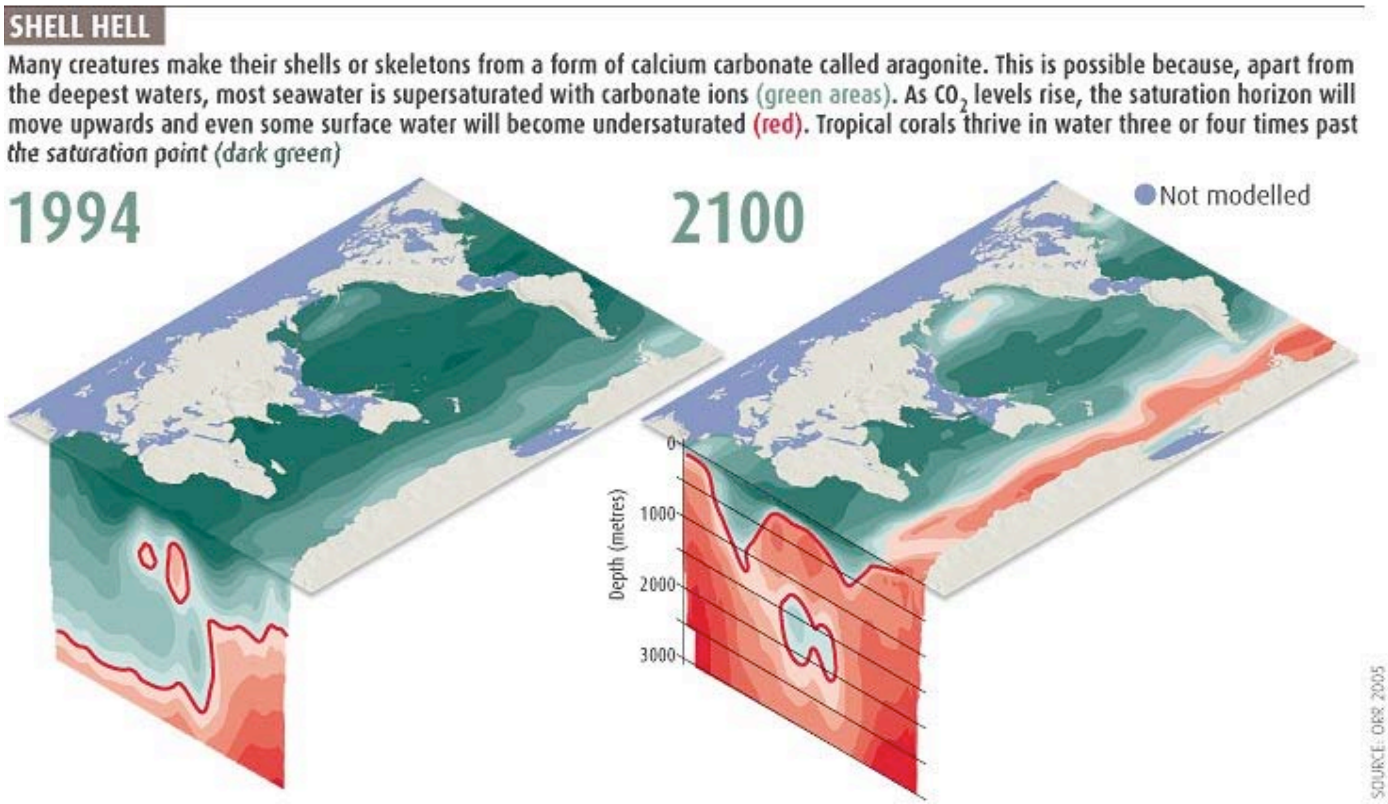
Orr et al. '05

# ocean acidification




*coccolithophorids** grown in low pH environments are deformed
(a - c = normal pH, d - f = low pH)

** ocean's most abundant calcite producer*




*The saturation horizon for $CaCO_3$ will rise dramatically (the more red, the more dissolution). Corals need water that is oversaturated by a factor of 3-4 (dark green). Those areas will shrink dramatically…..*

# more take home points

- dissolution of $CO_2$ into the ocean lowers pH and consumes $CO_3^{=}$ (and $CaCO_3$)
- carbonate and aragonite forming organisms require high levels of $CO_3^{=}$ saturation
- these organisms are threatened by the ongoing acidification of the ocean
- ocean uptake of $CO_2$ comes at a price!

# key points

- land use changes lead to early rise in $CO_2$ and remain a source of C to the atmosphere
- fossil fuel burning has increased steadily and is now 8 GTC/yr or more
- every molecule of emitted C counts, i.e. since the atmospheric lifetime of $CO_2$ is long, emitted C accumulates in the atmosphere
- presently Earth's ambient C reservoirs soak up about half of all emissions
- *this may not last*

# learning goals

- be able to formulate and describe an observing strategy that tracks the fate of $CO_2$ emitted due to combustion of fossil fuels since the 1800's
- use a simple budget to determine whether the land has been a net source or "sink" of $CO_2$ since the 1800's
- describe the chemical and ecological consequences of $CO_2$ uptake by the oceans

# next class

- variations of $CO_2$, climate and sea level in deep time
- reading: Ch. 8 & 10