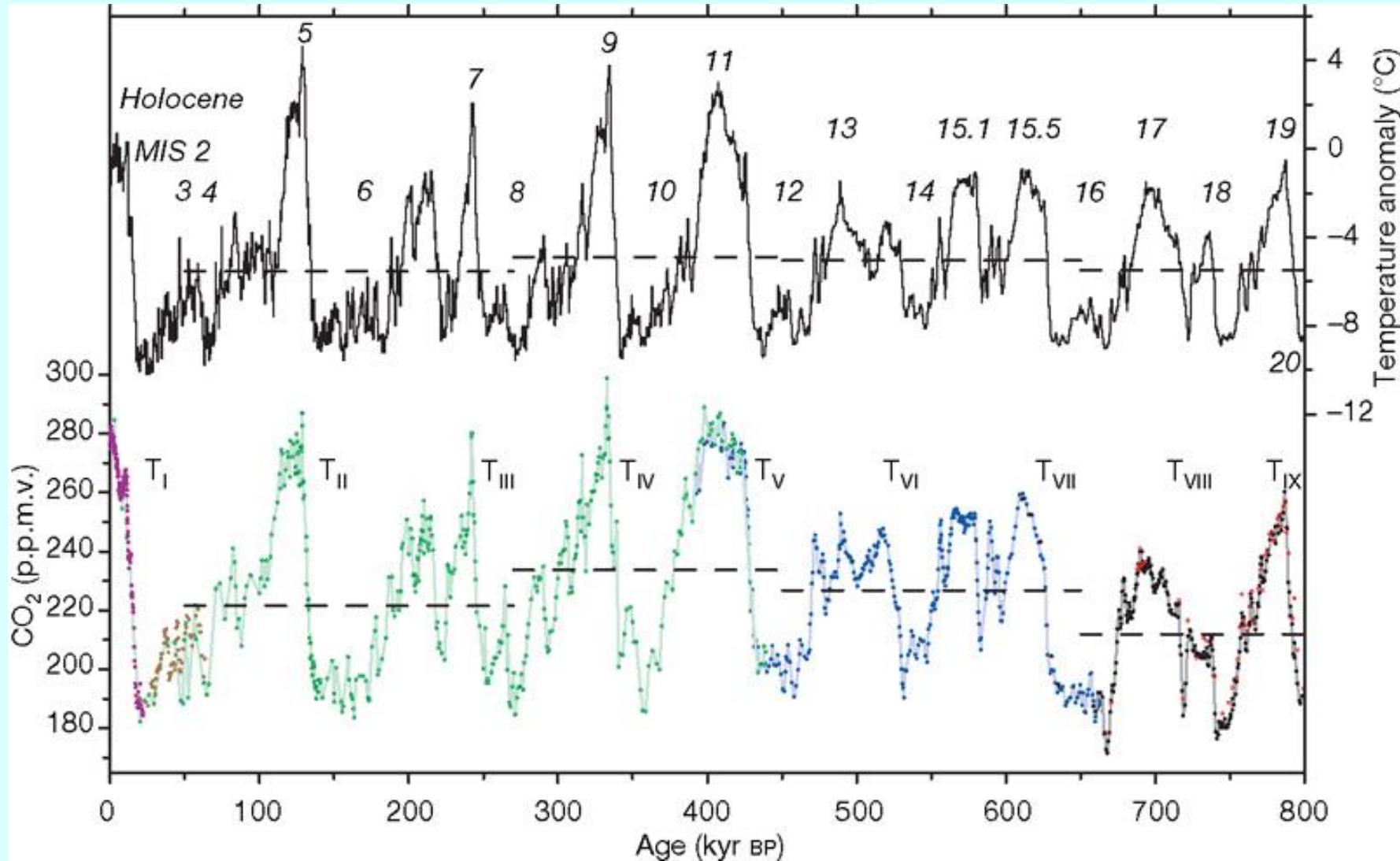


# Greenhouse Gases & Global Climate Change



Dieter Lüthi, Martine Le Floch, Bernhard Bereiter, Thomas Blunier, Jean-Marc Barnola, Urs Siegenthaler, Dominique Raynaud, Jean Jouzel, Hubertus Fischer, Kenji Kawamura & Thomas F. Stocker

*Nature* **453**, 379-382 (15 May 2008)

doi:10.1038/nature06949 PICA ice core , Antarctica

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS \*.

I. *Introduction : Observations of Langley on Atmospheric Absorption.*

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall † in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this : Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere ? Fourier‡ maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet § ; and Langley was by some of his researches led to the view, that "the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to  $-200^{\circ}$  C., if that atmosphere did not possess the quality of selective

\* Extract from a paper presented to the Royal Swedish Academy of Sciences, 11th December, 1895. Communicated by the Author.

† 'Heat a Mode of Motion,' 2nd ed. p. 405 (Lond., 1865).

‡ *Mém. de l'Ac. R. d. Sci. de l'Inst. de France*, t. vii. 1827.

§ *Comptes rendus*, t. vii. p. 41 (1838).

In 1896, Arrhenius made the connection between atmospheric CO<sub>2</sub> and global climate!

## Time Scales for Exchange

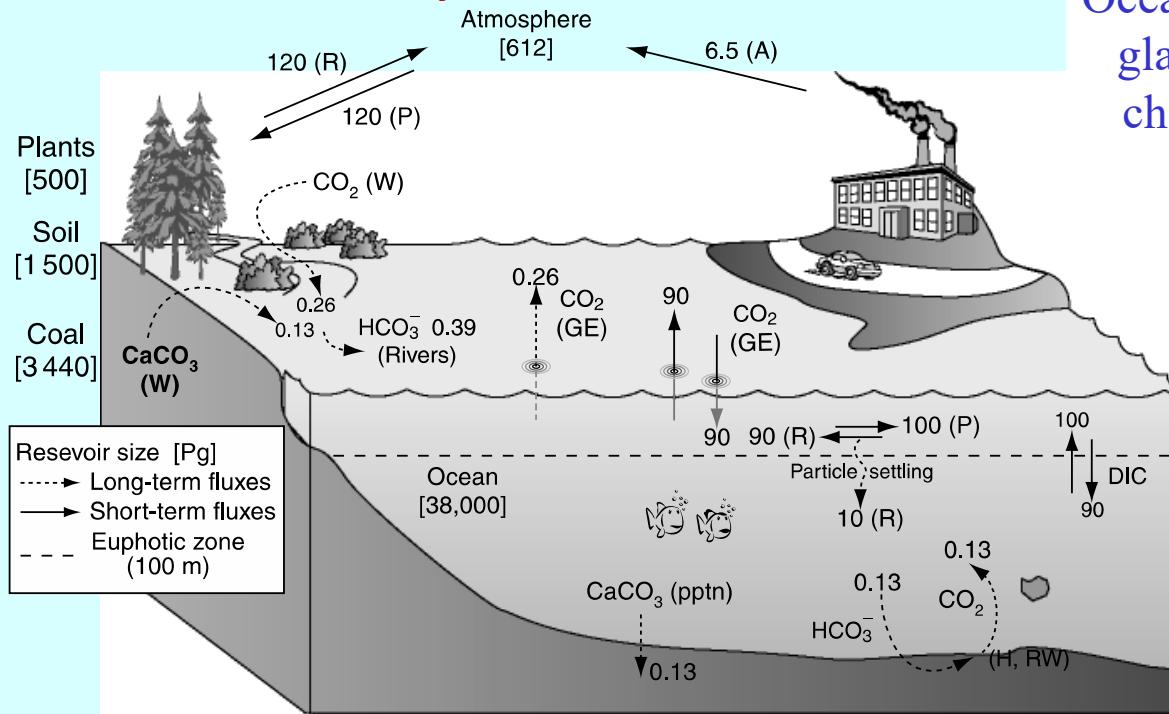
Atm.-surface ocean ~ 10 yr

Atm. - deep ocean ~1000 yr

Atm./Ocean - sediments ~  $10^5$  to  $10^7$  yr.

60X more CO<sub>2</sub> in ocean than in atmosphere!

Oceanic processes drive glacial to interglacial changes in atm. CO<sub>2</sub>



**Figure 11.1.** The global carbon cycle. Values in brackets are preanthropogenic reservoir sizes in Pg ( $10^{15}$  g); values on the arrows are fluxes in Pg  $y^{-1}$ . Dashed lines represent the long-term carbon cycle determined by weathering. Values are normalized to the flux of DIC from rivers (see Chapter 2). Solid arrows are the shorter-term carbon fluxes associated with photosynthesis and respiration. The wiggly vertical line indicates particulate C and DOC transport from the ocean euphotic zone to deep water. Symbols: W, weathering of carbonates ( $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+}$ ) and silicates (silicate +  $\text{CO}_2 + \text{H}_2\text{O} \rightarrow$  clay +  $\text{HCO}_3^- + \text{cations}$ ); GE, gas exchange; P, gross photosynthesis ( $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} (\text{OM}) + \text{O}_2$ ); R, respiration ( $\text{CH}_2\text{O} (\text{OM}) + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ ); PPT, calcite precipitation (the reverse of carbonate weathering); H, hydrothermal processes; RW, reverse weathering (the reverse of silicate weathering).

## Atmosphere

### Biological Pump

### Solubility Pump

Cold, Polar  
Surface Ocean

Warm, Temp/Tropical  
Surface Ocean

$\text{CaCO}_3$   
(decrease in ALK  
net increase in  $\text{pCO}_2$ )

Organic Matter  
(no change in ALK  
net decrease in  $\text{pCO}_2$ )

$\text{CaCO}_3/\text{OM}$  ratio  
Controlled by biology e.g.  
*diatoms vs coccolithophorids*

Cold, Deep  
Interior Ocean

Particle sinking

Particle sinking

Advection/ mixing  
and storage in  
large volume of  
very cold, deep  
ocean water

(increase in ALK  
net decrease in  $\text{pCO}_2$ )

No change in ALK  
net increase in  $\text{pCO}_2$

$\text{CO}_2$

$\text{CO}_2$

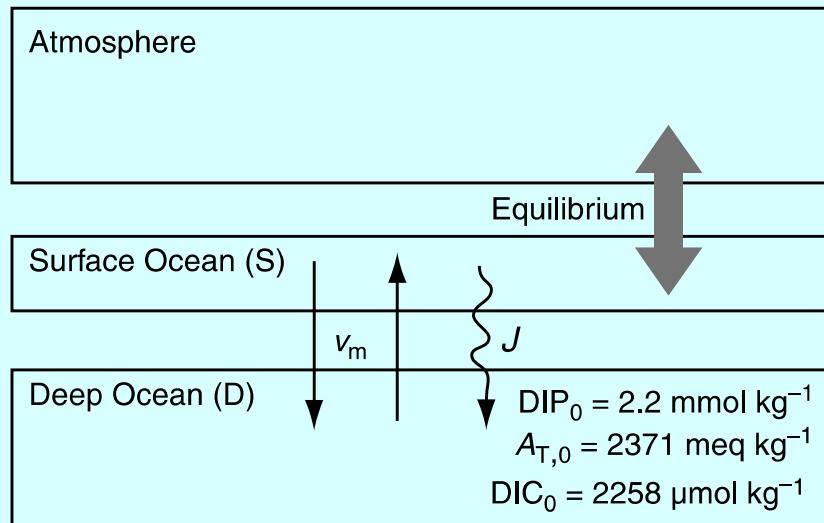
$\text{CO}_2$

$\text{CO}_2$

Higher solubility  
due to cold SST

$\text{CO}_2$

**Figure 11.2.** Sketch of the three-box model of the atmosphere, surface and deep ocean. Equations indicate the circulation dynamics ( $V_m$  in  $\text{m yr}^{-1}$ , is the mixing rate between the surface and deep ocean); stoichiometry of the particulate transport ( $J$  in  $\text{mol m}^{-2} \text{yr}^{-1}$ ); and chemical equilibria of the carbonate system.



$$\text{Dynamics: } V_D \times \frac{d[C_D]}{dt} = 0 = V_m \times ([C_S] - [C_D]) + J$$

$$\begin{aligned}\text{Stoichiometry: } \Delta P : \Delta N : \Delta DIC : \Delta A_T : \Delta Ca \\ 1 : 16 : 136 : 44 : 30\end{aligned}$$

Equilibrium:

$$DIC = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$$

$$A_{C\&B} = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{B(OH)}_4^-]$$

$$B_T = \text{B(OH)}_3 + \text{B(OH)}_4^-$$

$$K_{\text{H,CO}_2} = \frac{[\text{CO}_2]}{f_{\text{CO}_2}^a}$$

$$K_2' = \frac{[\text{CO}_3^{2-}] [\text{H}^+]}{[\text{HCO}_3^-]}$$

$$K_1' = \frac{[\text{HCO}_3^-] [\text{H}^+]}{[\text{CO}_2]}$$

$$K_B' = \frac{[\text{B(OH)}_4^-] [\text{H}^+]}{[\text{B(OH)}_3]}$$

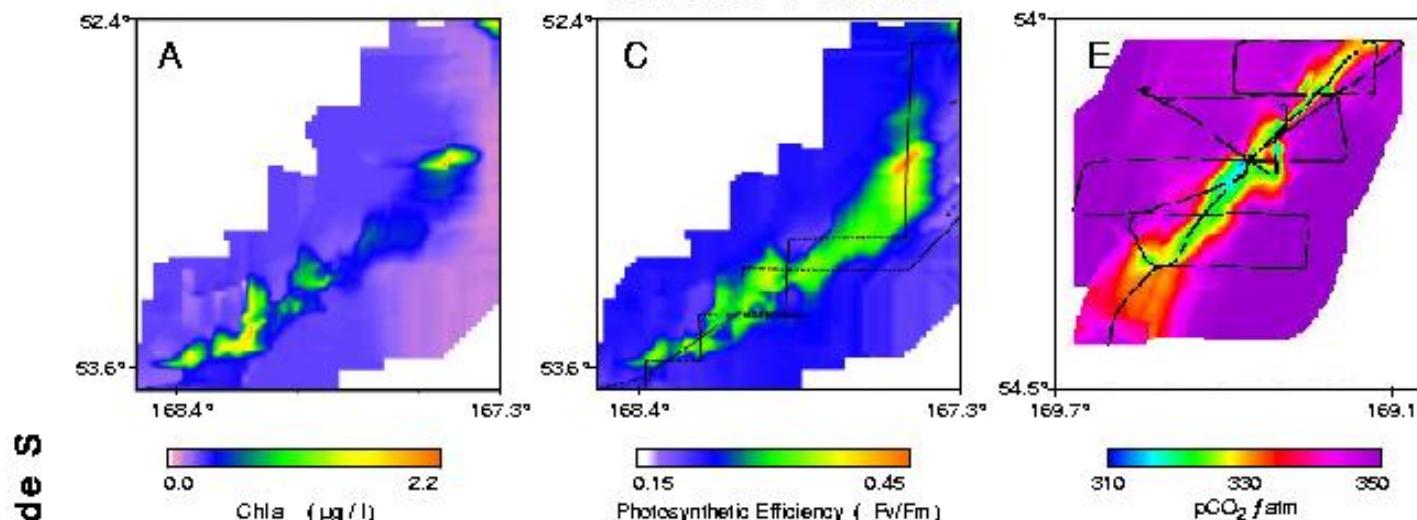
**Table 11.2.** The effect of the solubility and biological pumps on the fugacity of  $\text{CO}_2$  in the atmosphere,  $f_{\text{CO}_2}$ , determined by the simple two-layer ocean model depicted in Fig. 11.2

The first row is the standard case and the rows under this indicate changes due to temperature, carbon flux, circulation rate and the organic carbon to  $\text{CaCO}_3$  ratio of the particle flux,  $\text{OC} : \text{CaCO}_3$ .

| Case                                 | Temp<br>°C | $[\text{DIP}]_S$<br>$\mu\text{mol kg}^{-1}$ | $\tau_{\text{mix}}$<br>y | $R_{\text{OC:CA}}$ | $\text{DIC}_S$<br>$\mu\text{mol kg}^{-1}$ | $A_{T,S}$<br>$\mu\text{eq kg}^{-1}$ | $f_{\text{CO}_2}$<br>atm |
|--------------------------------------|------------|---|--------------------------|--------------------|---|-------------------------------------|--------------------------|
| Standard                             | 20         | 0.5   | 1000                     | 3.5                | 2027                                      | 2296                                | 375                      |
| Temp. effect                         | 15         |   |                          |                    |   |                                     | 304                      |
|                                      | 25         |   |                          |                    |   |                                     | 460                      |
| Biol. pump                           |            |   |                          |                    |   |                                     |                          |
| Carbon flux                          | 20         | 2.2   |                          |                    | 2258                                      | 2371                                | 1184                     |
|                                      |            | 0.0   |                          |                    | 1959                                      | 2274                                | 293                      |
| Circulation                          |            | 0.85  | 500                      |                    | 2074                                      | 2312                                | 446                      |
|                                      |            | 0.0   | 1500                     |                    | 1959                                      | 2274                                | 291                      |
| OC:CaCO <sub>3</sub><br>(P:OC = 106) |            | 0.5   | 1000                     | 10:1               | 2059                                      | 2361                                | 337                      |
|                                      |            |   |                          | 1.5:1              | 1957                                      | 2157                                | 485                      |

# SOFEX Fe Fertilization Study in Southern Ocean

## North Patch



## South Patch

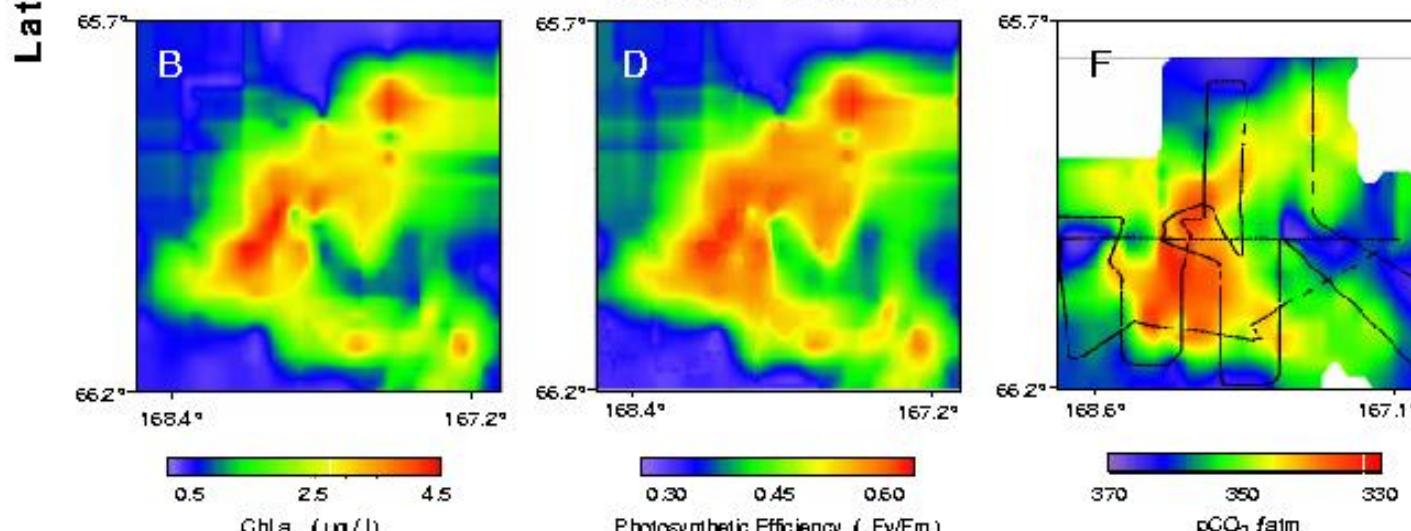
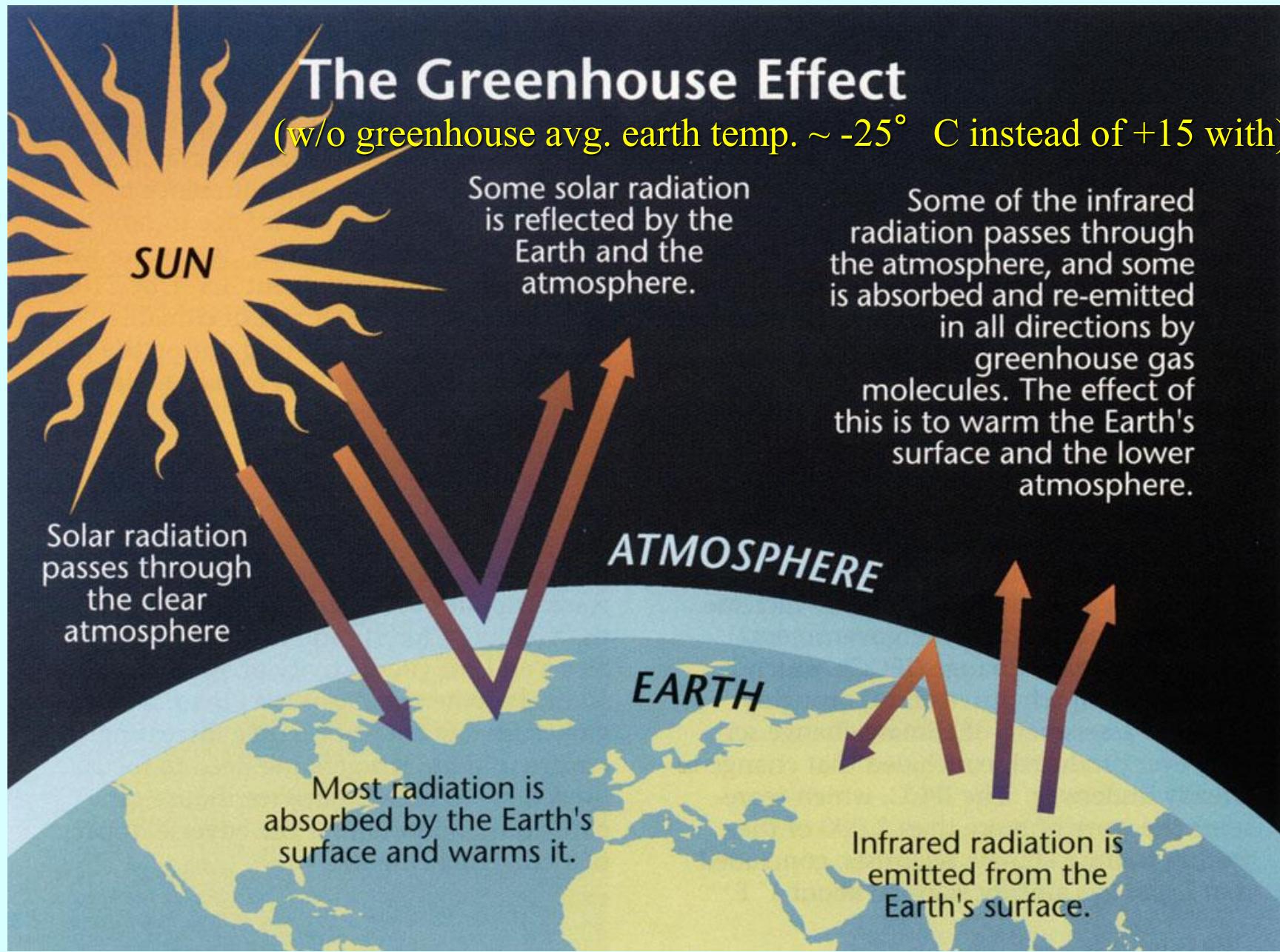


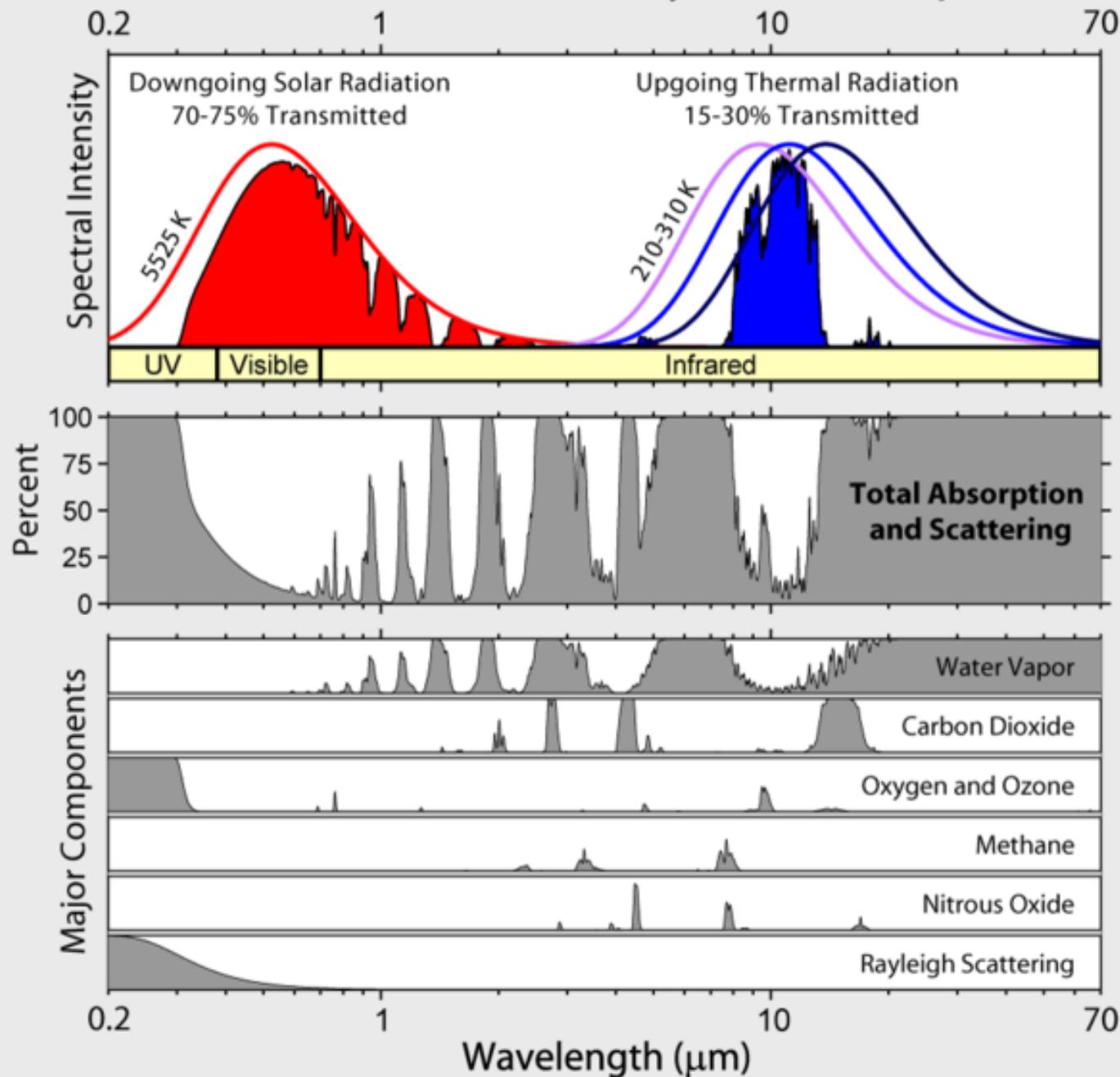
Fig. S3

# The Greenhouse Effect

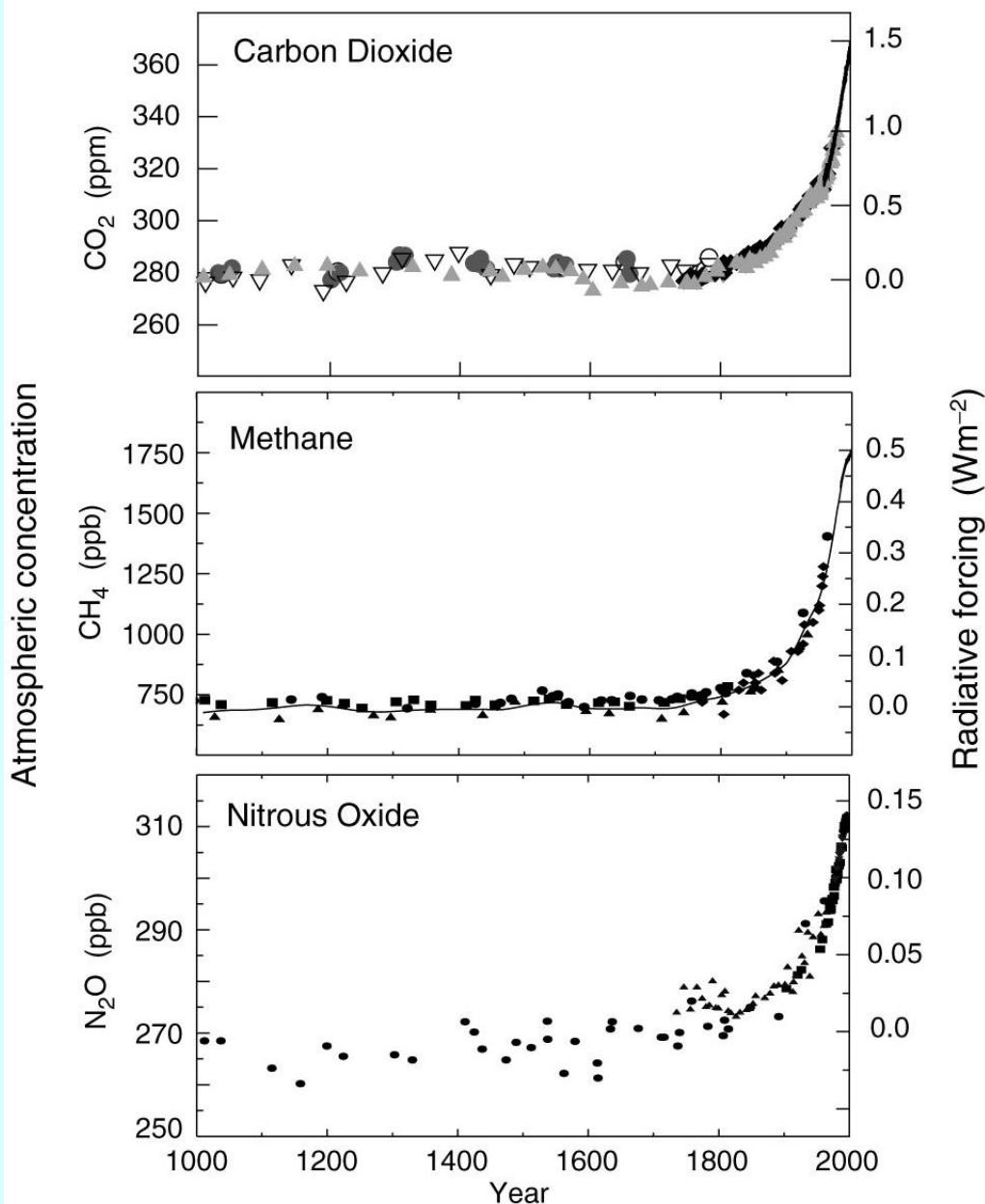
(w/o greenhouse avg. earth temp.  $\sim -25^{\circ}$  C instead of +15 with)



# Radiation Transmitted by the Atmosphere



**(a) Global atmospheric concentrations of three well mixed greenhouse gases**



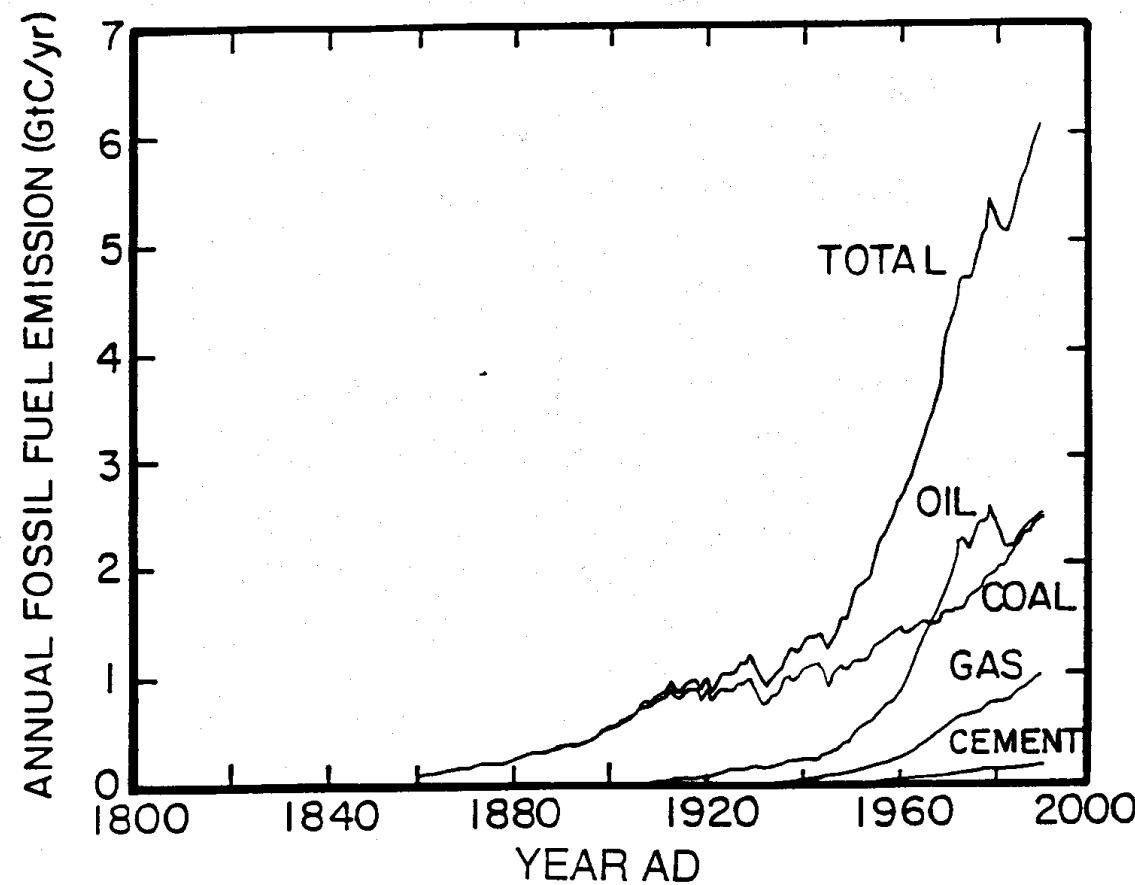
# Anthropogenic Influence on Atmospheric Concentration of Greenhouse Gases

Source: IPCC TAR 2001

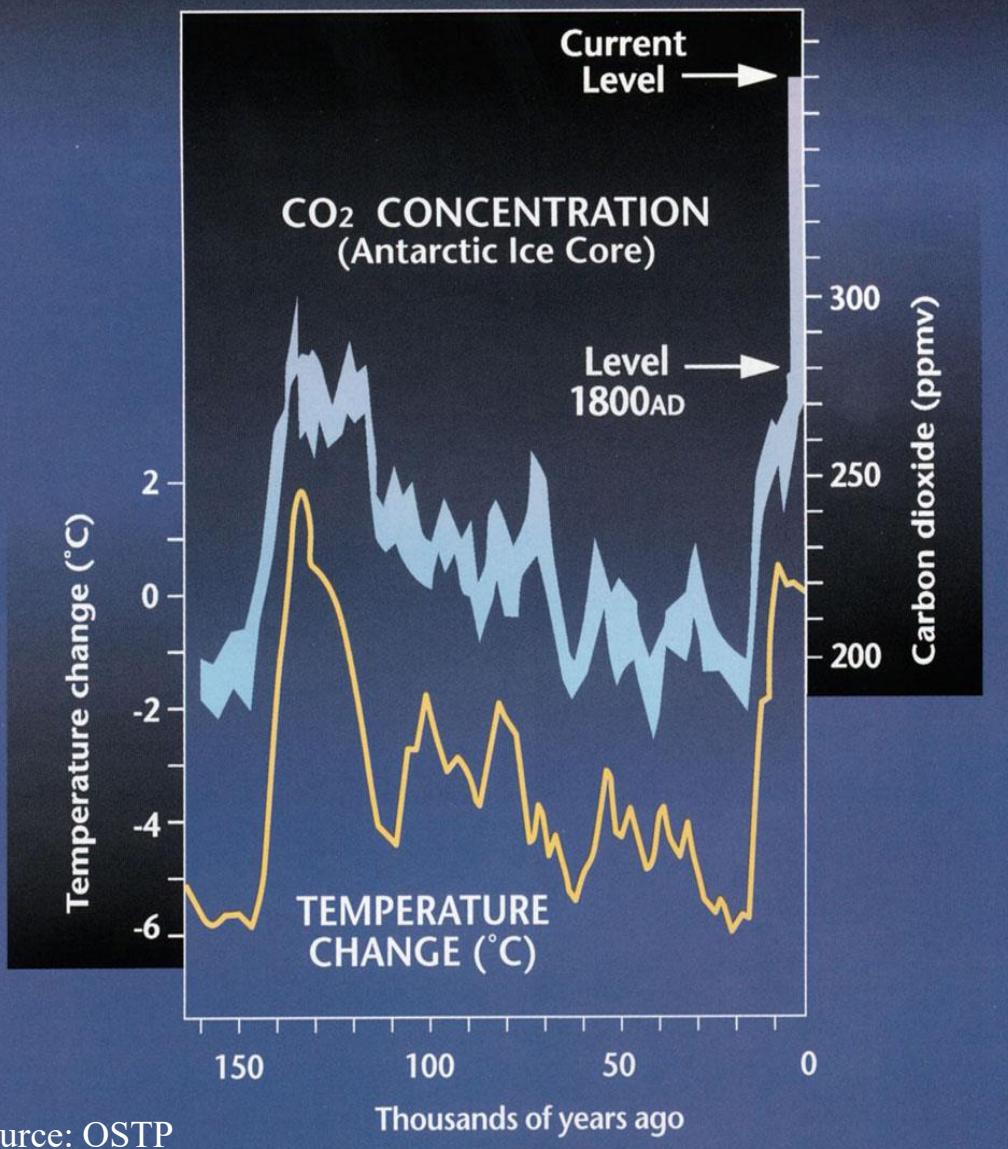


Union of  
Concerned  
Scientists

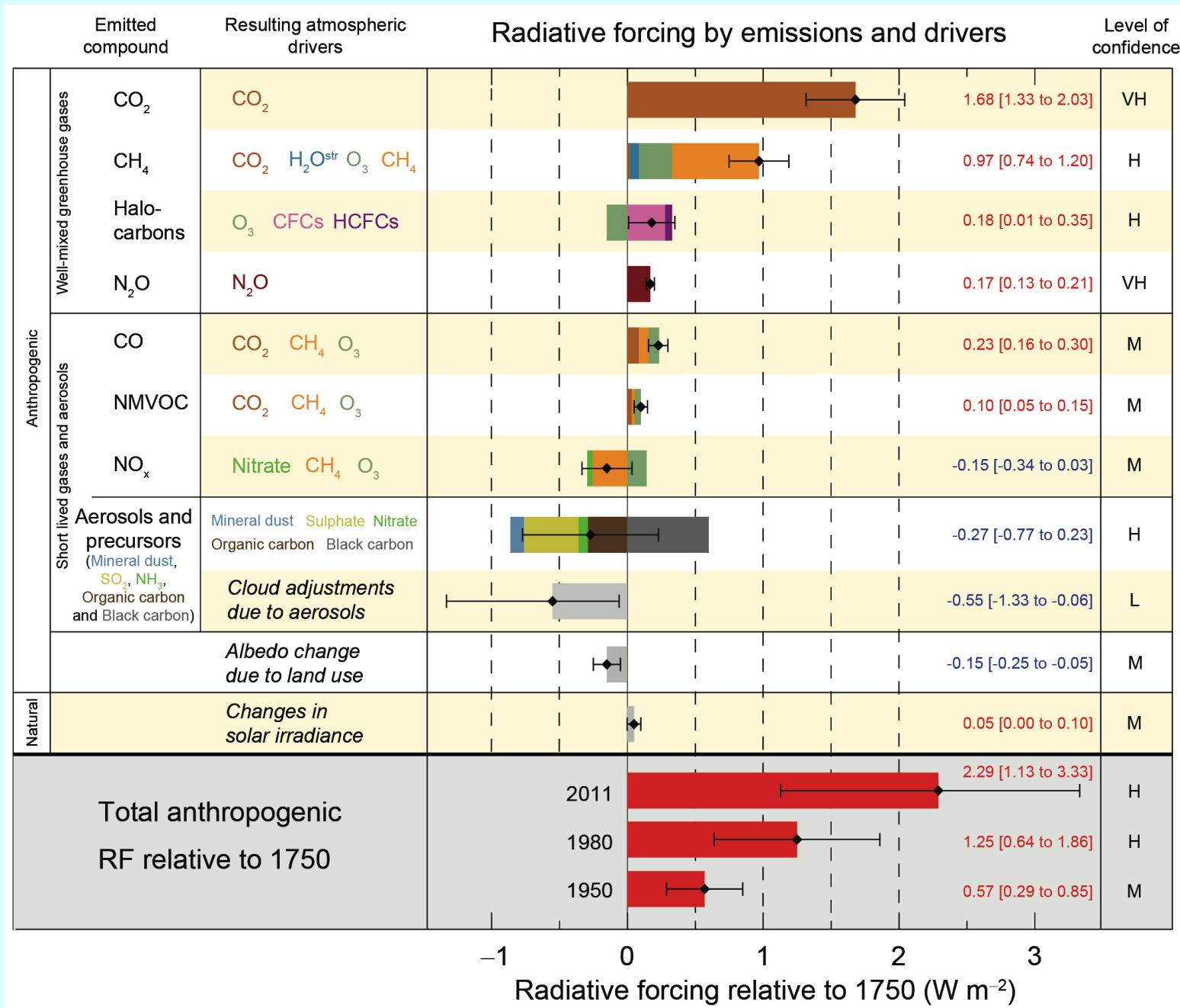
# TIME HISTORY OF FOSSIL FUEL CONSUMPTION



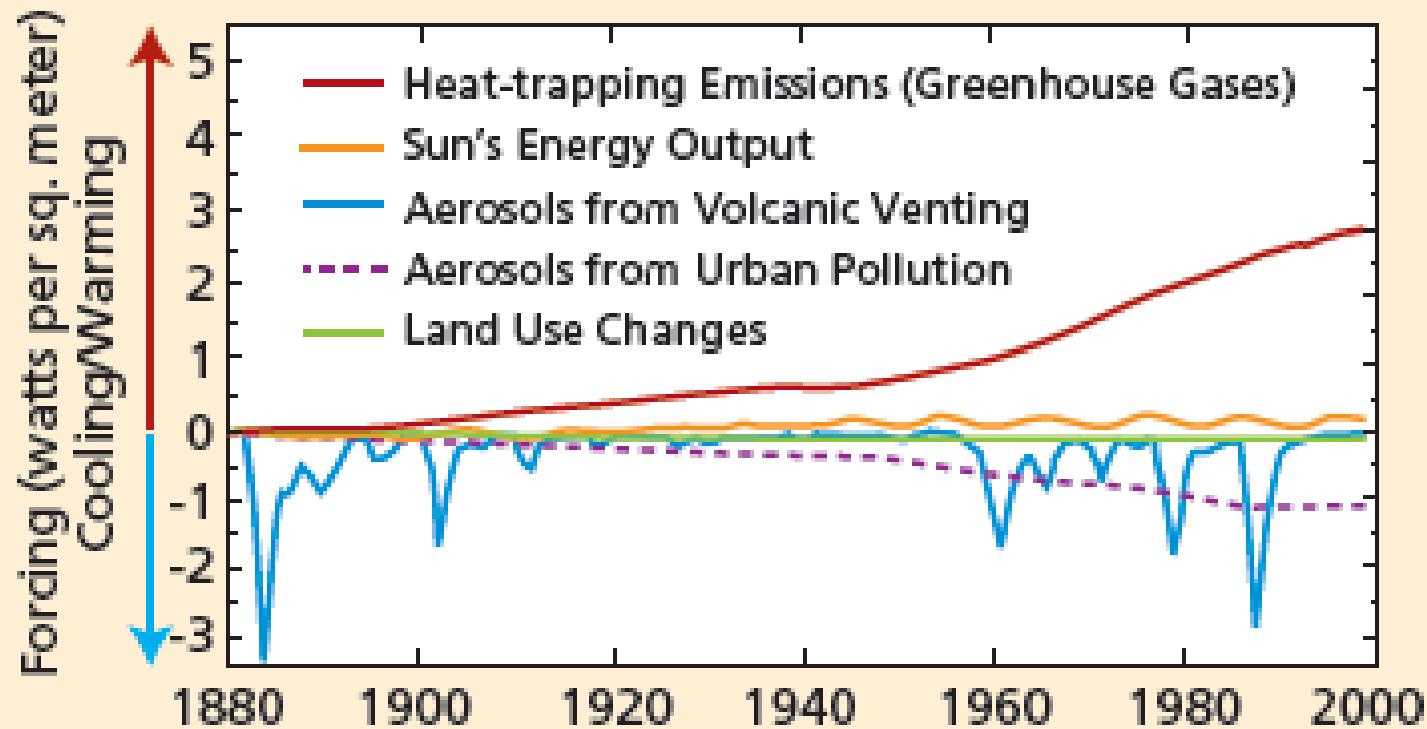
# Atmospheric Carbon Dioxide Concentration and Temperature Change



- Clear correlation between atmospheric CO<sub>2</sub> and temperature over last 160,000 years
- Current level of CO<sub>2</sub> is *outside* bounds of natural variability
- Rate of change of CO<sub>2</sub> is also unprecedented

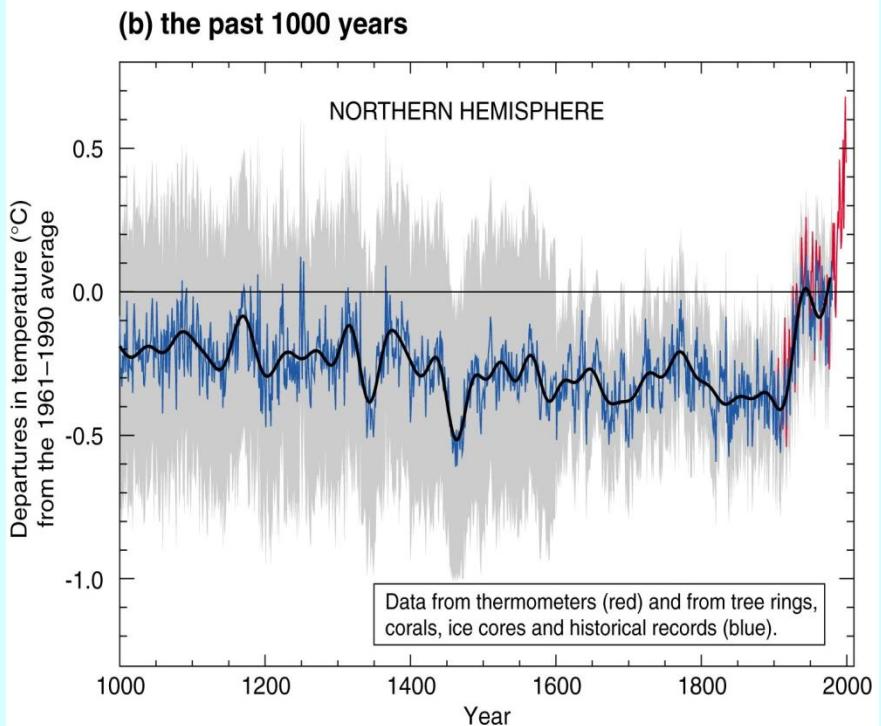
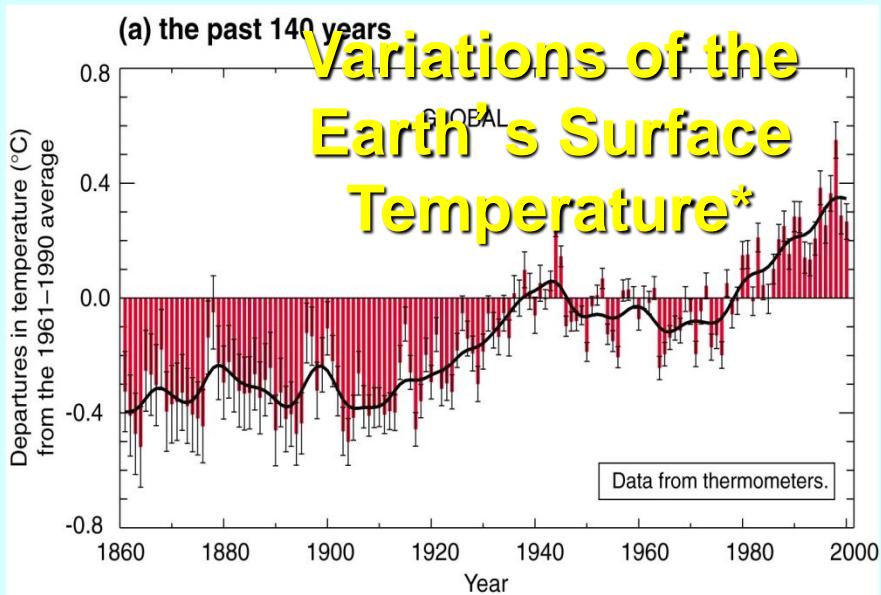


# Global Climate Drivers

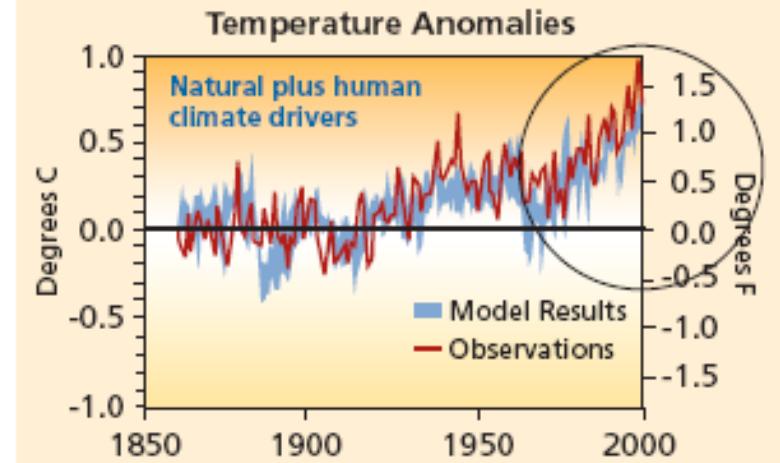
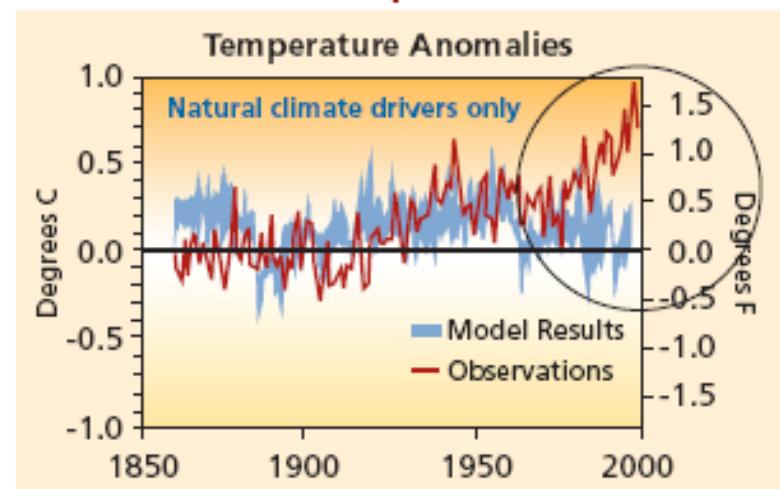


**Heat-trapping emissions (greenhouse gases) far outweigh the effects of other drivers acting on Earth's climate.**

Source: Hansen et al. 2005.

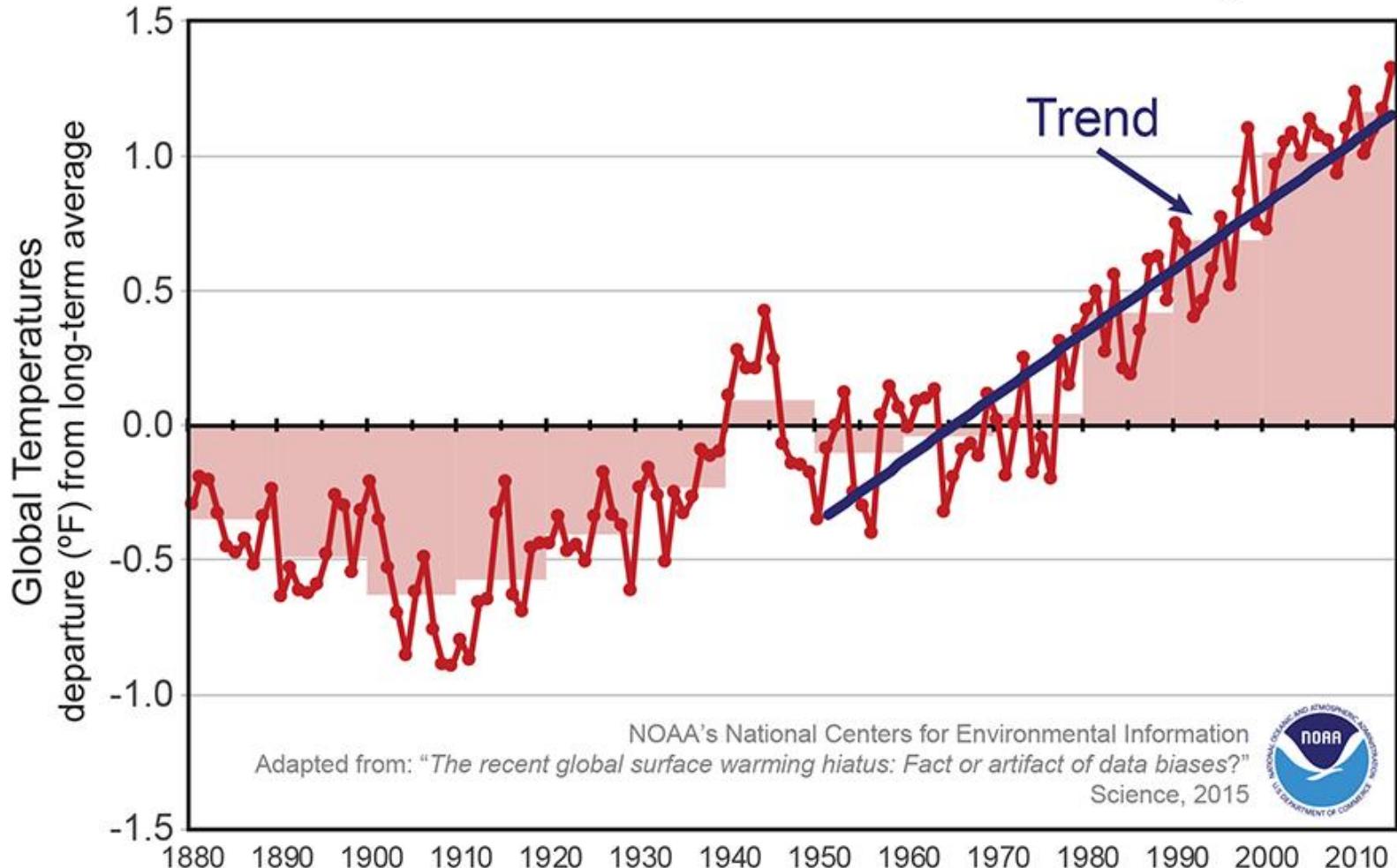


## Climate Drivers Compared with Global Surface Temperature

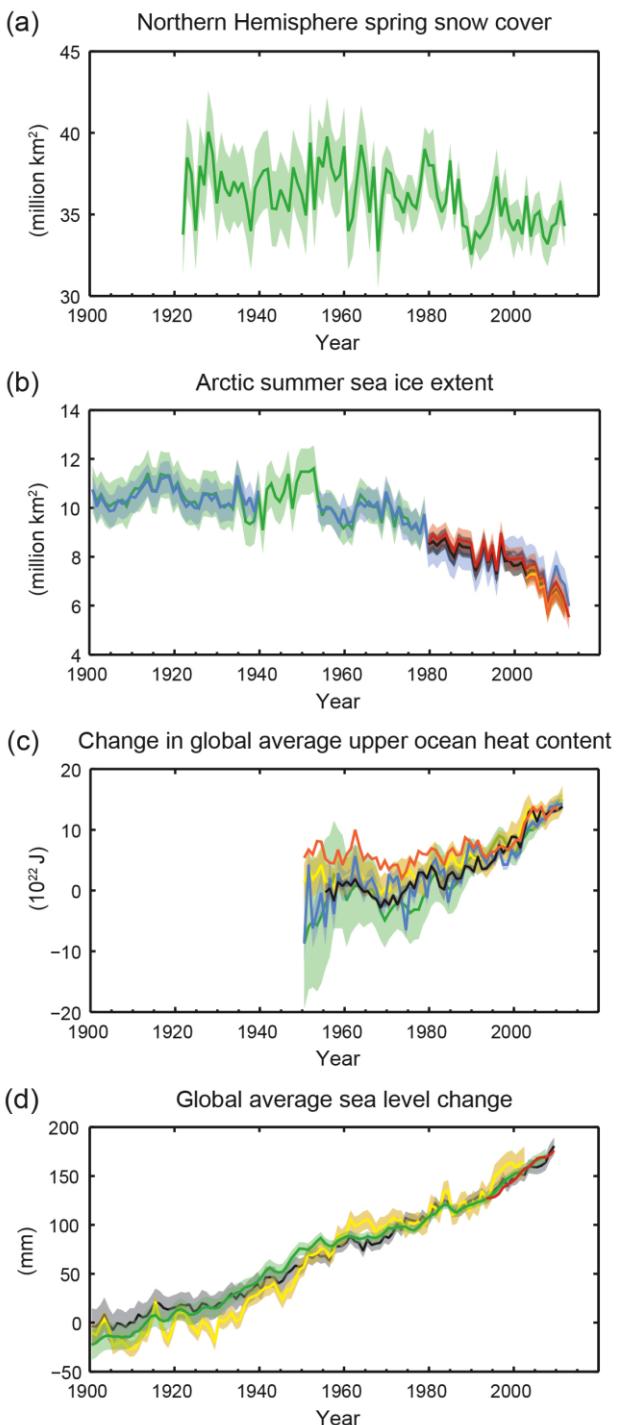
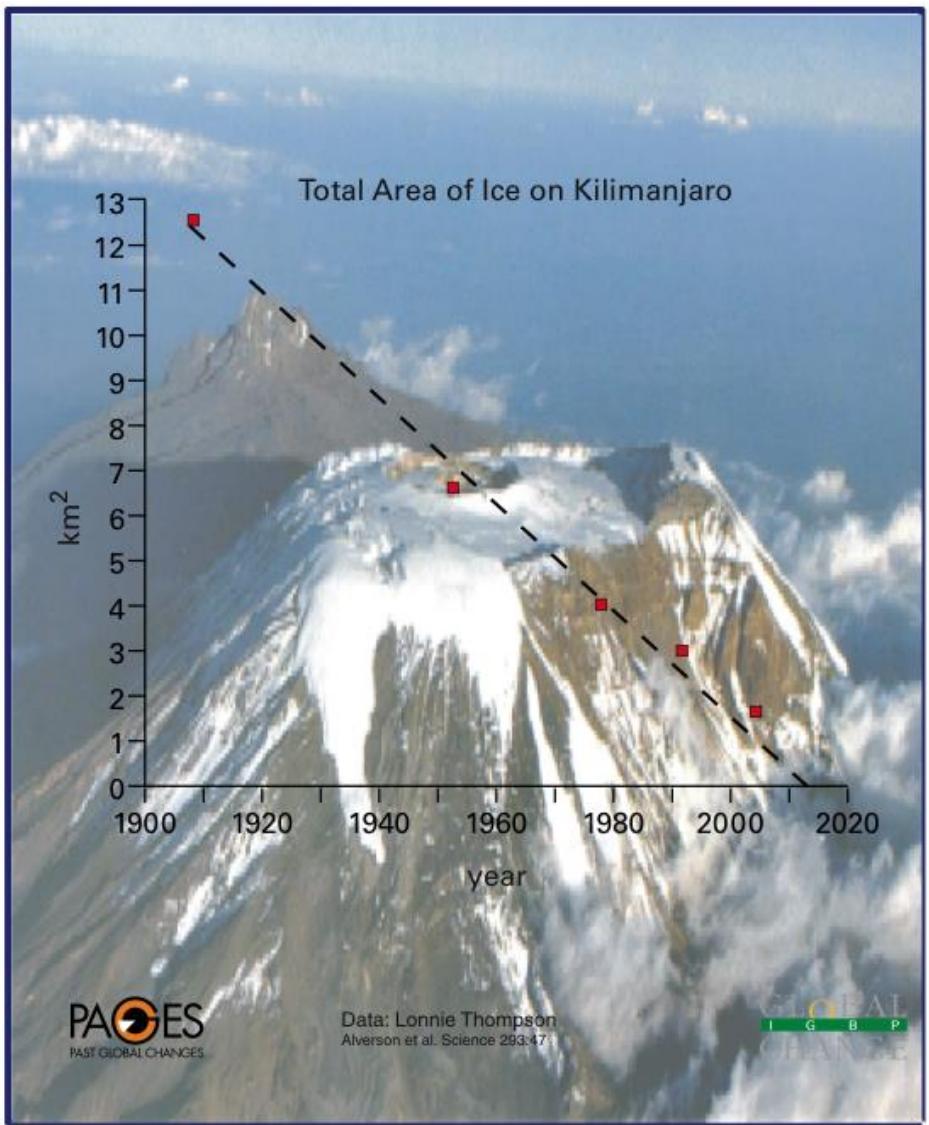


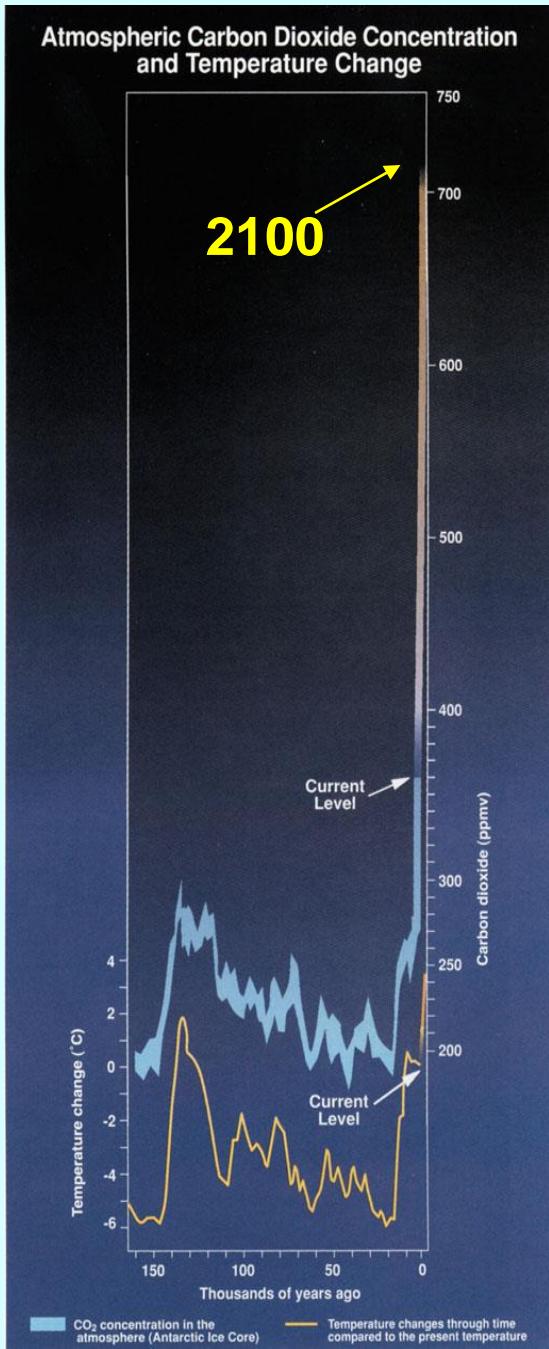
The model output (blue shading) that includes both natural and human-induced drivers (lower graph) gives a better match with the observed temperature response (red line). Source: IPCC TAR 2001.

# No Slow Down in Global Warming



Contrary to much recent discussion, the latest corrected analysis shows that the rate of global warming has continued, and there has been no slow down.





If business as usual:

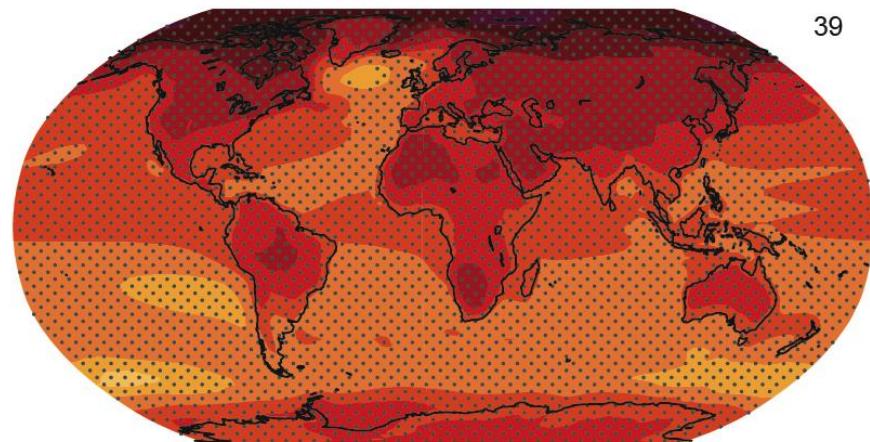
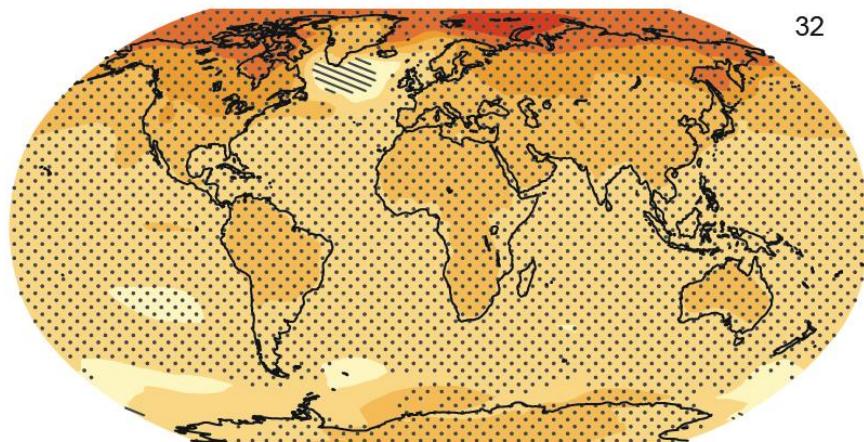
- CO<sub>2</sub> concentrations will likely be more than 700 ppm by 2100
- Global average temperatures projected to increase between 2.5 - 10.4° F

RCP 2.6

RCP 8.5

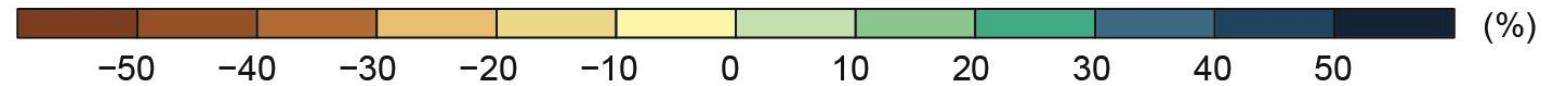
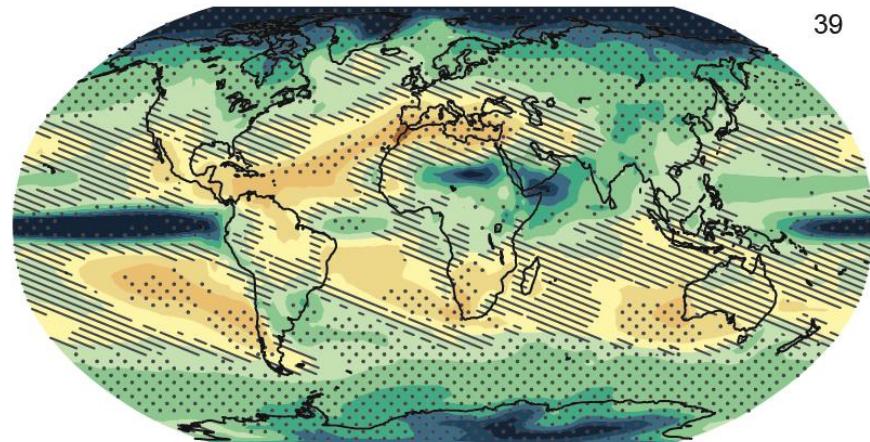
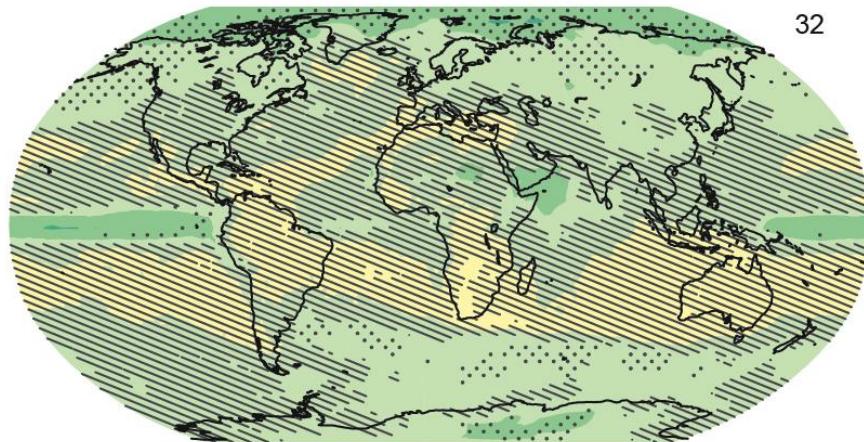
(a)

Change in average surface temperature (1986–2005 to 2081–2100)



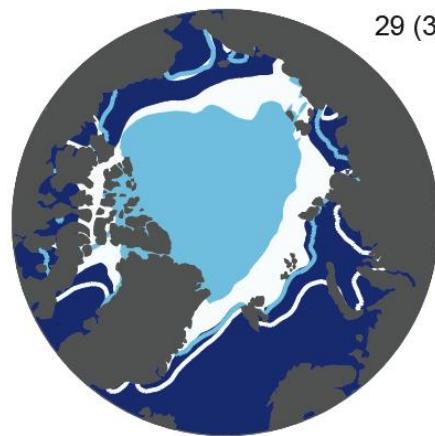
(b)

Change in average precipitation (1986–2005 to 2081–2100)

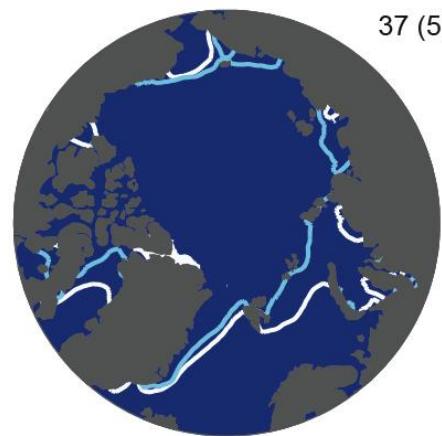


(c)

### Northern Hemisphere September sea ice extent (average 2081–2100)

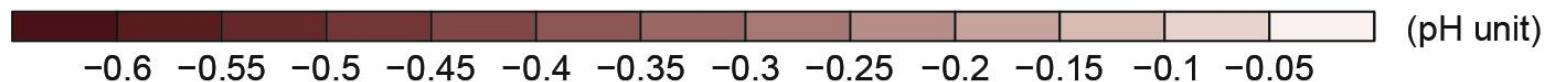
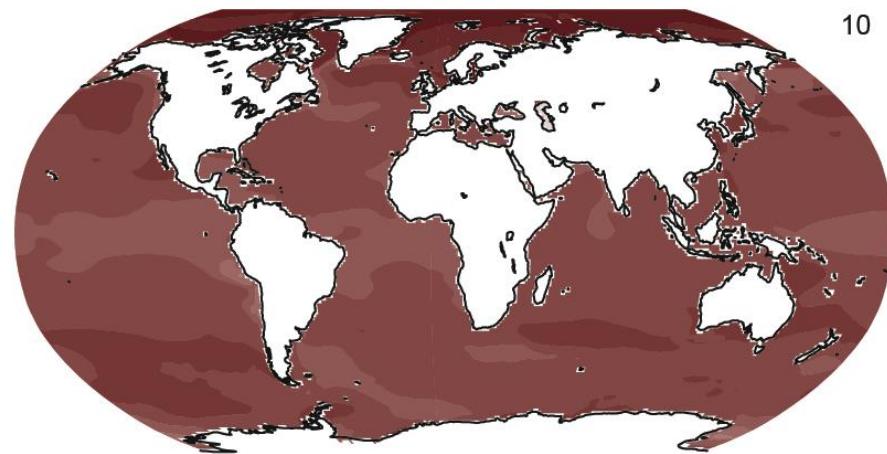
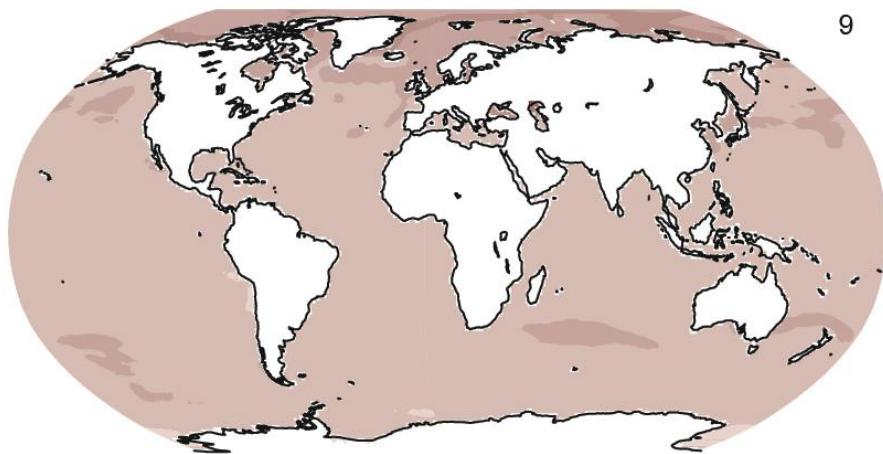


- CMIP5 multi-model average 1986–2005
- CMIP5 multi-model average 2081–2100
- CMIP5 subset average 1986–2005
- CMIP5 subset average 2081–2100



(d)

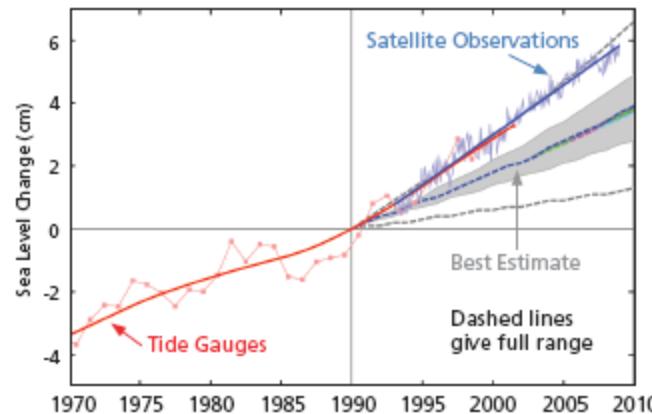
### Change in ocean surface pH (1986–2005 to 2081–2100)





10 m sea level rise

FIGURE 2 Sea Level Rise In Line with Highest Projection



Changes in sea level since 1973, compared with IPCC scenarios (dashed lines and gray ranges), based on tide gauges (red) and satellites (blue). From Rahmstorf et al. (2007) updated by Rahmstorf (personal communication).

FIGURE 3 Sea Level Rise by End of This Century

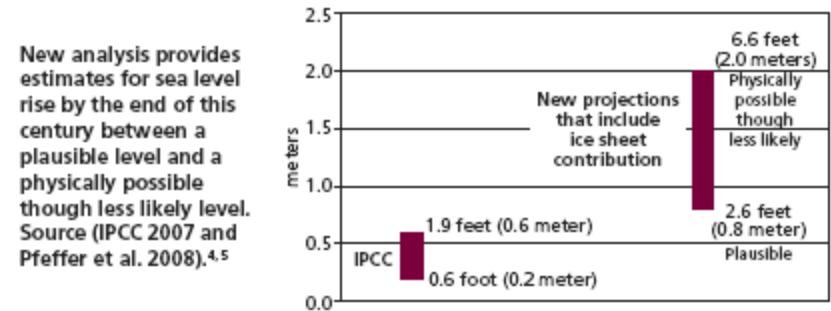
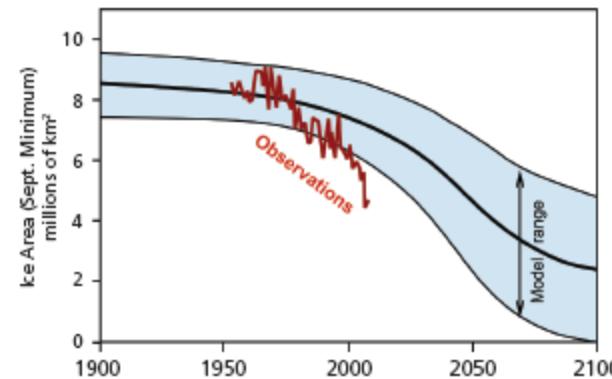


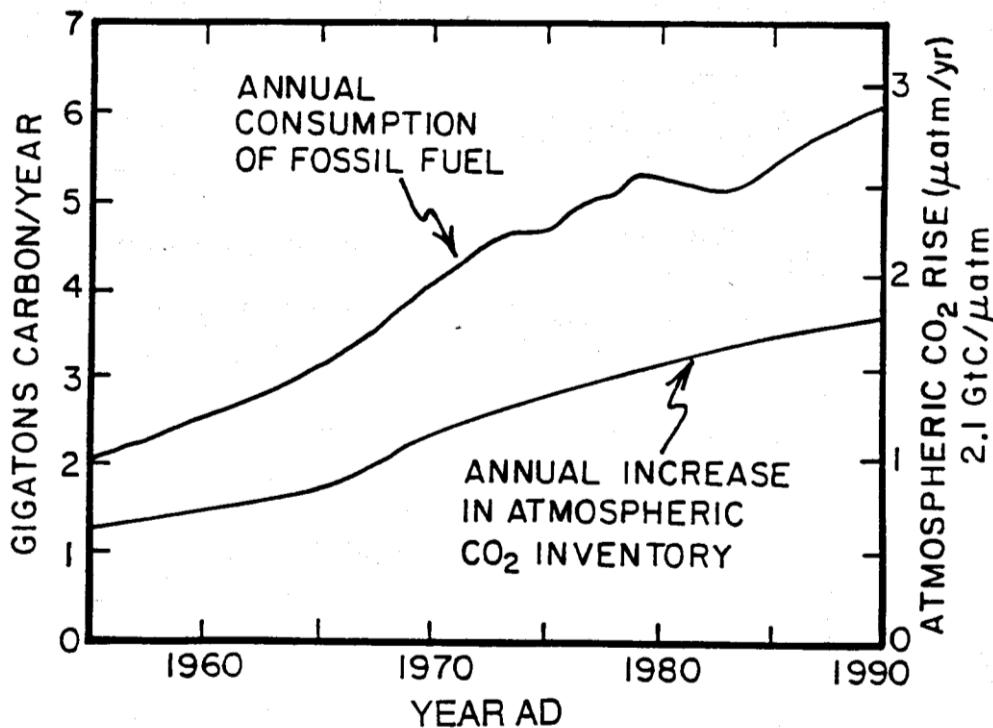
FIGURE 4 Shrinking Summer Arctic Sea Ice Area



Arctic models of September sea ice area underestimate the rate of observed sea ice retreat. Based on Stroeve et al. 2007.

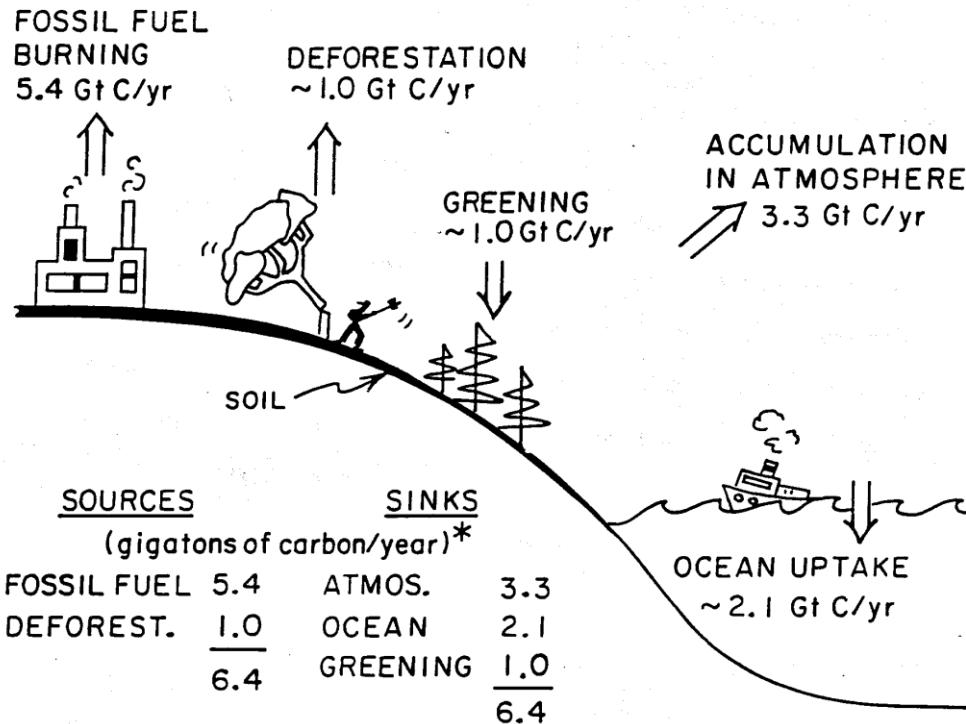
Sources: Dirk Notz from Hamburg adapted figure from <http://www.nslc.org/news/Images20070430Figure1.png>.

## COMPARISON WITH THE RATE OF ACCUMULATION OF CO<sub>2</sub> IN THE ATMOSPHERE



OVER THE TIME PERIOD DURING WHICH THE ATMOSPHERE HAS BEEN ACCURATELY MONITORED, ITS CO<sub>2</sub> CONTENT HAS BEEN RISING AT A RATE ONLY ABOUT 60% THE RATE EXPECTED IF ALL THE FOSSIL FUEL CO<sub>2</sub> RELEASED REMAINED AIRBORNE.

**APROXIMATE  
EARTH CARBON BUDGET  
FOR THE 1980s;  
THE ANTHROPOGENIC PERTURBATION**



$$\text{FRAC. TO ATMOS. } \frac{3.3}{6.4} = .52$$

\* 1 Gt =  $1 \times 10^{15}$  grams

$$\text{FRAC. TO SEA } \frac{2.1}{6.4} = .33$$

$= 1 \times 10^9$  tons

$$\text{FRAC. TO CONT. } \frac{1.0}{6.4} = .15$$

1.00

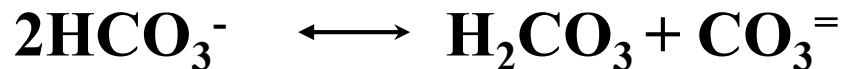
## Atmosphere

*Net transfer to ocean due to disequilibrium in pCO<sub>2</sub>*

Warm, Temp/Tropical  
Surface Ocean



Air/sea exchange  
calibrated with <sup>14</sup>C and  
Rn tracers



Surface/deep  
exchange primary  
brake on net CO<sub>2</sub>  
transfer

Whole ocean has the capacity to absorb 5/6  
of the atm. increase in CO<sub>2</sub> through this  
mechanism, but can only occur on time scale of  
surface to deep mixing ~ hundreds of years.

Cold, Deep  
Interior Ocean



# THERMODYNAMIC CAPACITY FOR CO<sub>2</sub> UPTAKE

IDEALIZED SEA WATER (NO BORATE)

CHARGE BALANCE

$$[Na^+] + [K^+] + 2[Mg^{++}] + 2[Ca^{++}] = [Cl^-] + 2[SO_4^{=}] + [HCO_3^-] + 2[CO_3^{=}]$$

OR

$$[Na^+] + [K^+] + 2[Mg^{++}] + 2[Ca^{++}] - [Cl^-] - 2[SO_4^{=}] = [HCO_3^-] + 2[CO_3^{=}]$$

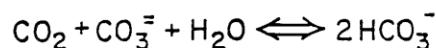
OR

$$[ALKALINITY] = [HCO_3^-] + 2[CO_3^{=}]$$

MASS BALANCE FOR DISSOLVED INORGANIC CARBON

$$[\Sigma CO_2] = [CO_2] + [HCO_3^-] + [CO_3^{=}]$$

CHEMICAL EQUILIBRIUM



$$K_c' = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{=}]} , \quad \alpha = \frac{[CO_2]}{pCO_2} = 0.342 \frac{\mu\text{mol/kg}}{\mu\text{atm}}$$

EXAMPLE T=18°C S=35‰ K<sub>c</sub>' = 1445 ALK = 2100

| pCO <sub>2</sub> = 280 μatm             | pCO <sub>2</sub> = 360 μatm             | Δ            |
|---|---|--------------|
| [CO <sub>2</sub> ] = 9.6                | [CO <sub>2</sub> ] = 12.3               | +2.6 μmol/kg |
| [HCO <sub>3</sub> <sup>-</sup> ] = 1700 | [HCO <sub>3</sub> <sup>-</sup> ] = 1769 | +69 μmol/kg  |
| [CO <sub>3</sub> <sup>=</sup> ] = 200   | [CO <sub>3</sub> <sup>=</sup> ] = 166   | -34 μmol/kg  |
| [ALK] = 2100                            | [ALK] = 2100                            | 0 μmol/kg    |
| [ΣCO <sub>2</sub> ] = 1910              | [ΣCO <sub>2</sub> ] = 1948              | +38 μmol/kg  |

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2 / pCO_2}{\Delta \Sigma CO_2 / \Sigma CO_2} = \frac{80/280}{38/1910} = 14.4$$

# ACTUAL SEA WATER (INCLUDING BORATE)

## CHARGE BALANCE

$$[\text{ALKALINITY}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{H}_4\text{BO}_4^-]$$

## MASS BALANCE BORON

$$[\Sigma \text{B}] = [\text{H}_3\text{BO}_3^0] + [\text{H}_4\text{BO}_4^-] = 410.6 \frac{\text{S}}{35} \mu\text{mol/kg}$$

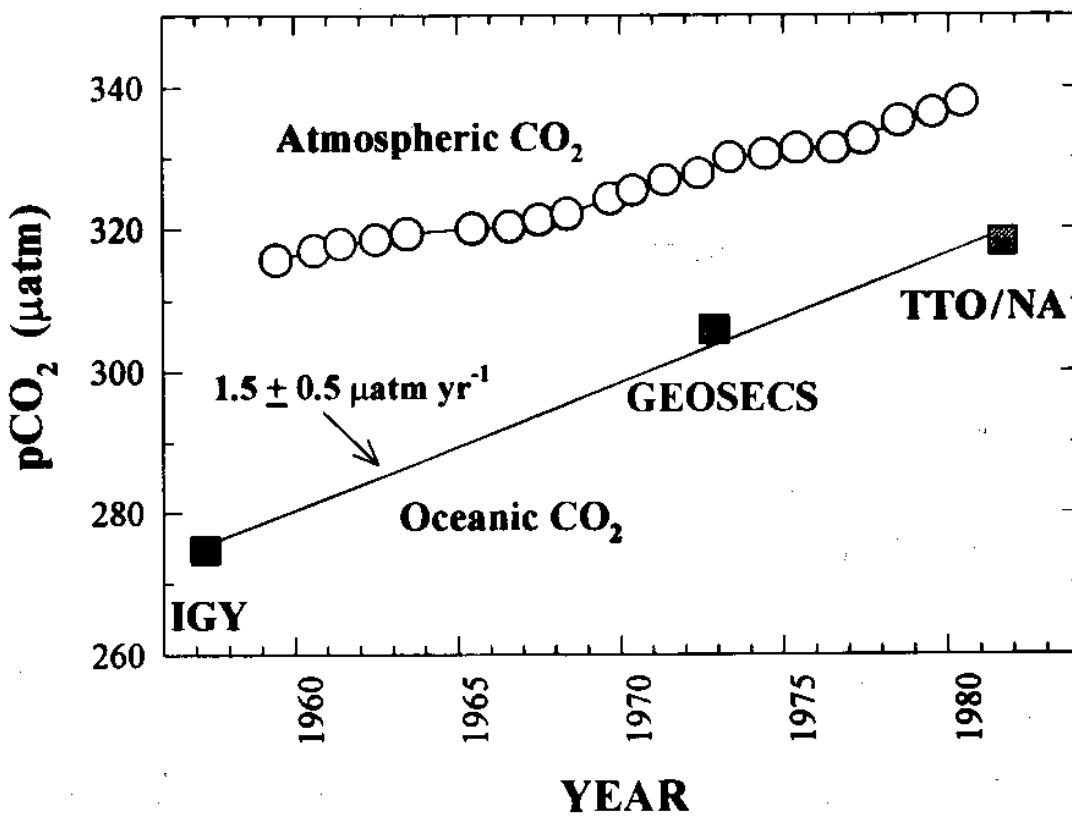
## CHEMICAL EQUILIBRIUM

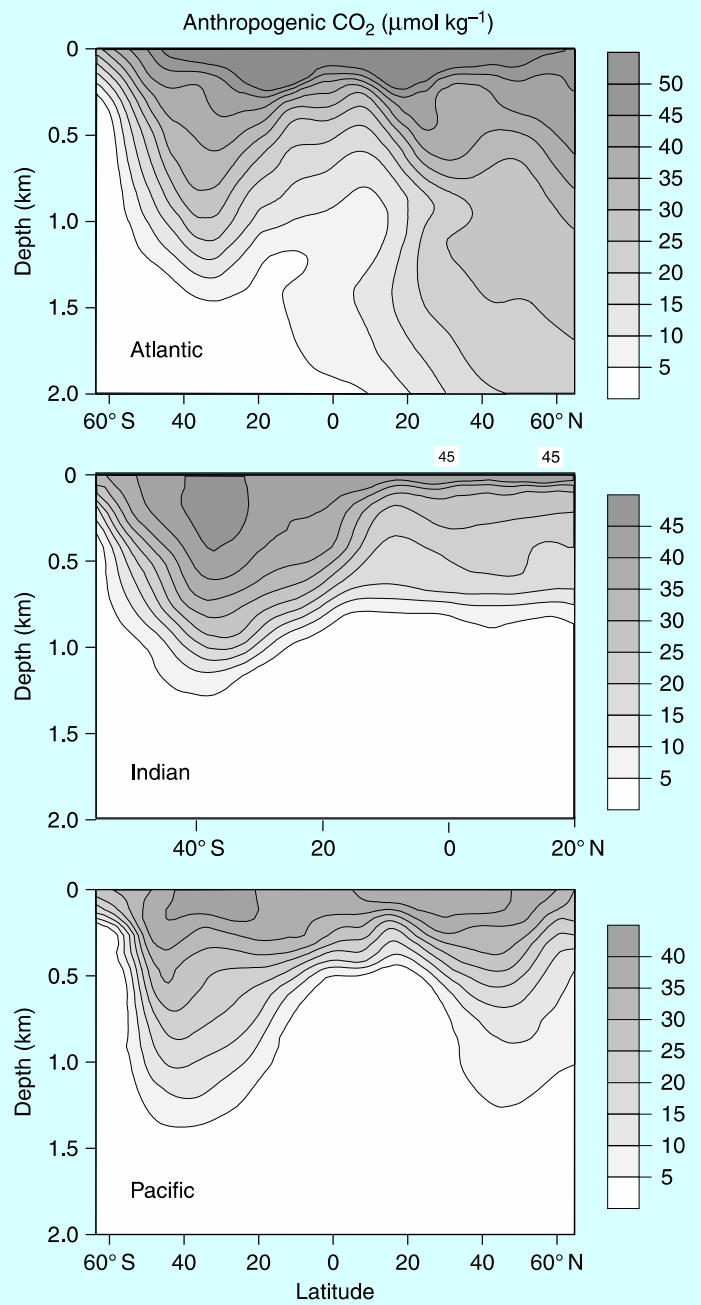
$$K_B' = \frac{[\text{H}_4\text{BO}_4^-][\text{HCO}_3^-]}{[\text{H}_3\text{BO}_3^0][\text{CO}_3^{=}]}$$

EXAMPLE T = 18°C S = 35‰  $K_C' = 1482$   $K_B' = 2.75$   
 ALK = 2216 SiO<sub>2</sub> = 0 NO<sub>3</sub> = 0 PO<sub>4</sub> = 0

| $\text{pCO}_2 = 280 \mu\text{atm}$  | $\text{pCO}_2 = 360 \mu\text{atm}$  | $\Delta$                 |
|-------------------------------------|-------------------------------------|--------------------------|
| $[\text{CO}_2] = 9.6$               | $[\text{CO}_2] = 12.3$              | $+2.6 \mu\text{mol/kg}$  |
| $[\text{HCO}_3^-] = 1702.5$         | $[\text{HCO}_3^-] = 1779.5$         | $+77.0 \mu\text{mol/kg}$ |
| $[\text{CO}_3^{=}] = 203.7$         | $[\text{CO}_3^{=}] = 173.1$         | $-30.6 \mu\text{mol/kg}$ |
| $[\Sigma \text{CO}_2] = 1915.8$     | $[\Sigma \text{CO}_2] = 1964.9$     | $+49.1 \mu\text{mol/kg}$ |
| $[\text{H}_3\text{BO}_3^0] = 308.9$ | $[\text{H}_3\text{BO}_3^0] = 323.9$ | $+15.0 \mu\text{mol/kg}$ |
| $[\text{H}_4\text{BO}_4^-] = 101.7$ | $[\text{H}_4\text{BO}_4^-] = 86.7$  | $-15.0 \mu\text{mol/kg}$ |
| $[\Sigma \text{B}] = 410.6$         | $[\Sigma \text{B}] = 410.6$         | $0.0 \mu\text{mol/kg}$   |
| $[\text{OH}^-] = 4.4$               | $[\text{OH}^-] = 3.6$               | $-0.8 \mu\text{mol/kg}$  |
| $[\text{ALK}] = 2216.0$             | $[\text{ALK}] = 2216.0$             | $0.0 \mu\text{mol/kg}$   |

$$\text{REVELLE FACTOR} = \frac{\Delta \text{pCO}_2 / \text{pCO}_2}{\Delta \Sigma \text{CO}_2 / \Sigma \text{CO}_2} = \frac{80/280}{49.1/1915.8} = 11.1$$





**Figure II.7.** A cross section of the anthropogenic  $\text{CO}_2$  in the ocean as determined by the  $\text{C}^*$  method. Robert Key, personal communication; Key *et al.* (2004).