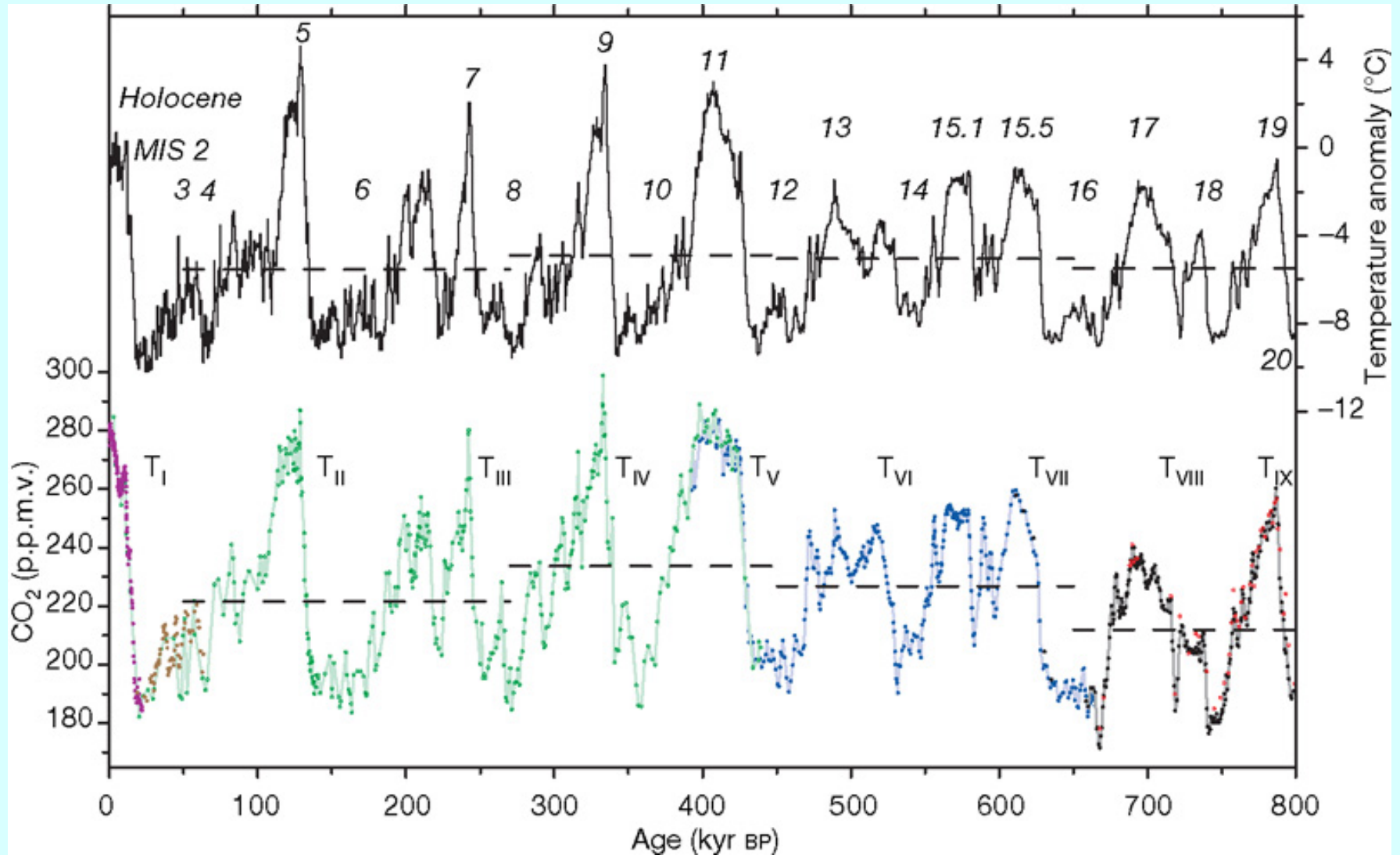


# Greenhouse Gases & Global Climate Change



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 hothouse, 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**

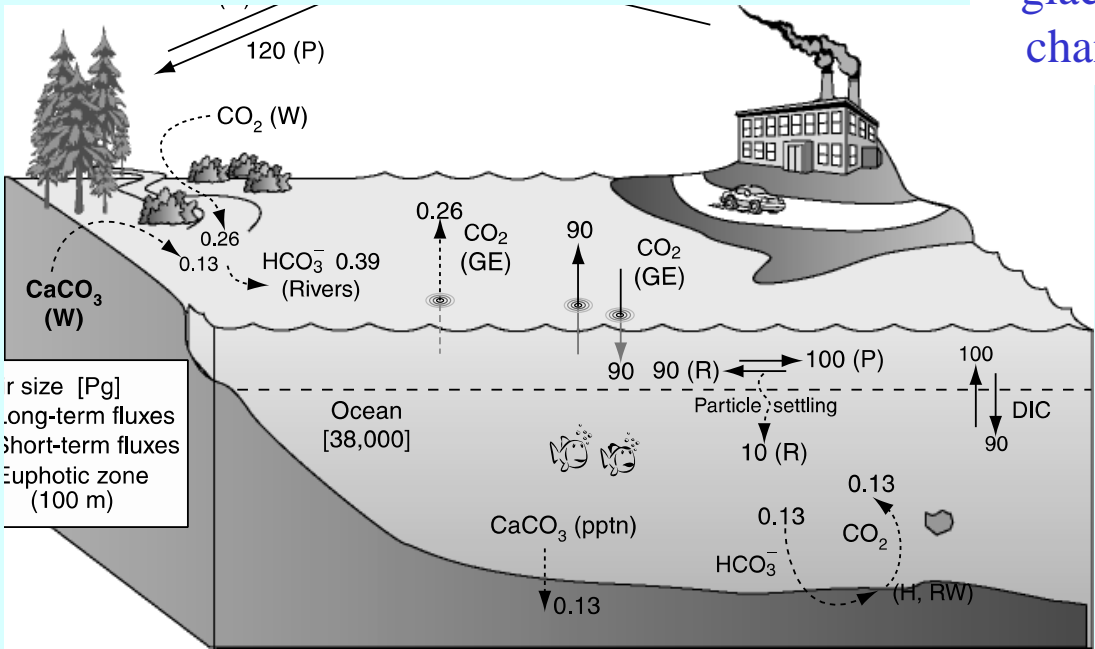
**Atm.-surface ocean ~ 10 yr**

**Atm. - deep ocean ~1000 yr**

**Atm./Ocean - sediments ~ 10<sup>5</sup> to 10<sup>7</sup> 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>



reverse weathering (the reverse of silicate weathering). thermal processes; RW,

# Atmosphere

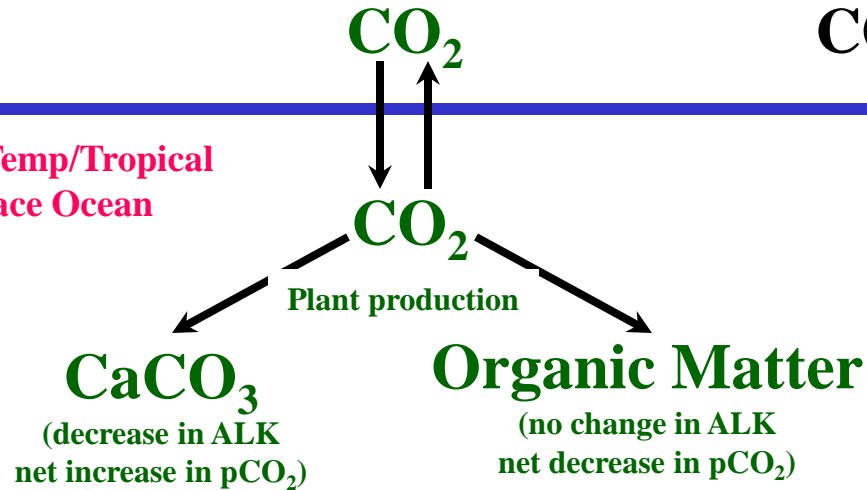
## Biological Pump

## Solubility Pump

Cold, Polar  
Surface Ocean

Warm, Temp/Tropical  
Surface Ocean

Higher solubility  
due to cold SST

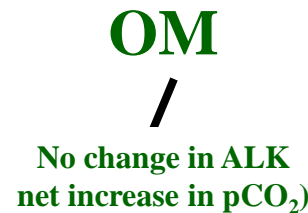
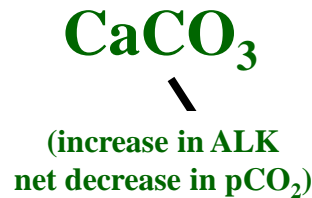


Particle sinking

Particle sinking

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

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



Cold, Deep  
Interior Ocean

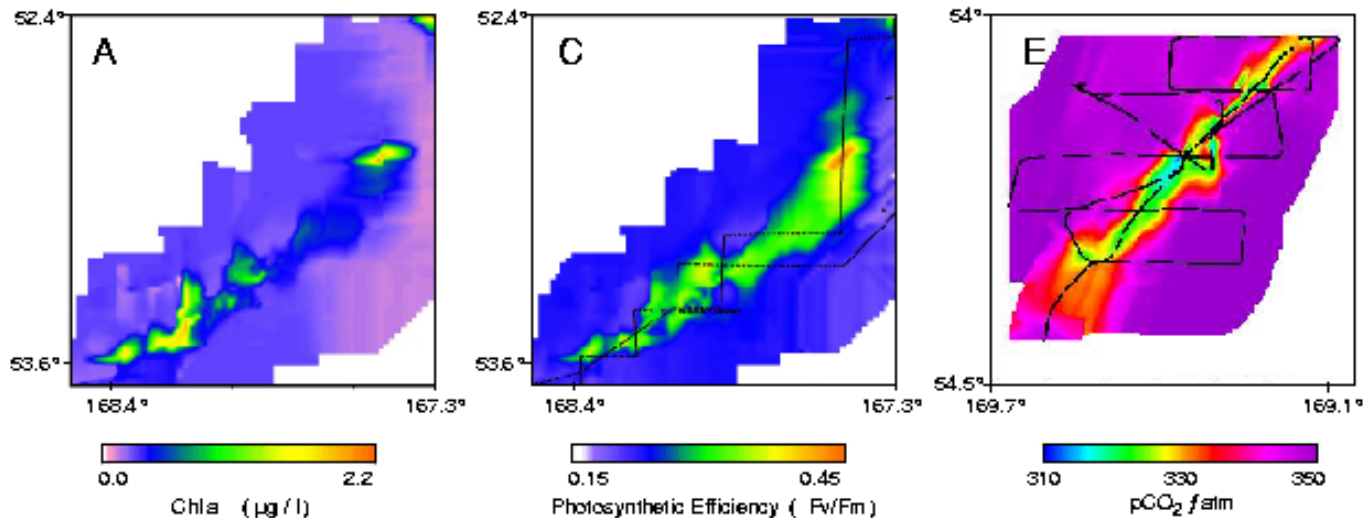
Table 11.2. The effect of the solubility and biological pumps on the fugacity of  $\text{CO}_2$  in the atmosphere,  $f_{\text{CO}_2}$ , determined by the simple two-layer ocean model depicted in Fig. 11.2

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, OC :  $\text{CaCO}_3$ .

Case	Temp °C	[DIP] <sub>s</sub> μmol kg <sup>-1</sup>	$\tau_{\text{mix}}$ y	$R_{\text{OC:CA}}$	DIC <sub>s</sub> μmol kg <sup>-1</sup>	$A_{\text{T,S}}$ μeq kg <sup>-1</sup>	$f_{\text{CO}_2}$ 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> (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

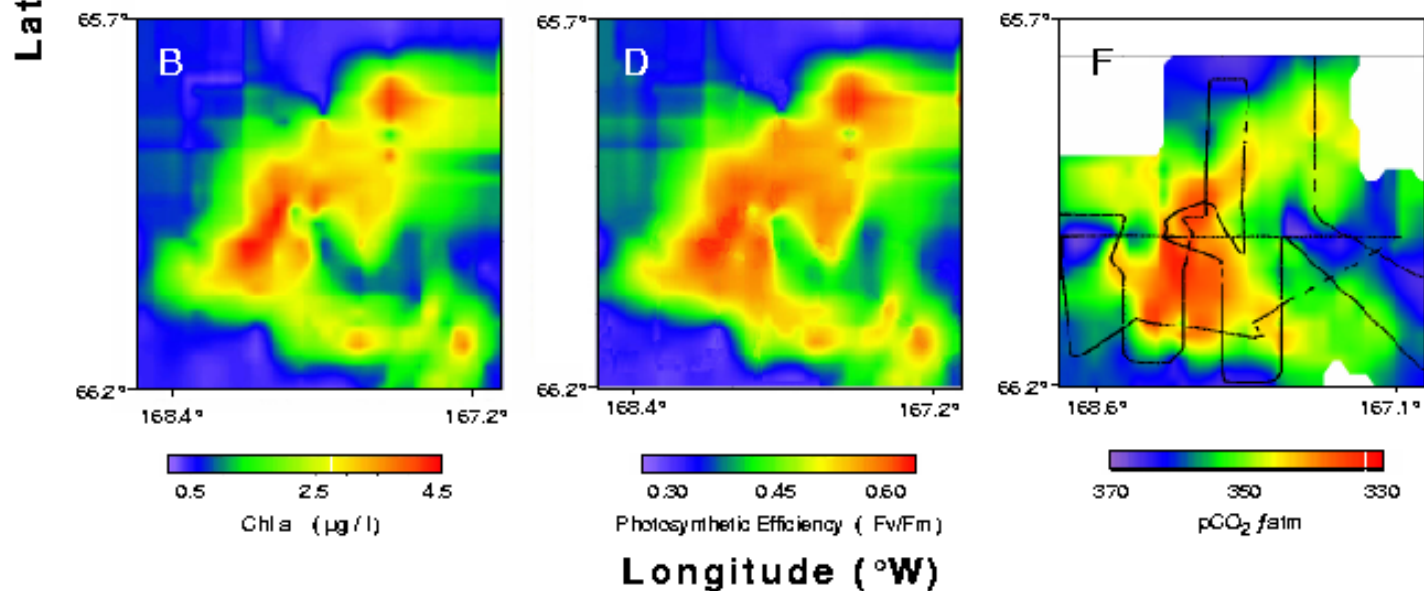
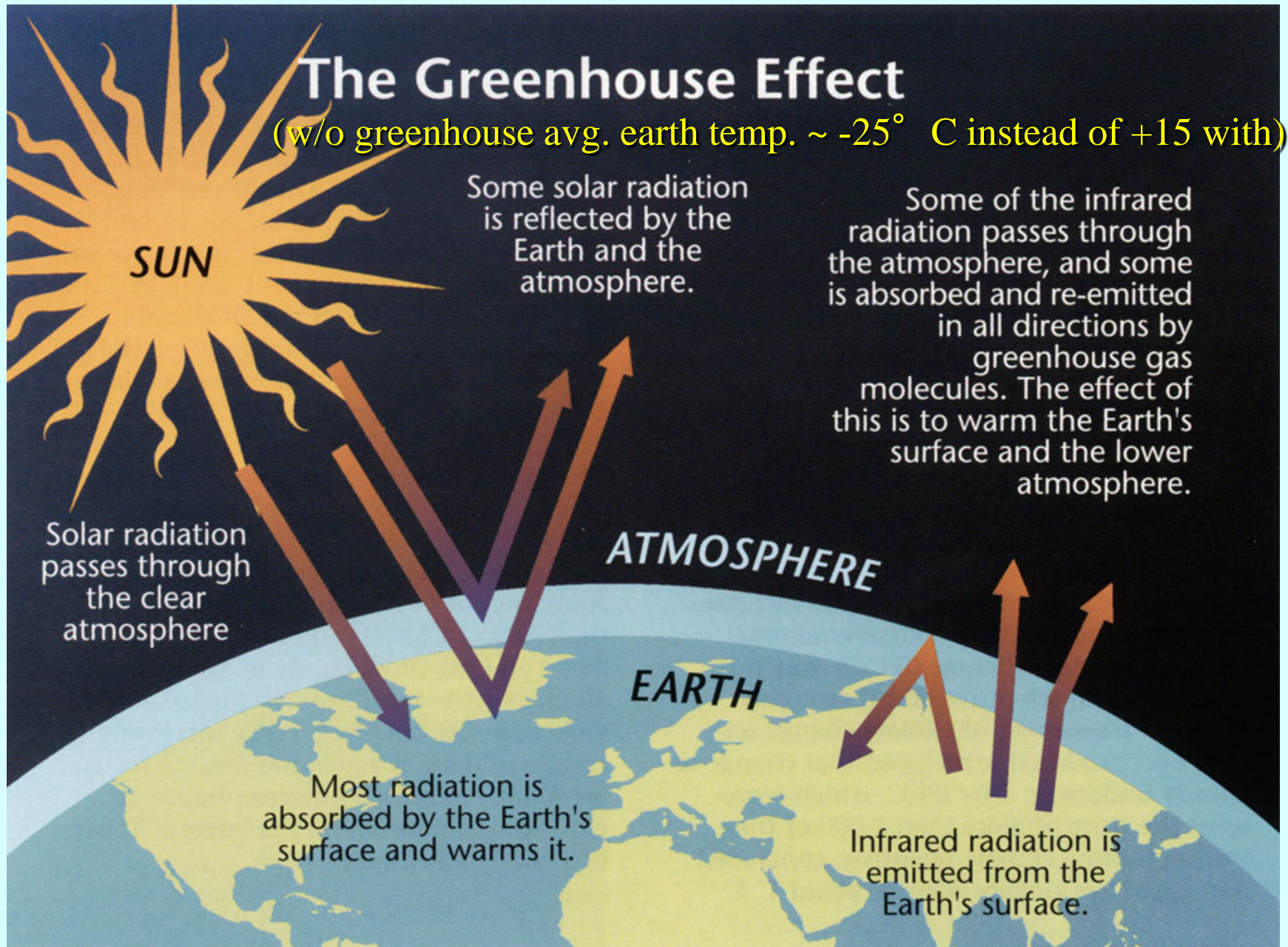


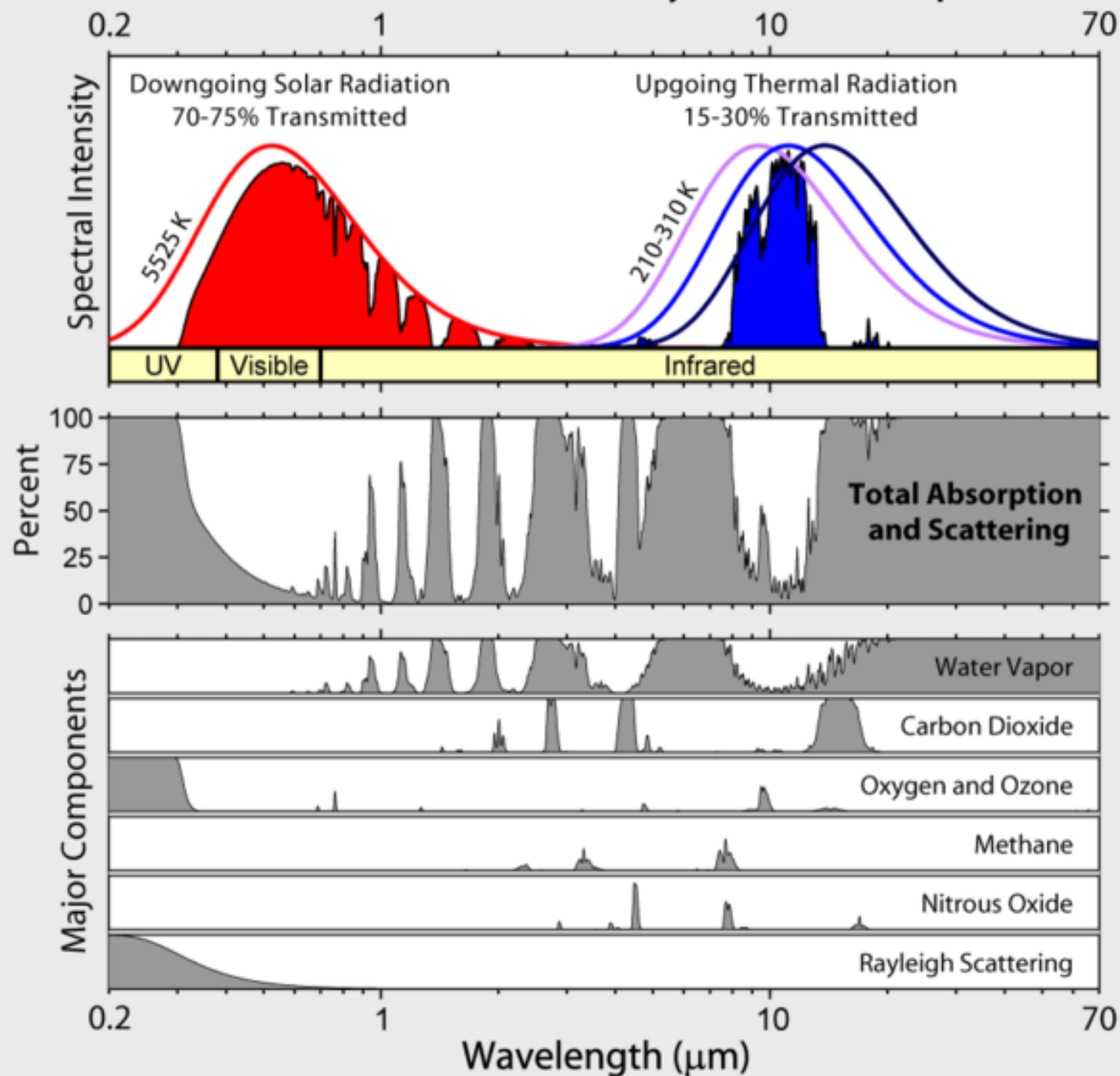
Fig. S3

# The Greenhouse Effect

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



# Radiation Transmitted by the Atmosphere



**FIGURE 5.17.** The adsorption of infrared radiation by gases in the atmosphere.

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**TABLE 5.5**  
**Trapping of IR Radiation by Trace Gases**  
**( $\Delta Q$ ,  $W m^{-2}$ )**

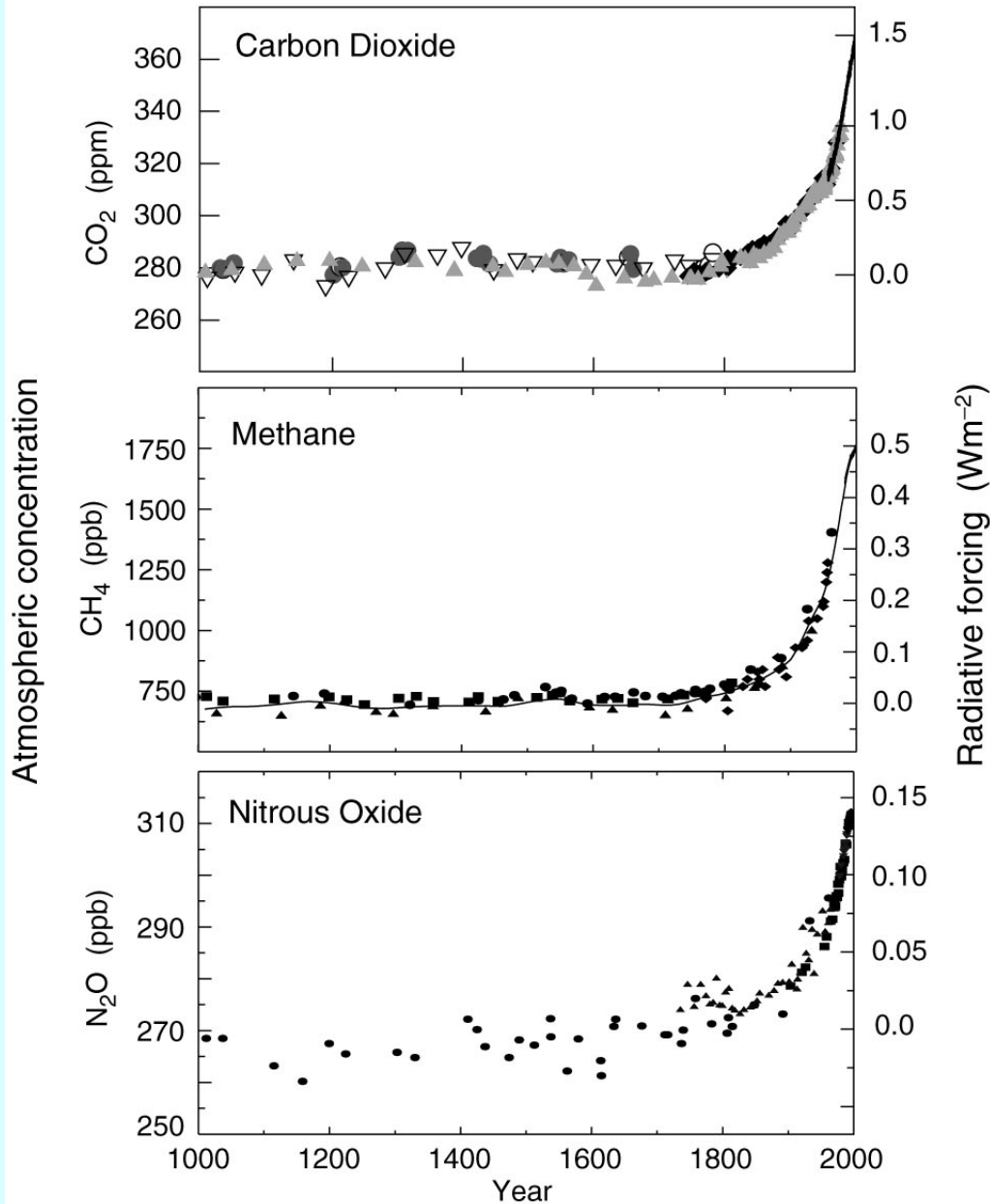
<b>Gas</b>	<b>Present level</b>	<b>Present <math>\Delta Q</math></b>	<b>Lifetime</b>
CO <sub>2</sub>	345 ppm	2.0	10–15 y
CH <sub>4</sub>	1.7 ppm	1.7	7–10
O <sub>3</sub>	10–100 ppb	1.3	0.5
N <sub>2</sub> O	340 ppb	1.3	100
CFC-11 <sup>a</sup>	0.22 ppb	0.06	75
CFC-12 <sup>b</sup>	0.38 ppb	0.12	100
Total		6.5	

<sup>a</sup> CCl<sub>3</sub>F.

<sup>b</sup> CCl<sub>2</sub>F<sub>2</sub>.

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



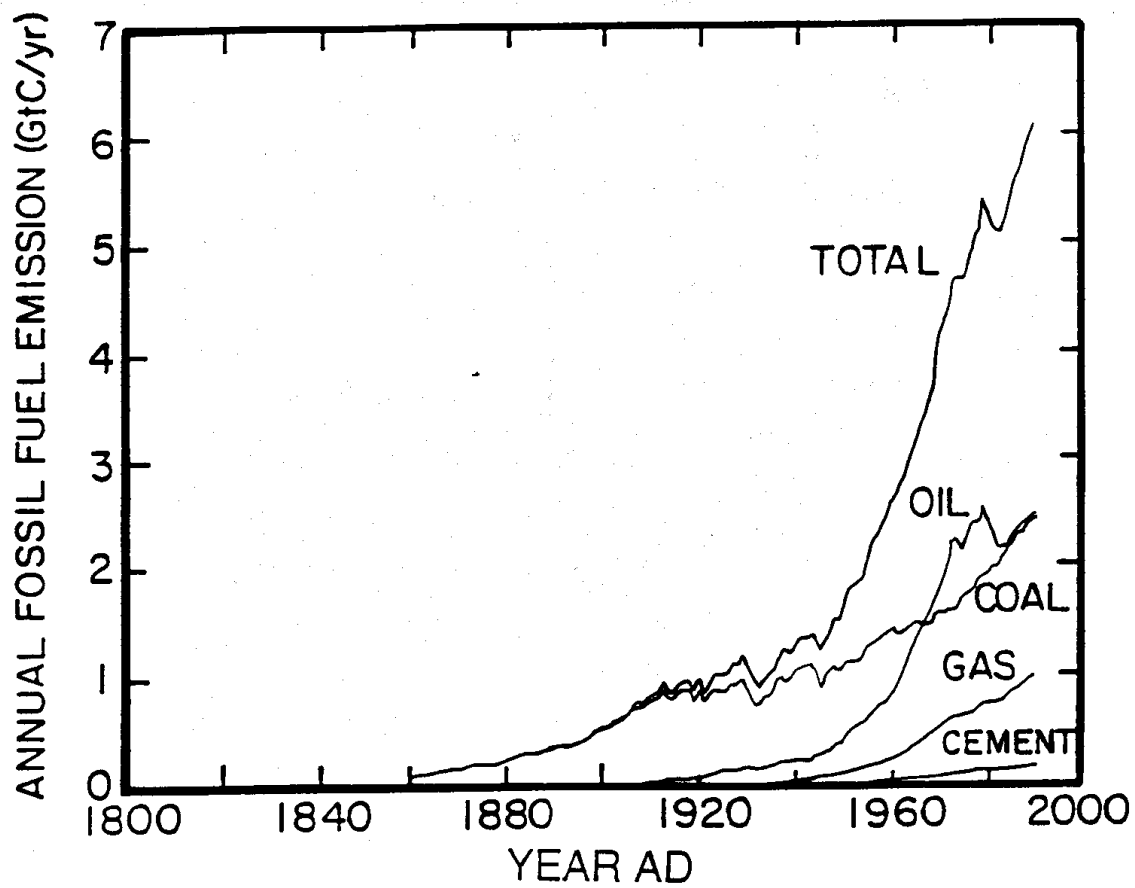
# Anthropogenic Influence on Atmospheric Concentration of Greenhouse Gases

Source: IPCC TAR 2001

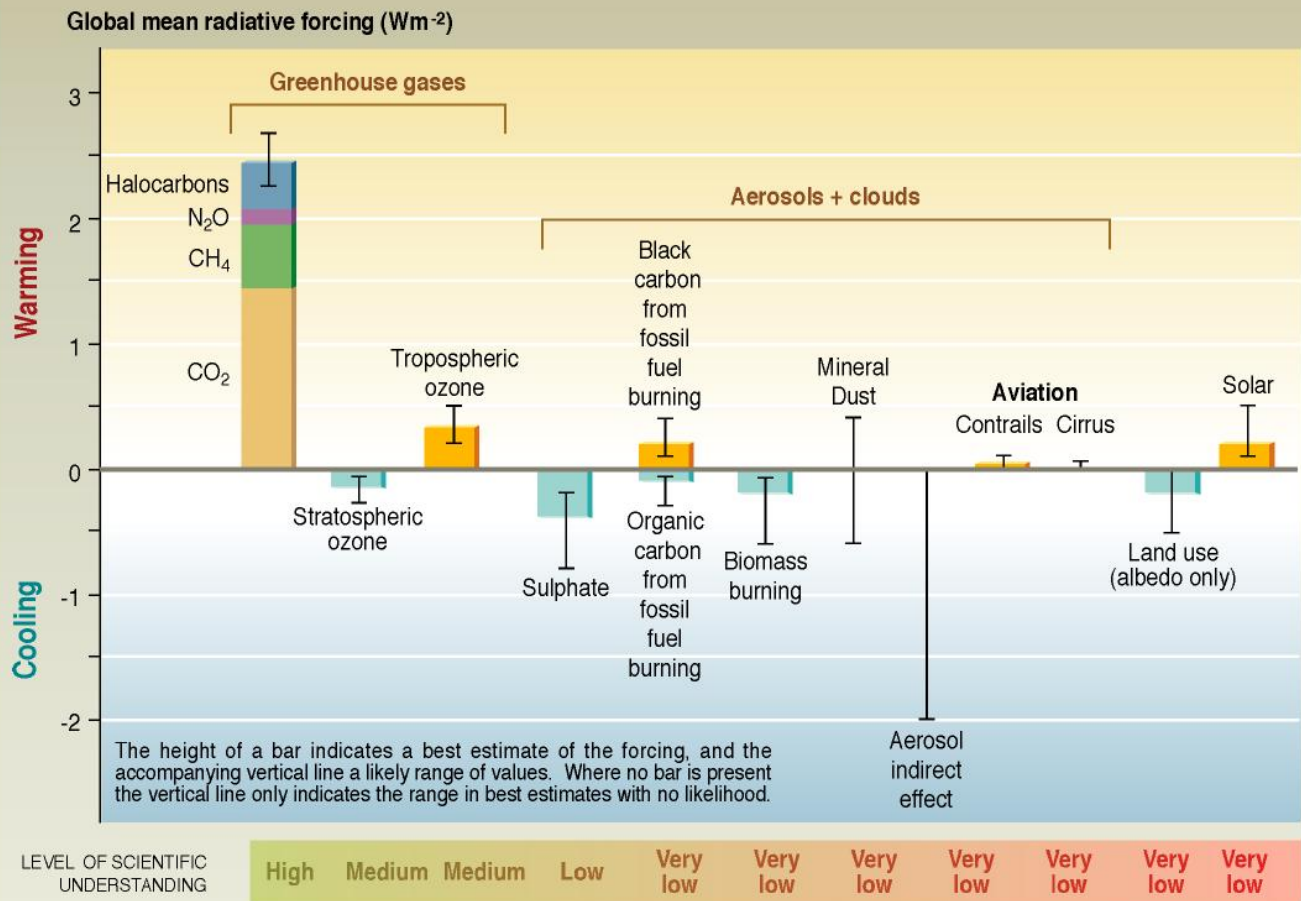


Union of  
Concerned  
Scientists

# TIME HISTORY OF FOSSIL FUEL CONSUMPTION

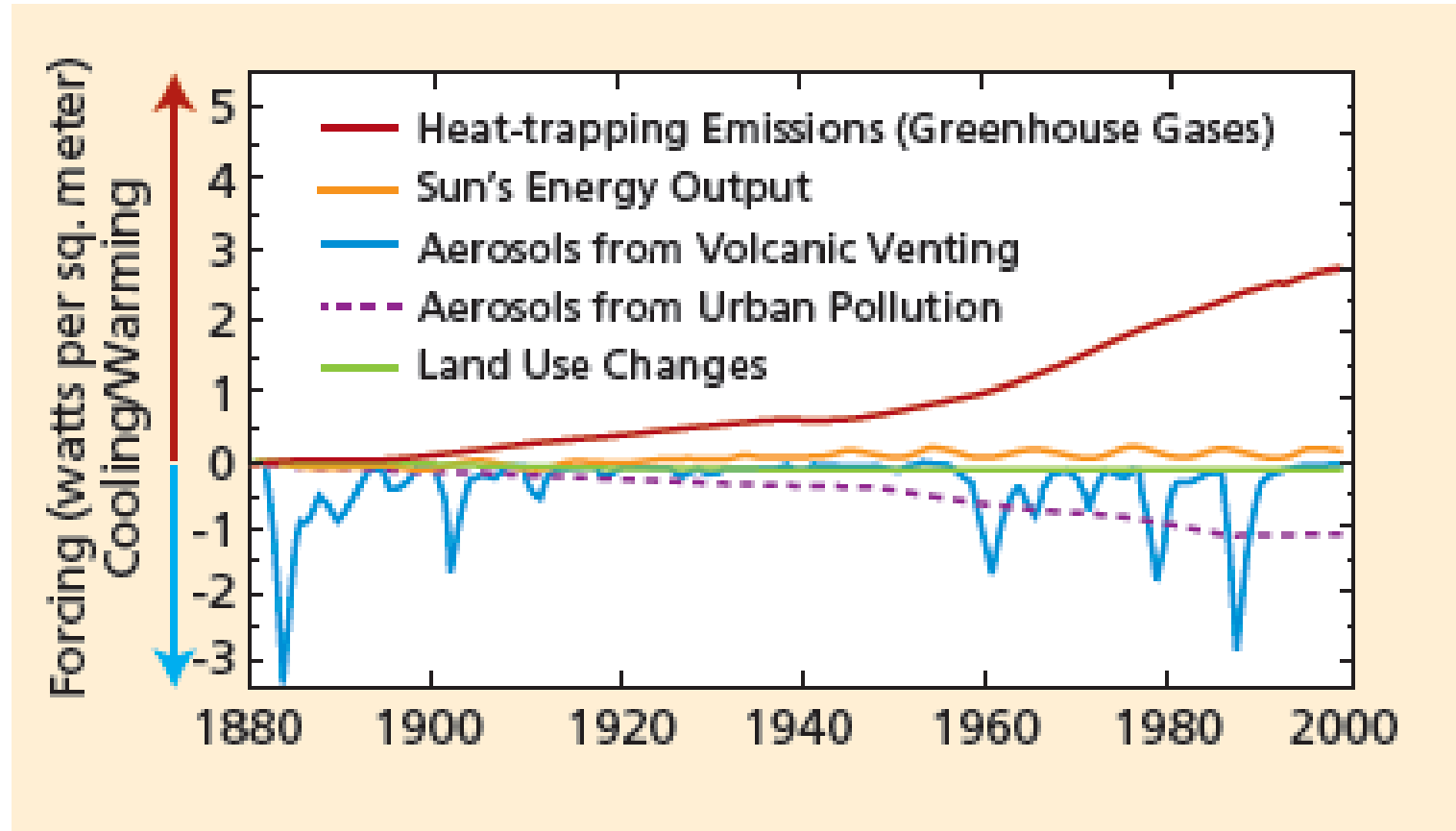


# Anthropogenic and natural forcing of the climate for the year 2000, relative to 1750



SYR - FIGURE 2-2

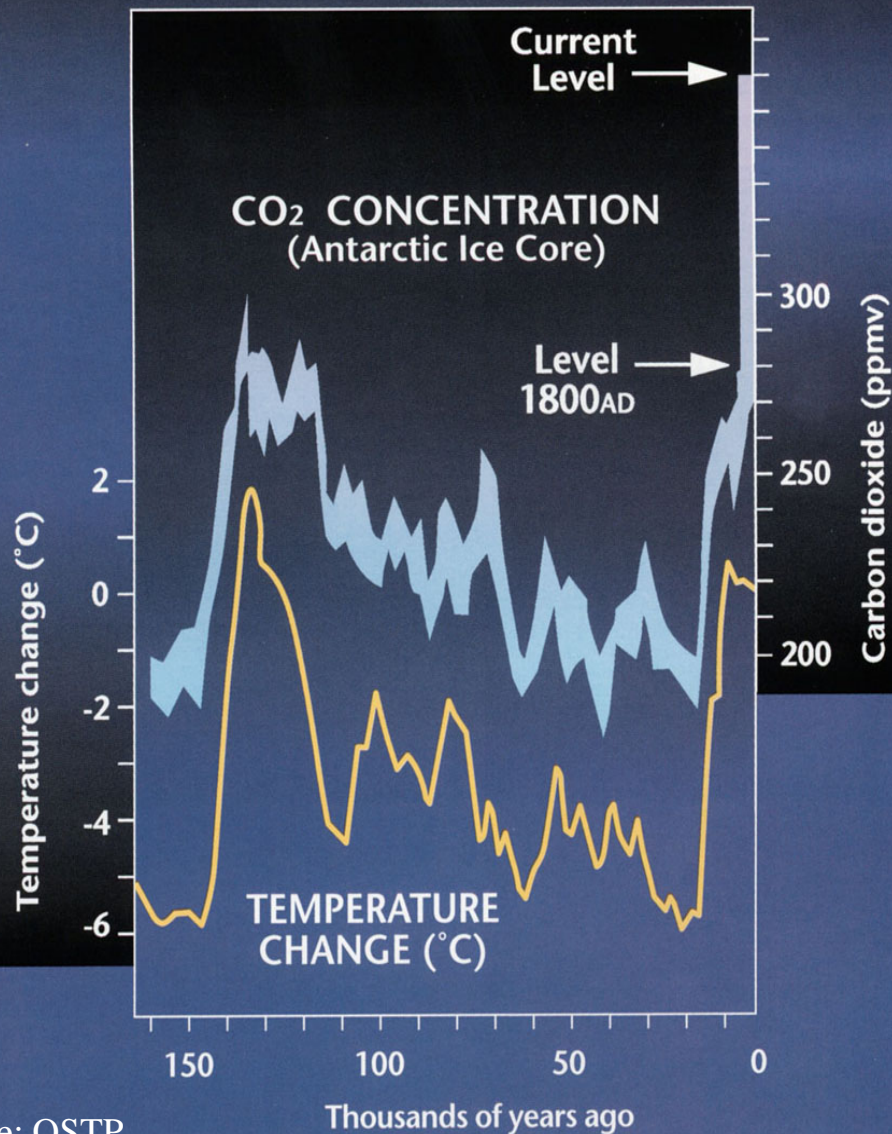
# Global Climate Drivers



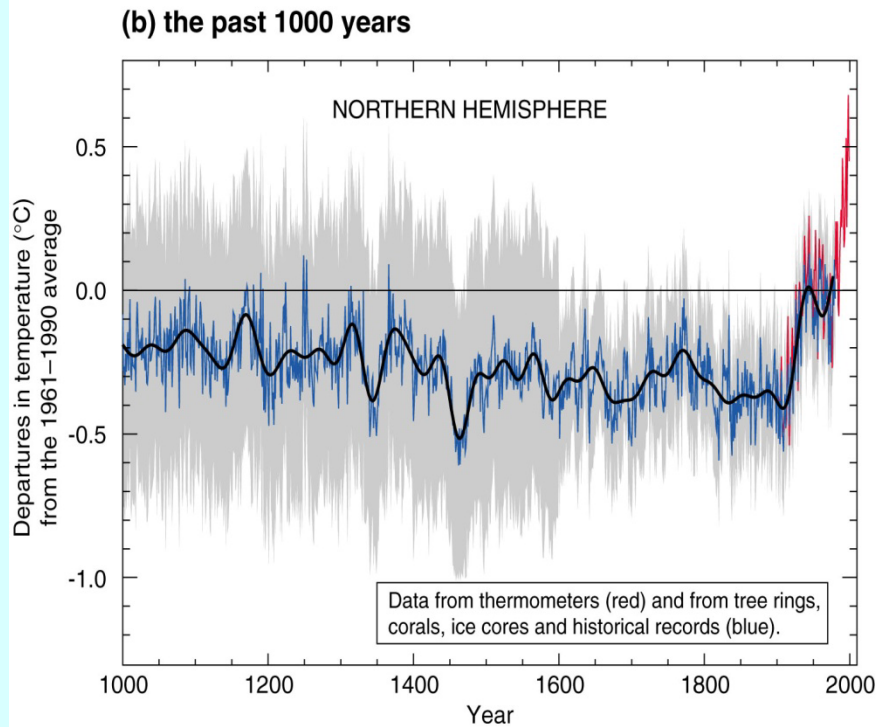
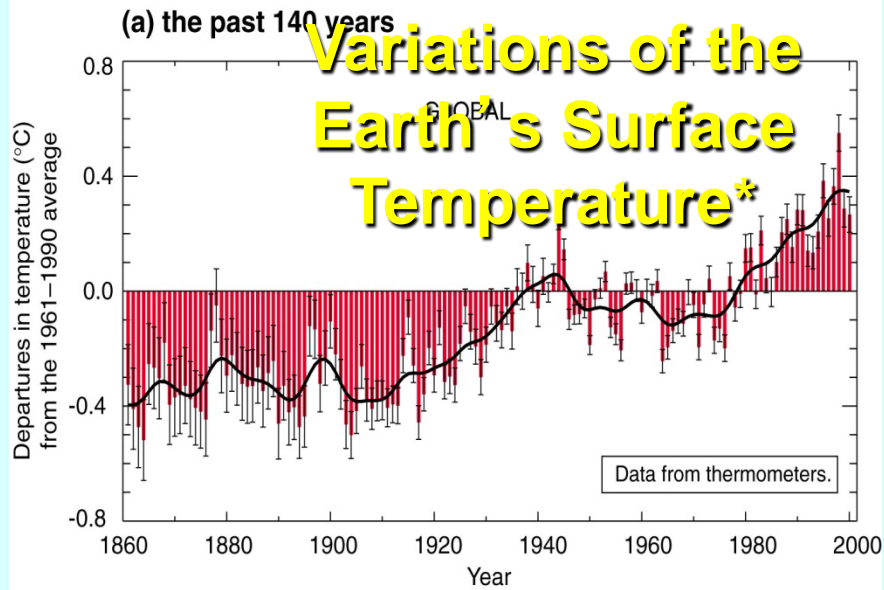
**Heat-trapping emissions (greenhouse gases) far outweigh the effects of other drivers acting on Earth's climate.**

Source: Hansen et al. 2005.

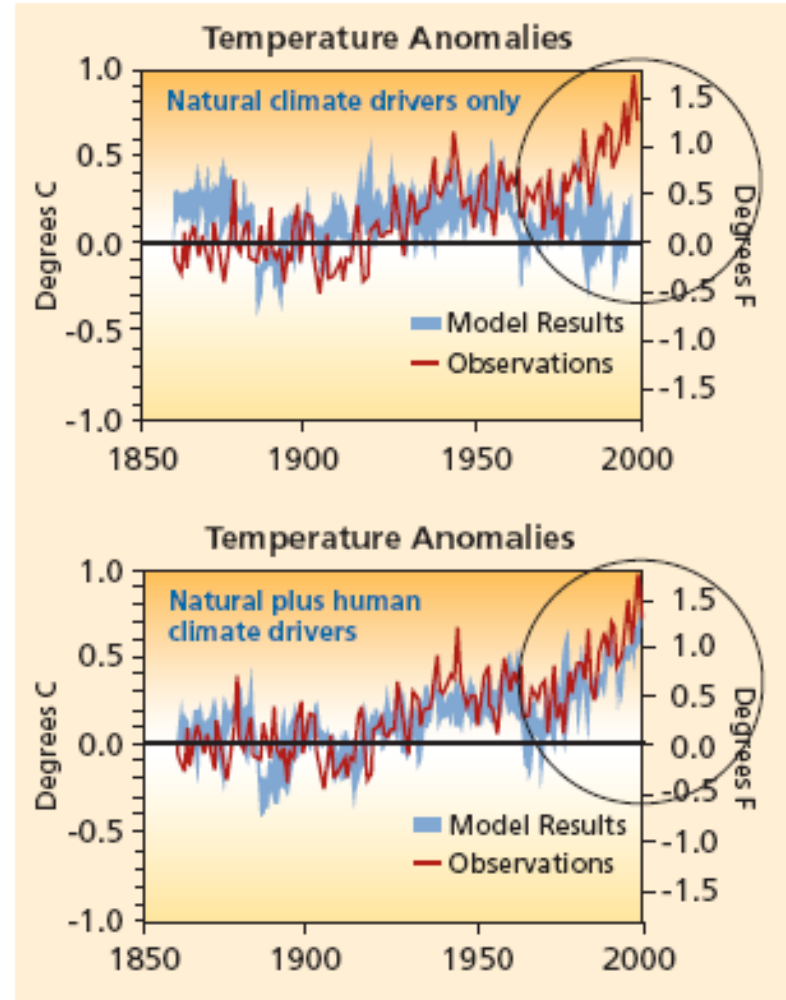
# Atmospheric Carbon Dioxide Concentration and Temperature Change



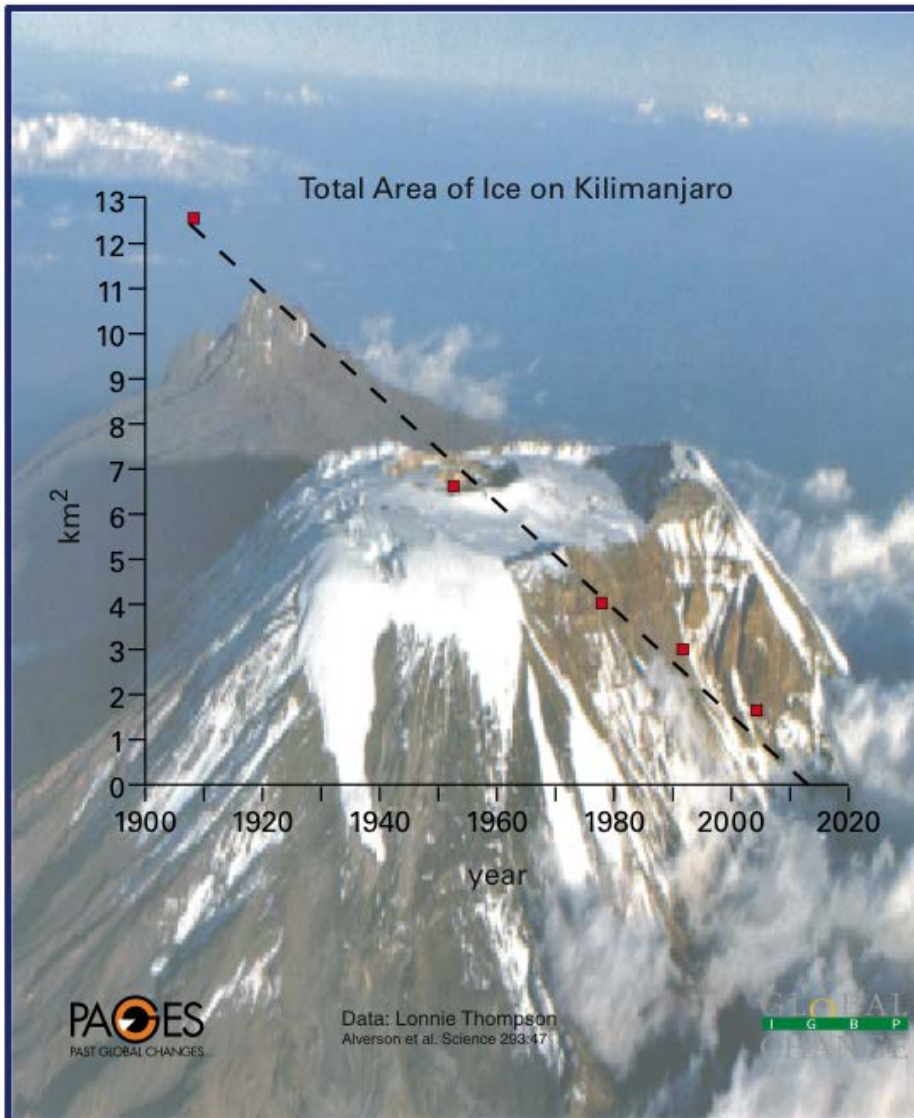
- Clear correlation between atmospheric CO<sub>2</sub> and temperature over last 160,000 years
- Current level of CO<sub>2</sub> is *outside* bounds of natural variability
- *Rate* of change of CO<sub>2</sub> is also unprecedented



## Climate Drivers Compared with Global Surface Temperature



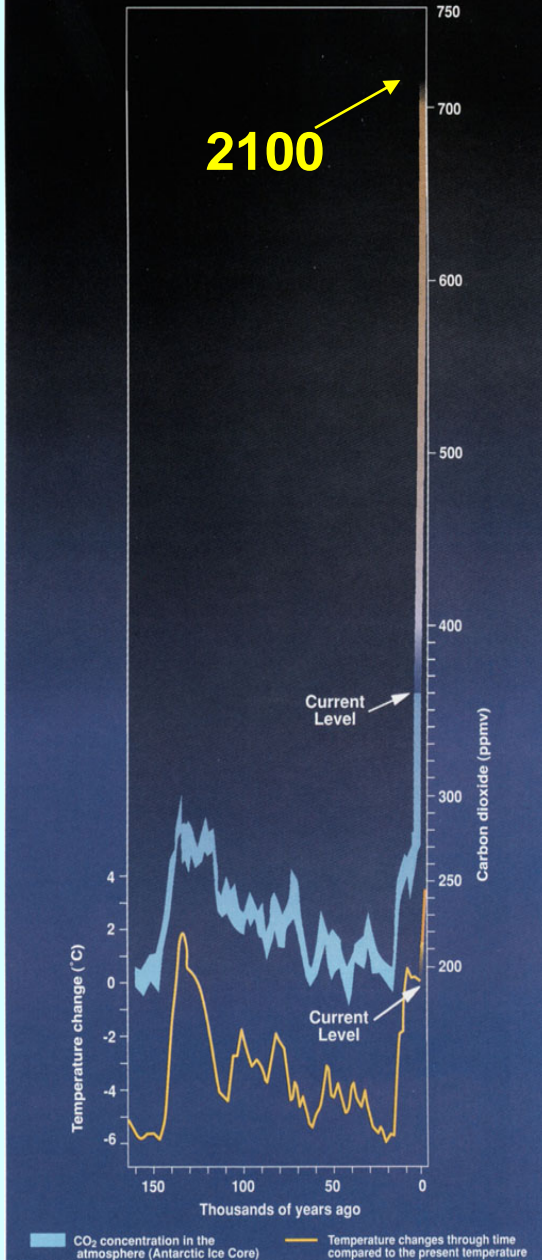
The model output (blue shading) that includes both natural and human-induced drivers (lower graph) gives a better match with the observed temperature response (red line). Source: IPCC TAR 2001.



Also:

- 1) Reduced arctic sea ice cover
- 2) Longer growing season
- 3) Change in time of seasonal migrations
- 4) Lower stratospheric temp.

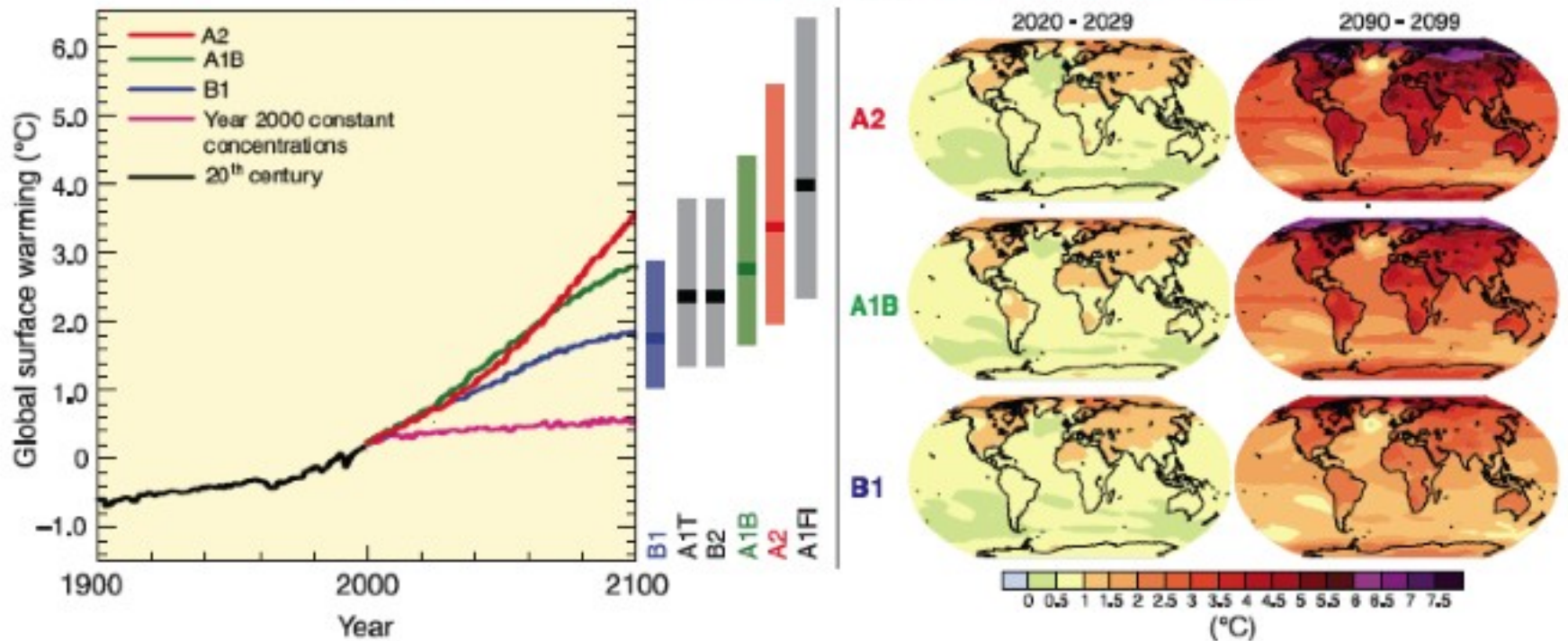
## Atmospheric Carbon Dioxide Concentration and Temperature Change



## If business as usual:

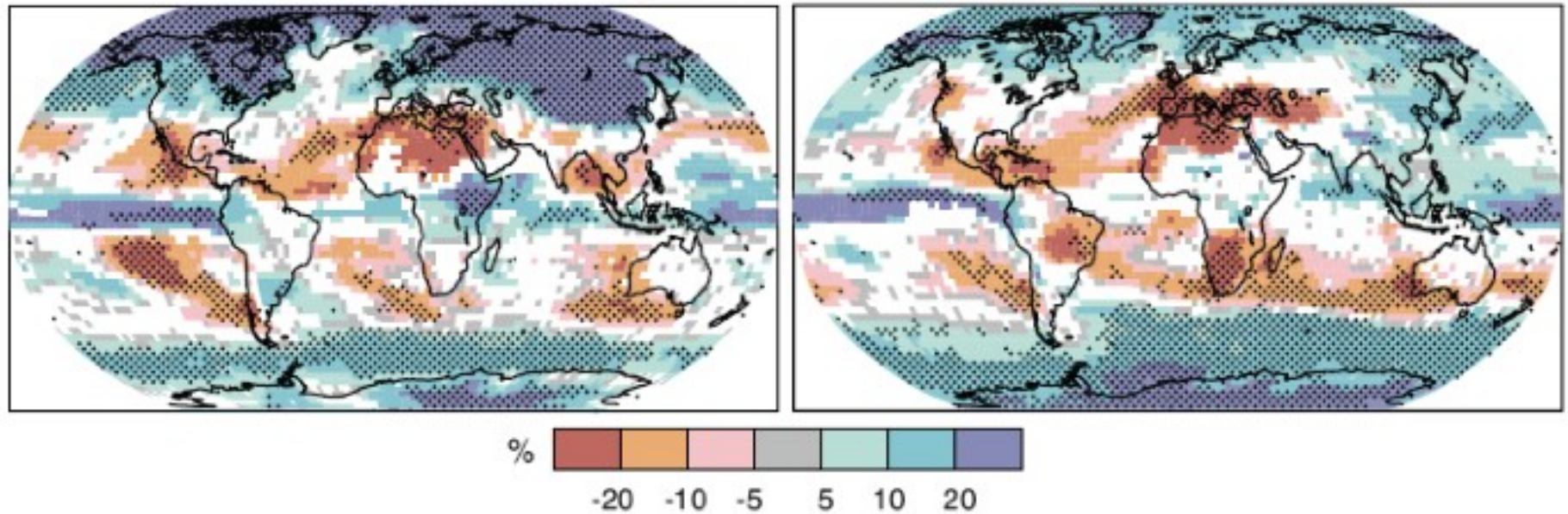
- CO<sub>2</sub> concentrations will likely be more than 700 ppm by 2100
- Global average temperatures projected to increase between 2.5 - 10.4° F

### Atmosphere-Ocean General Circulation Model projections of surface warming



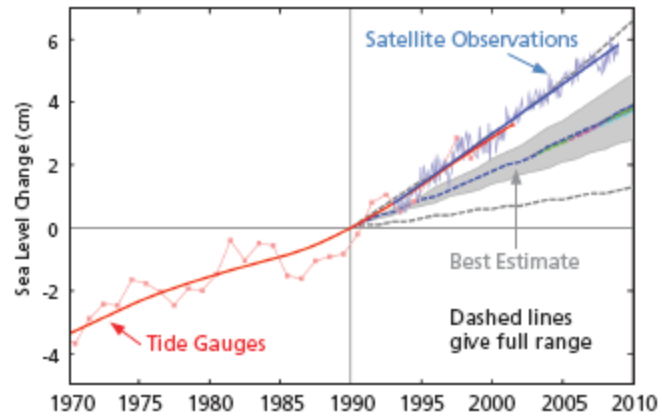
**Figure 3.2.** Left panel: Solid lines are multi-model global averages of surface warming (relative to 1990-1999) for the SRES scenarios A2, A1B and B1, shown as continuations of the 20<sup>th</sup> century simulations. The orange line is for the experiment where concentrations were held constant at year 2000 values. The bars in the middle of the figure indicate the best estimate (solid line within each bar) and the likely range assessed for the six SRES marker scenarios at 2090-2099 relative to 1980-1999. The assessment of the best estimate and likely ranges in the bars includes the Atmosphere-Ocean General Circulation Models (AOGCMs) in the left part of the figure, as well as results from a hierarchy of independent models and observational constraints. Right panels: Projected surface temperature changes for the early and late 21<sup>st</sup> century relative to the period 1980-1999. The panels show the multi-AOGCM average projections for the A2 (top), A1B (middle) and B1 (bottom) SRES scenarios averaged over decades 2020-2029 (left) and 2090-2099 (right). (WGI 10.4, 10.8, Figures 10.28, 10.29, SPM)

### Multi-model projected patterns of precipitation changes



**Figure 3.3.** Relative changes in precipitation (in percent) for the period 2090-2099, relative to 1980-1989. Values are multi-model averages based on the SRES A1B scenario for December to February (left) and June to August (right). White areas are where less than 66% of the models agree in the sign of the change and stippled areas are where more than 90% of the models agree in the sign of the change. (WGI Figure 10.9, SPM)

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

New analysis provides estimates for sea level rise by the end of this century between a plausible level and a physically possible though less likely level. Source (IPCC 2007 and Pfeffer et al. 2008).<sup>4,5</sup>

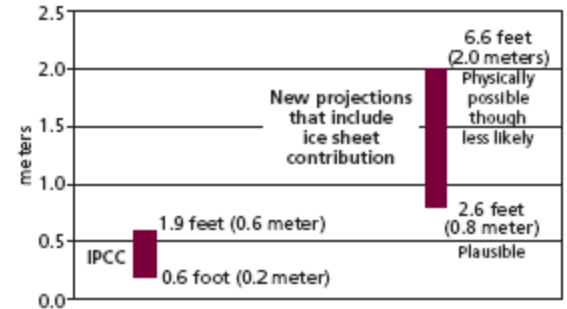
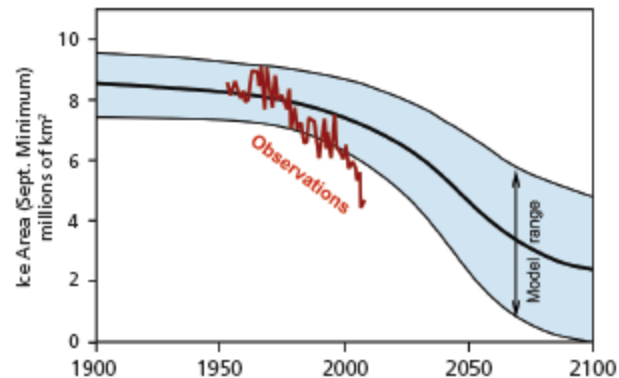


FIGURE 4 Shrinking Summer Arctic Sea Ice Area



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

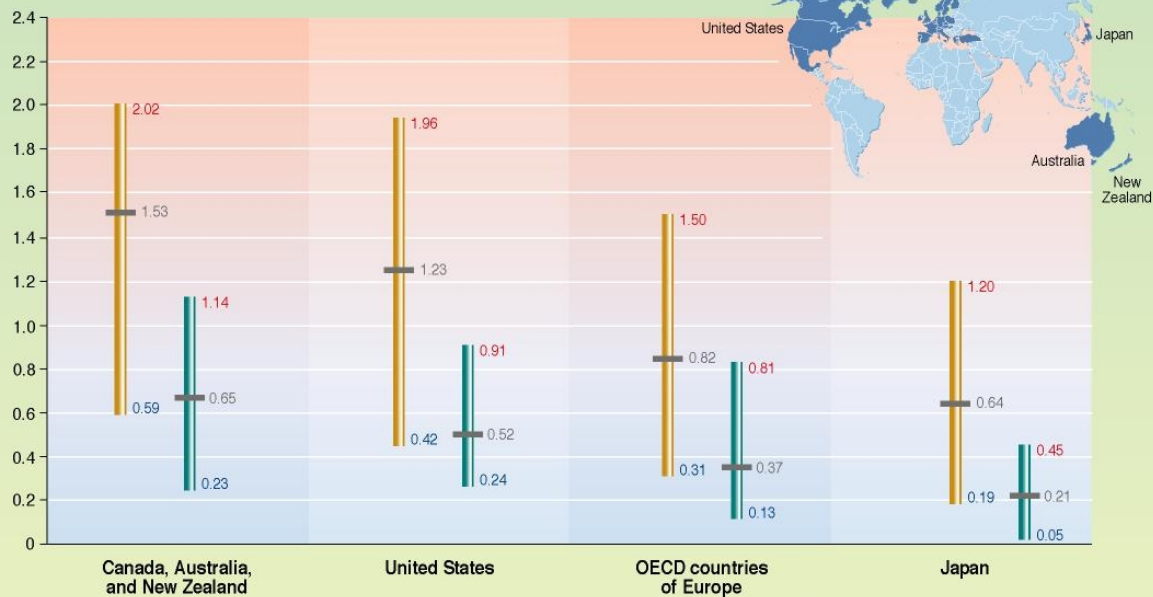
Source: Dirk Notz from Hamburg adapted figure from <http://www.nsidc.org/news/images20070430Figure1.png>.

10 m sea level rise





## Projections of GDP losses in Annex II countries in the year 2010 from global models

Percentage of GDP loss in the year 2010



### Range of outcomes for two scenarios

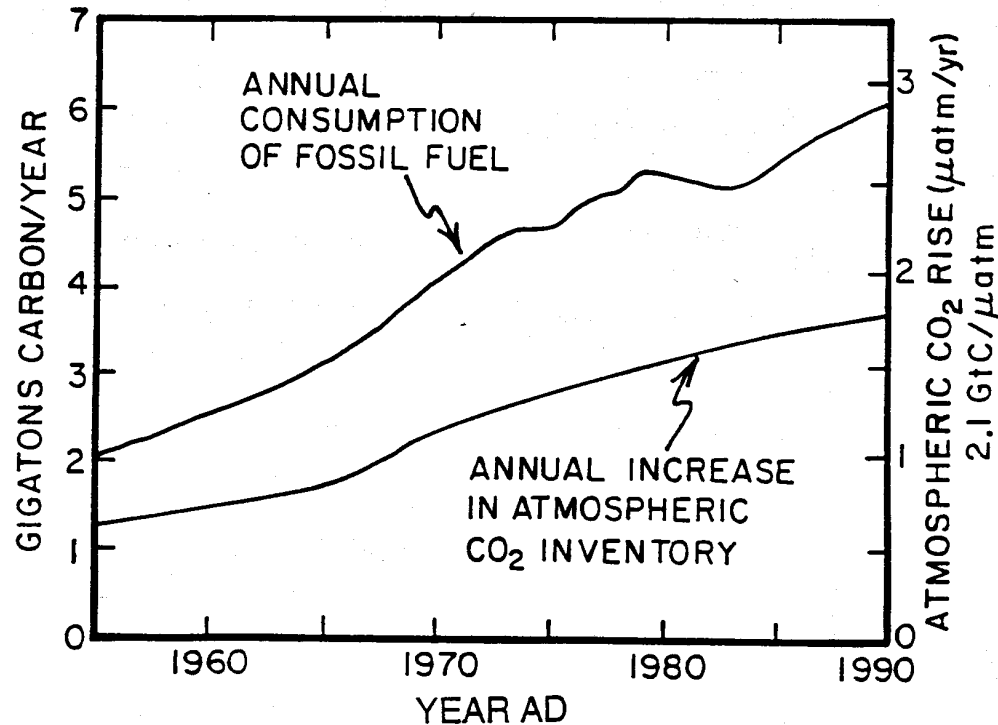
 Absence in international trade in carbon emissions rights: each region must take the prescribed reduction

 Full annex B trading of carbon emissions rights permitted

The three numbers on each bar represent the highest, mean, and lowest projections from the set of models.

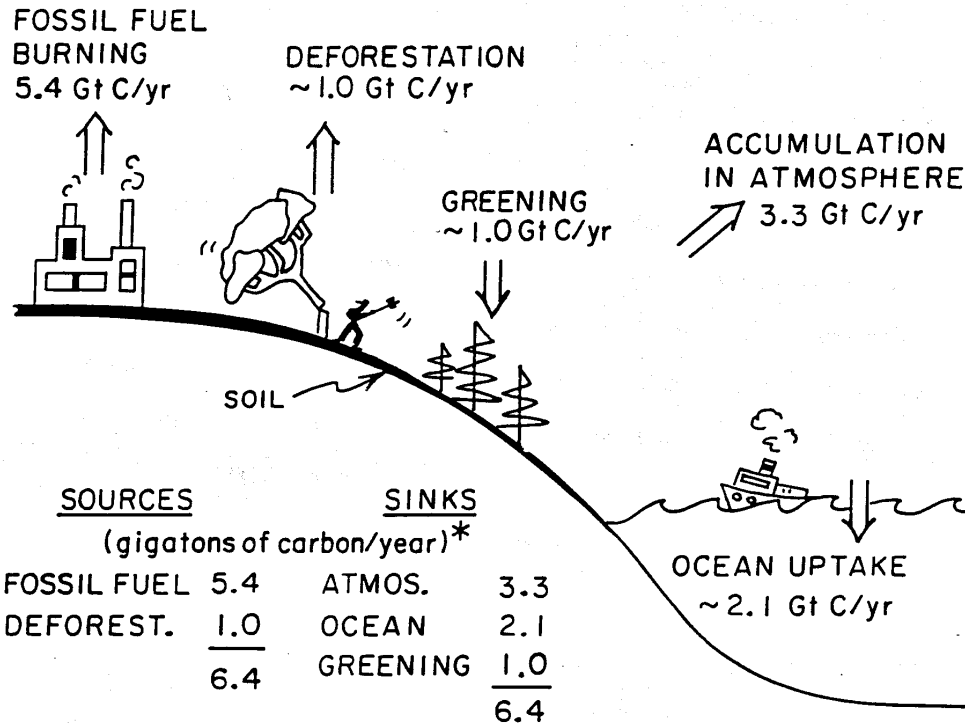
SYR - FIGURE 7-2 a

## 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



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

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

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

---

1.00

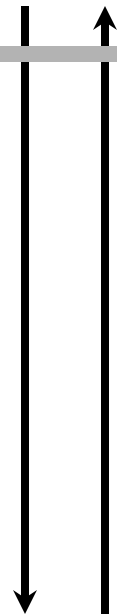
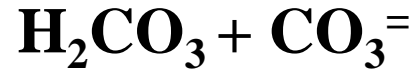
\*1 Gt =  $1 \times 10^{15}$  grams  
=  $1 \times 10^9$  tons

# Atmosphere

Net transfer to ocean due to disequilibrium in  $p\text{CO}_2$



Air/sea exchange calibrated with  $^{14}\text{C}$  and Rn tracers



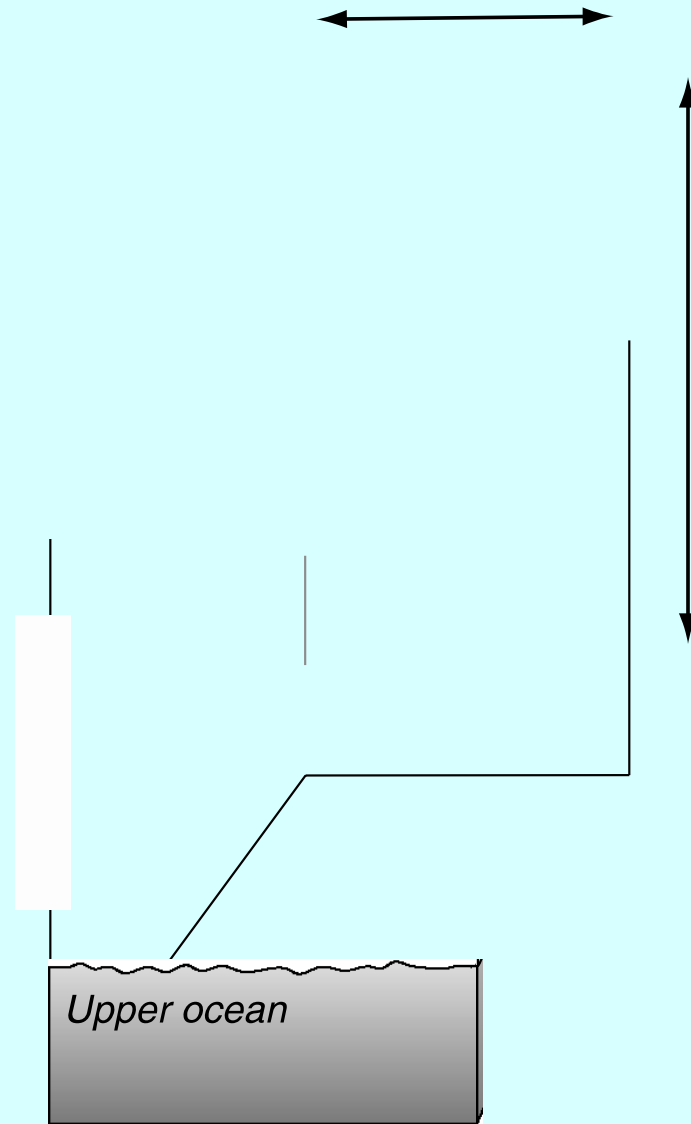
Surface/deep exchange primary brake on net  $\text{CO}_2$  transfer

Whole ocean has the capacity to absorb 5/6 of the atm. increase in  $\text{CO}_2$  through this mechanism, but can only occur on time scale of surface to deep mixing ~ hundreds of years.

Cold, Deep Interior Ocean



and water carbon concentrations indicated. This hypothetical system is used to illustrate the effect of carbonate reactions in controlling the distribution of a perturbation of  $\text{CO}_2$  between the atmosphere and ocean at chemical equilibrium.



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

## IDEALIZED SEA WATER (NO BORATE)

### CHARGE BALANCE

$$[\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{++}] + 2[\text{Ca}^{++}] = [\text{Cl}^-] + 2[\text{SO}_4^{=}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{=}]$$

OR

$$[\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{++}] + 2[\text{Ca}^{++}] - [\text{Cl}^-] - 2[\text{SO}_4^{=}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}]$$

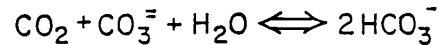
OR

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

### MASS BALANCE FOR DISSOLVED INORGANIC CARBON

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

### CHEMICAL EQUILIBRIUM



$$K'_c = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{=}]}, \quad \alpha = \frac{[\text{CO}_2]}{p\text{CO}_2} = 0.342 \frac{\mu\text{mol/kg}}{\mu\text{atm}}$$

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

$$\text{REVELLE FACTOR} = \frac{\Delta p\text{CO}_2 / p\text{CO}_2}{\Delta \Sigma\text{CO}_2 / \Sigma\text{CO}_2} = \frac{80/280}{38/1910} = 14.4$$

## ACTUAL SEA WATER ( INCLUDING BORATE )

### CHARGE BALANCE

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

### MASS BALANCE BORON

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

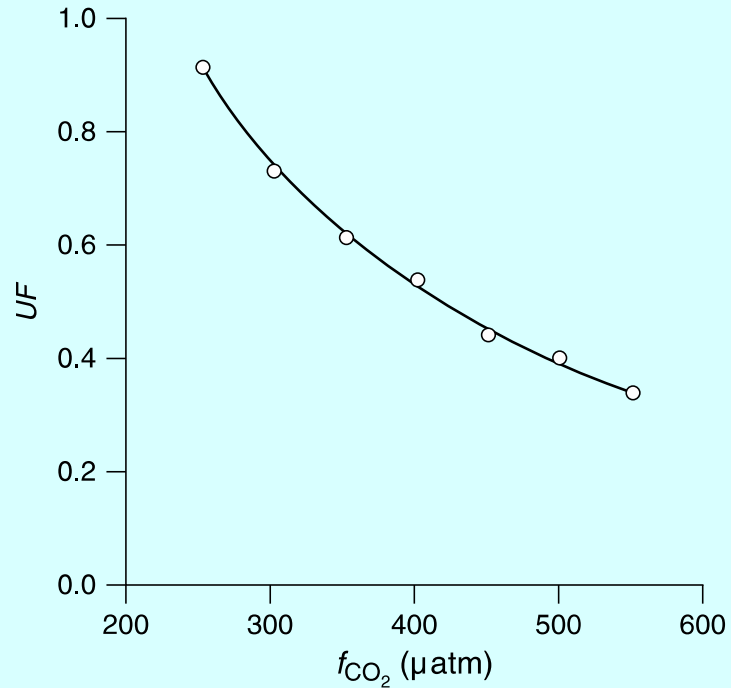
### CHEMICAL EQUILIBRIUM

$$K_B' = \frac{[\text{H}_4\text{BO}_4^-][\text{HCO}_3^-]}{[\text{H}_3\text{BO}_3^0][\text{CO}_3^{2-}]}$$

EXAMPLE  $T=18^\circ\text{C}$   $S=35\text{‰}$   $K_c' = 1482$   $K_B' = 2.75$   
 $\text{ALK} = 2216$   $\text{SiO}_2 = 0$   $\text{NO}_3 = 0$   $\text{PO}_4 = 0$

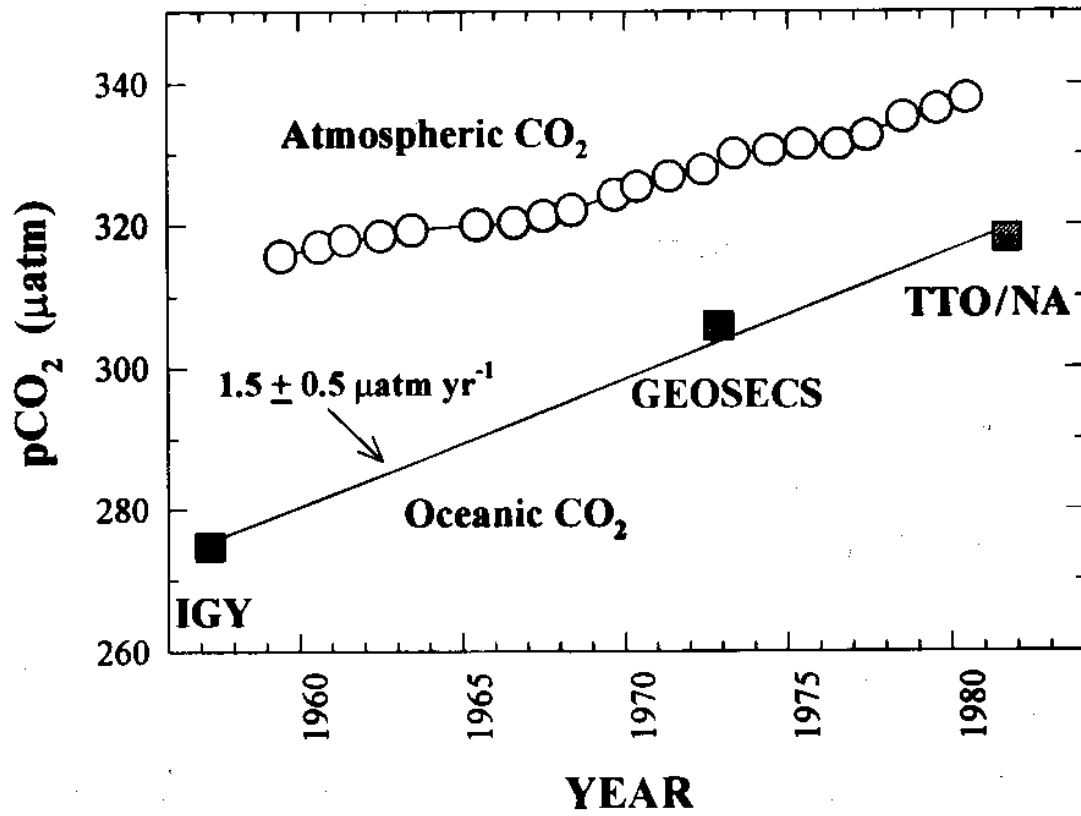
$p\text{CO}_2 = 280 \mu\text{atm}$	$p\text{CO}_2 = 360 \mu\text{atm}$	$\Delta$
$[\text{CO}_2] = 9.6$	$[\text{CO}_2] = 12.3$	$+2.6 \mu\text{mol/kg}$
$[\text{HCO}_3^-] = 1702.5$	$[\text{HCO}_3^-] = 1779.5$	$+77.0 \mu\text{mol/kg}$
$[\text{CO}_3^{2-}] = 203.7$	$[\text{CO}_3^{2-}] = 173.1$	$-30.6 \mu\text{mol/kg}$
$[\Sigma\text{CO}_2] = 1915.8$	$[\Sigma\text{CO}_2] = 1964.9$	$+49.1 \mu\text{mol/kg}$
$[\text{H}_3\text{BO}_3^0] = 308.9$	$[\text{H}_3\text{BO}_3^0] = 323.9$	$+15.0 \mu\text{mol/kg}$
$[\text{H}_4\text{BO}_4^-] = 101.7$	$[\text{H}_4\text{BO}_4^-] = 86.7$	$-15.0 \mu\text{mol/kg}$
$[\Sigma\text{B}] = 410.6$	$[\Sigma\text{B}] = 410.6$	$0.0 \mu\text{mol/kg}$
$[\text{OH}^-] = 4.4$	$[\text{OH}^-] = 3.6$	$-0.8 \mu\text{mol/kg}$
$[\text{ALK}] = 2216.0$	$[\text{ALK}] = 2216.0$	$0.0 \mu\text{mol/kg}$

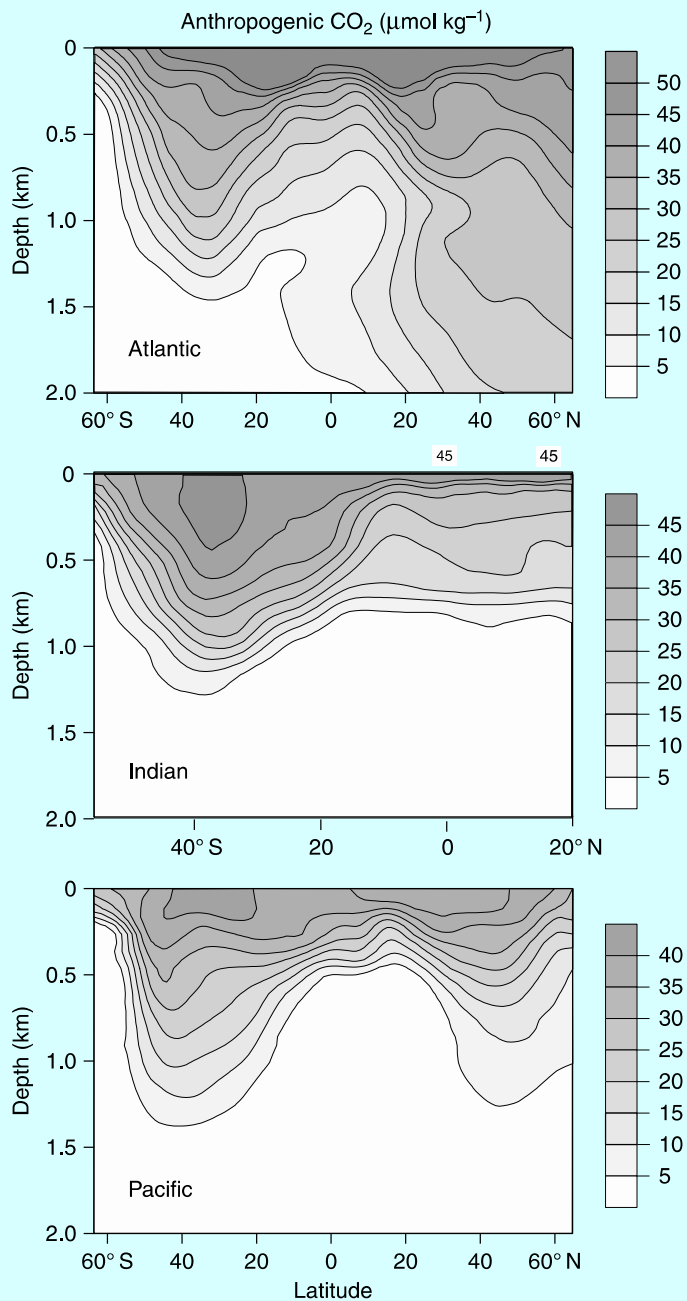
$$\text{REVELLE FACTOR} = \frac{\Delta p\text{CO}_2 / p\text{CO}_2}{\Delta \Sigma\text{CO}_2 / \Sigma\text{CO}_2} = \frac{80/280}{49.1/1915.8} = 11.1$$



**Figure 11.5.** The change in the uptake Factor ( $UF$ ) and Revelle Factor ( $R$ ) as a function of the  $f_{\text{CO}_2}$  in equilibrium with a seawater solution containing a total alkalinity of  $2300 \mu\text{eq kg}^{-1}$ .

$f_{\text{CO}_2}$ ( $\mu\text{atm}$ )	DIC ( $\mu\text{mol kg}^{-1}$ )	$[\text{CO}_3^{2-}]$ ( $\mu\text{mol kg}^{-1}$ )	$\text{pH}_T$	$UF$ ( $\mu\text{mol kg}^{-1} \mu\text{atm}^{-1}$ )	$R$
250	1928	264	8.21	0.90	8.6
300	1968	234	8.15	0.72	9.1
350	2000	216	8.10	0.60	9.6
400	2028	199	8.05	0.52	10.1
450	2051	184	8.00	0.43	10.6
500	2071	171	7.96	0.38	11.0
550	2088	160	7.93	0.33	11.5





**Figure 11.7.** A cross section of the anthropogenic CO<sub>2</sub> in the ocean as determined by the C\* method. Robert Key, personal communication; Key *et al.* (2004).

