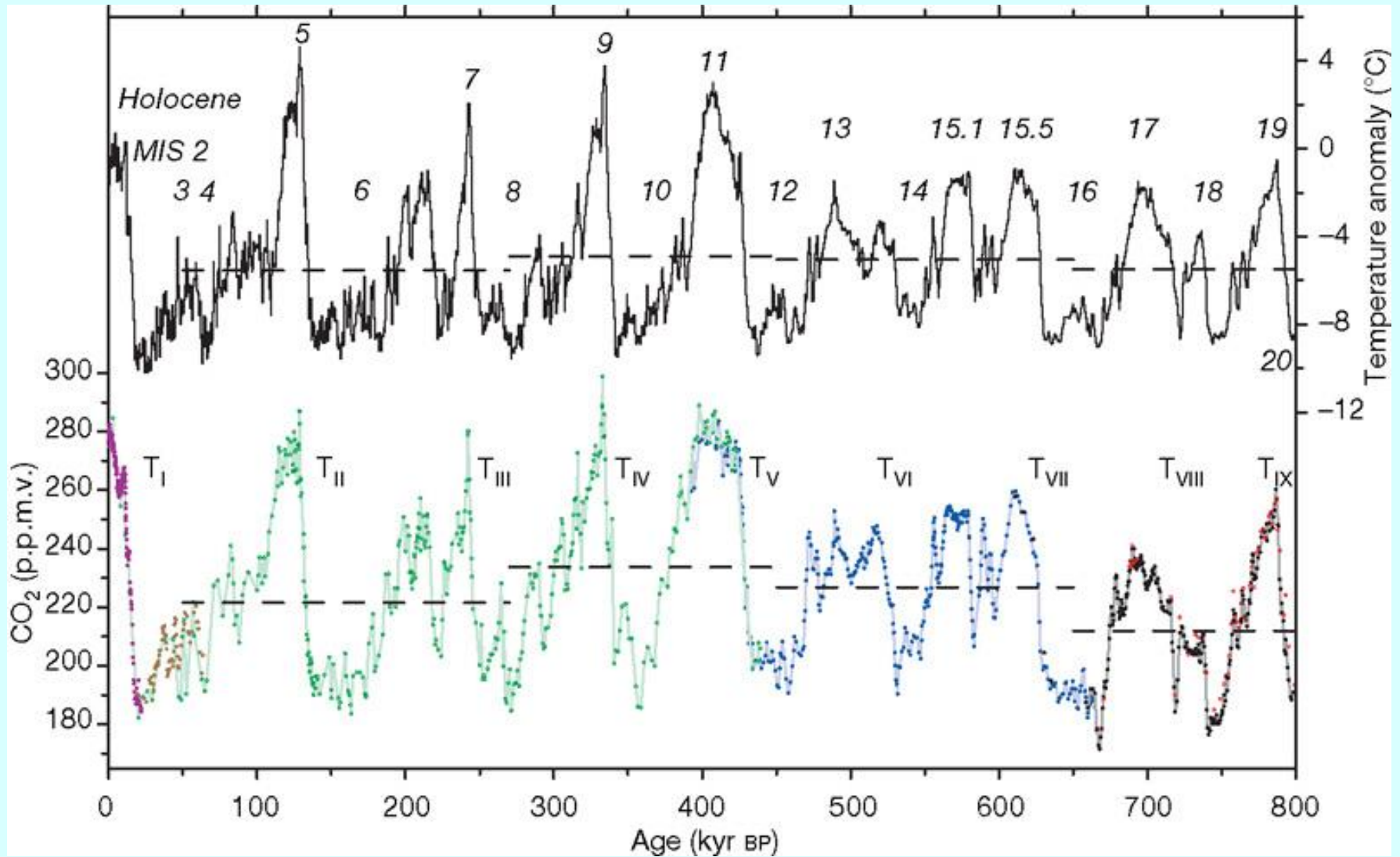


Greenhouse Gases & Global Climate Change



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° 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 CO₂ 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 CO₂ in ocean than in atmosphere!

Oceanic processes drive glacial to interglacial changes in atm. CO₂

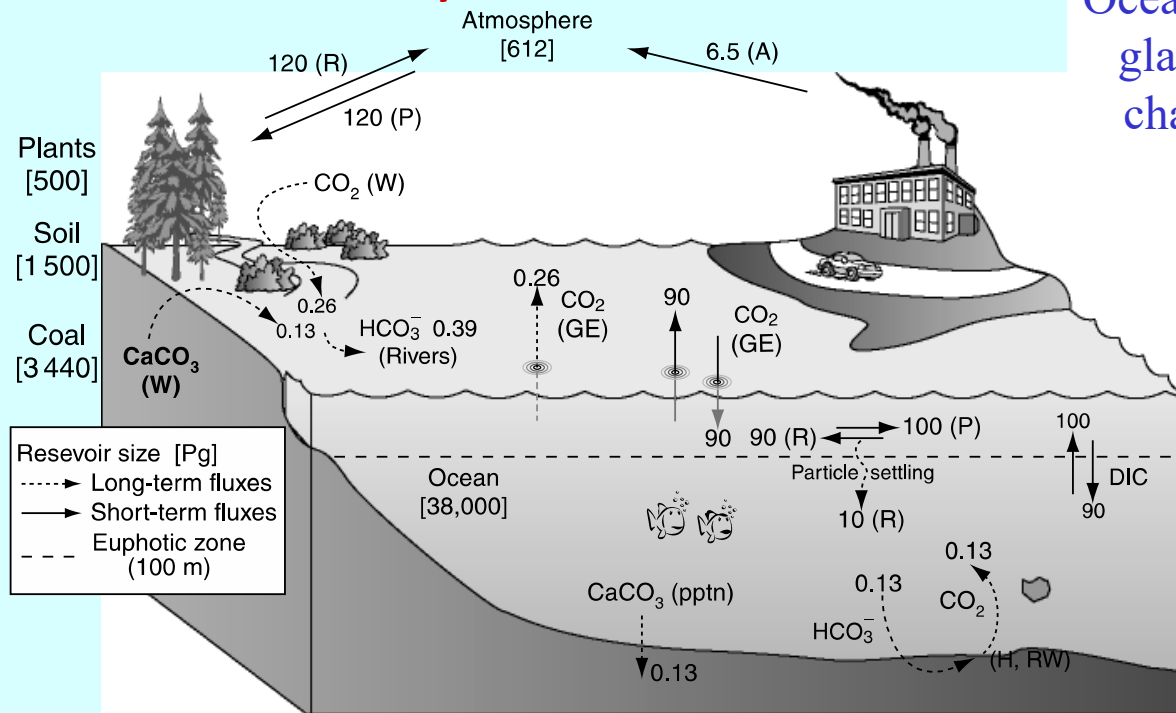


Figure 11.1. The global carbon cycle. Values in brackets are preanthropogenic reservoir sizes in Pg (10^{15} g); values on the arrows are fluxes in Pg y^{-1} . Dashed lines represent the long-term carbon cycle determined by weathering. Values are normalized to the flux of DIC from rivers (see Chapter 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 + HCO_3^- + cations); GE, gas exchange; P, gross photosynthesis ($\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O (OM)} + \text{O}_2$); R, respiration ($\text{CH}_2\text{O (OM)} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$); PPT, calcite precipitation (the reverse of carbonate weathering); H, hydrothermal processes; RW, reverse weathering (the reverse of silicate weathering).

Atmosphere

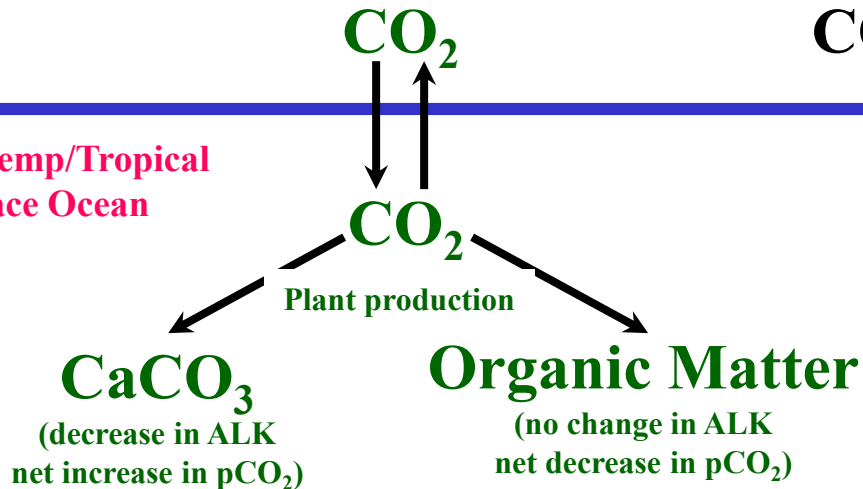
Biological Pump

Solubility Pump

Cold, Polar
Surface Ocean

Warm, Temp/Tropical
Surface Ocean

Higher solubility
due to cold SST



CO_2

Particle sinking

Particle sinking

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

CaCO_3/OM ratio
Controlled by biology e.g.
diatoms vs coccolithophorids

CaCO_3

OM

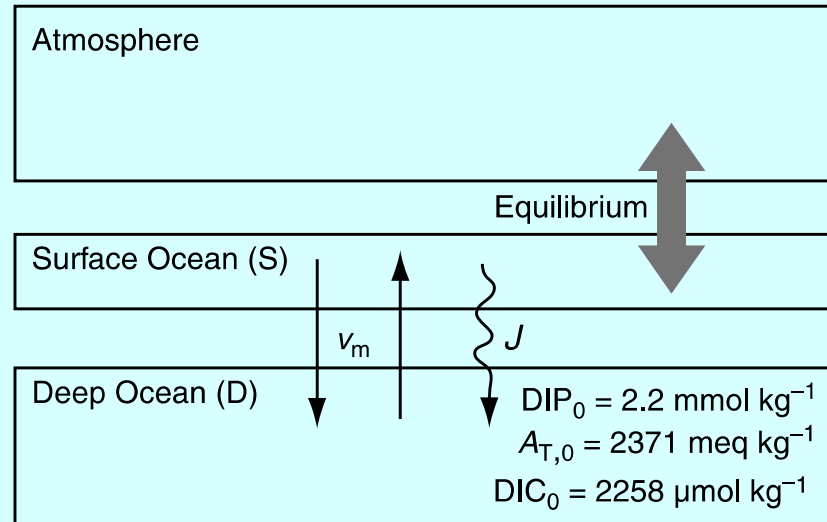
(increase in ALK
net decrease in pCO_2)

No change in ALK
net increase in pCO_2)

Cold, Deep
Interior Ocean

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 m y^{-1} , is the mixing rate between the surface and deep ocean.); stoichiometry of the particulate transport (J in $\text{mol m}^{-2} \text{y}^{-1}$); and chemical equilibria of the carbonate system.



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

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

Equilibrium:

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

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

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

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

$$K'_2 = \frac{[\text{CO}_3^{2-}] [\text{H}^+]}{[\text{HCO}_3^-]}$$

$$K'_1 = \frac{[\text{HCO}_3^-] [\text{H}^+]}{[\text{CO}_2]}$$

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

Table 11.2. The effect of the solubility and biological pumps on the fugacity of CO_2 in the atmosphere, f_{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 CaCO_3 ratio of the particle flux, OC : CaCO_3 .

	Temp	[DIP] _s	τ_{mix}	$R_{\text{OC:CA}}$	DIC _s	$A_{\text{T,S}}$	f_{CO_2}
Case	°C	$\mu\text{mol kg}^{-1}$	y		$\mu\text{mol kg}^{-1}$	$\mu\text{eq kg}^{-1}$	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 ₃		0.5	1000	10:1	2059	2361	337
(P:OC = 106)				1.5:1	1957	2157	485

SOFEX Fe Fertilization Study in Southern Ocean

North Patch

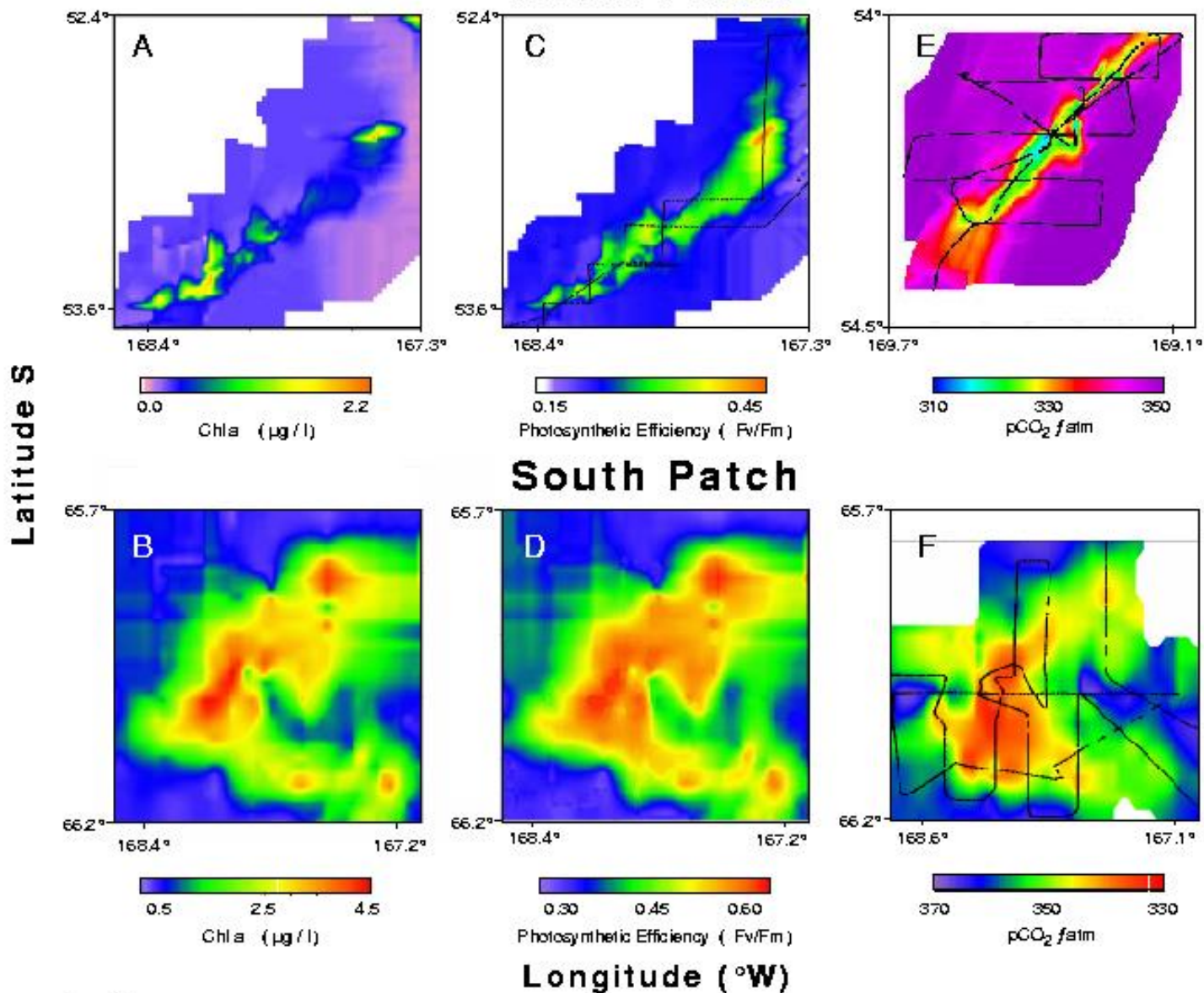
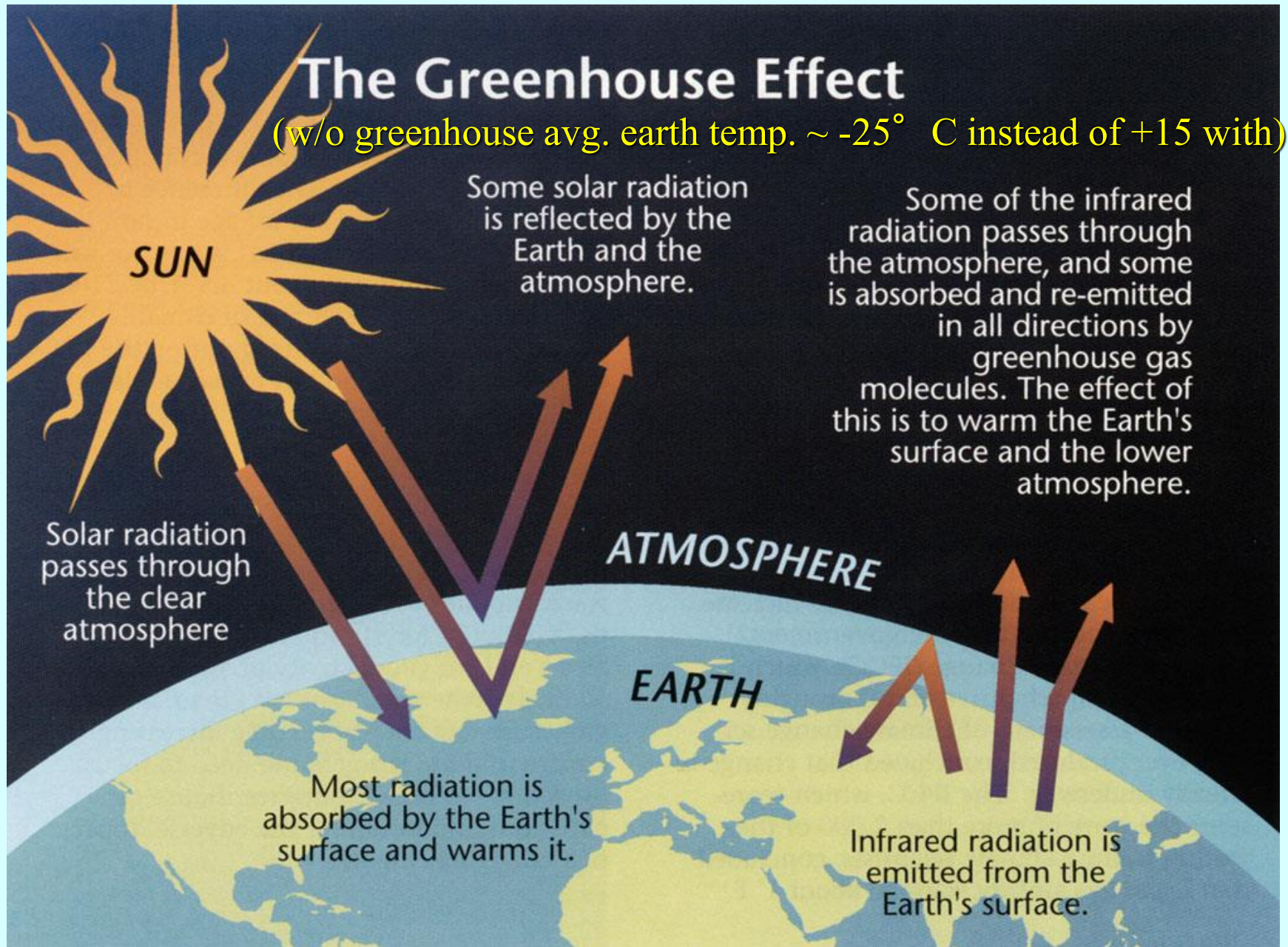


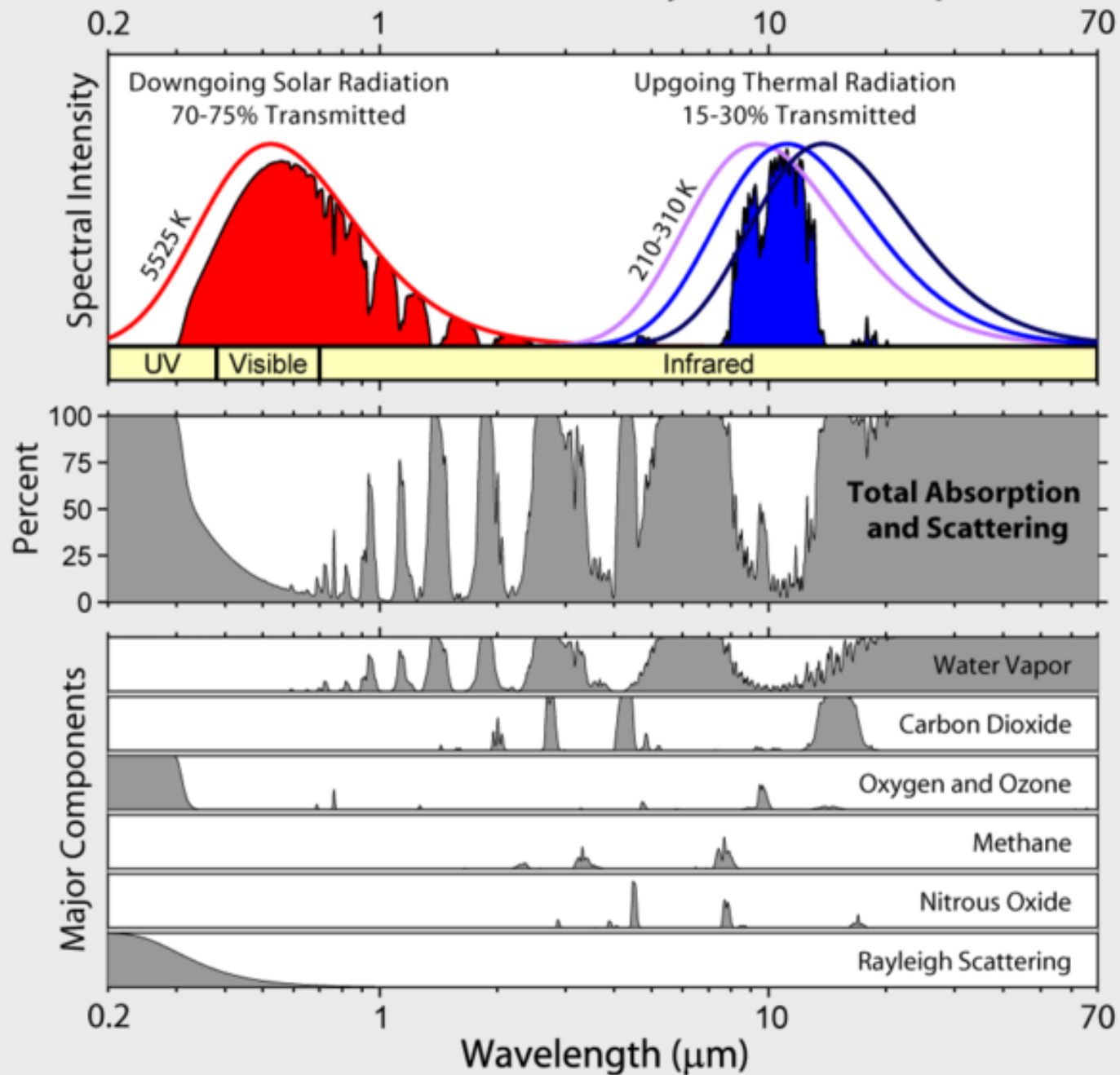
Fig. S3

The Greenhouse Effect

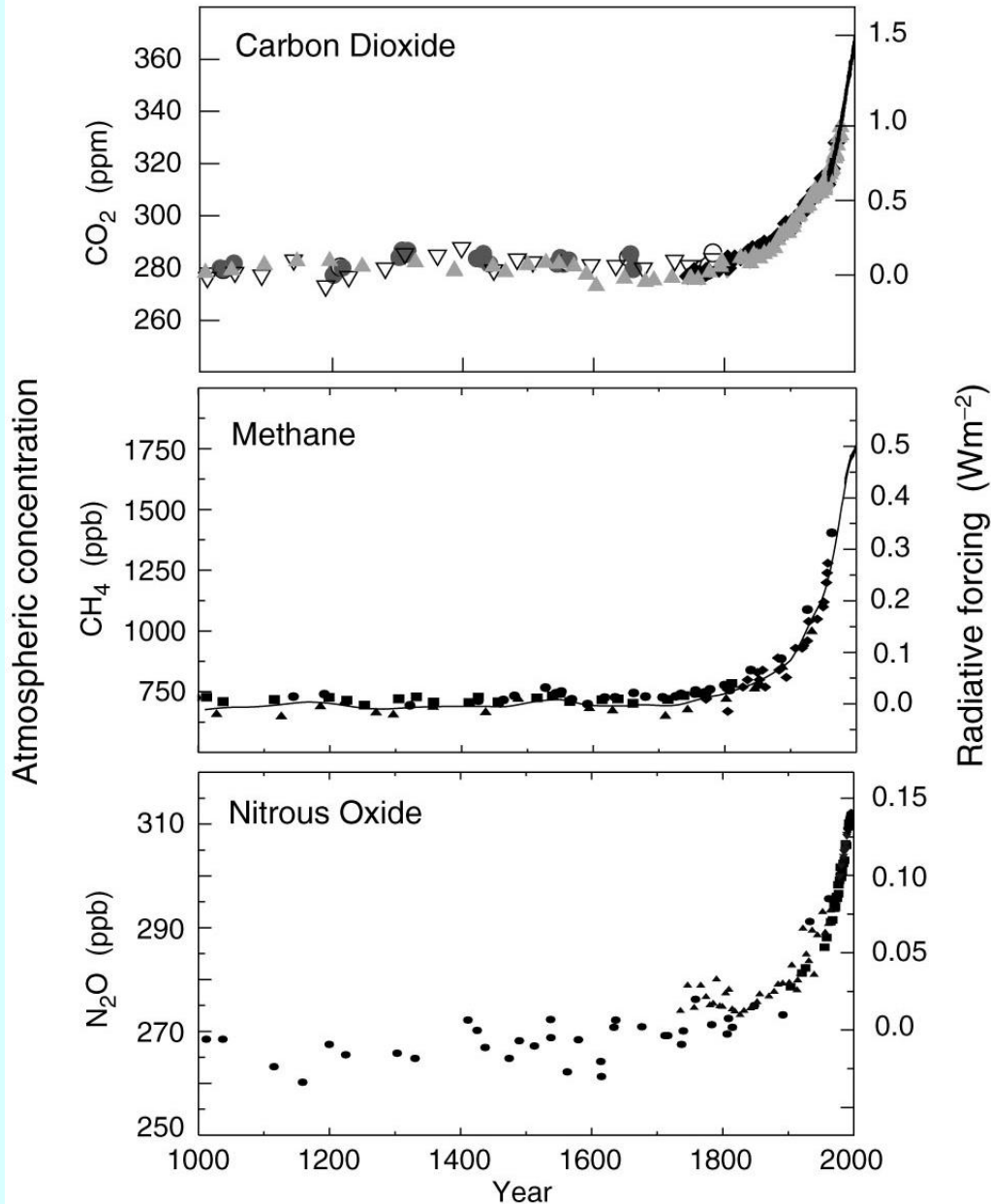
(w/o greenhouse avg. earth temp. $\sim -25^{\circ}$ C instead of $+15$ with)



Radiation Transmitted by the Atmosphere



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



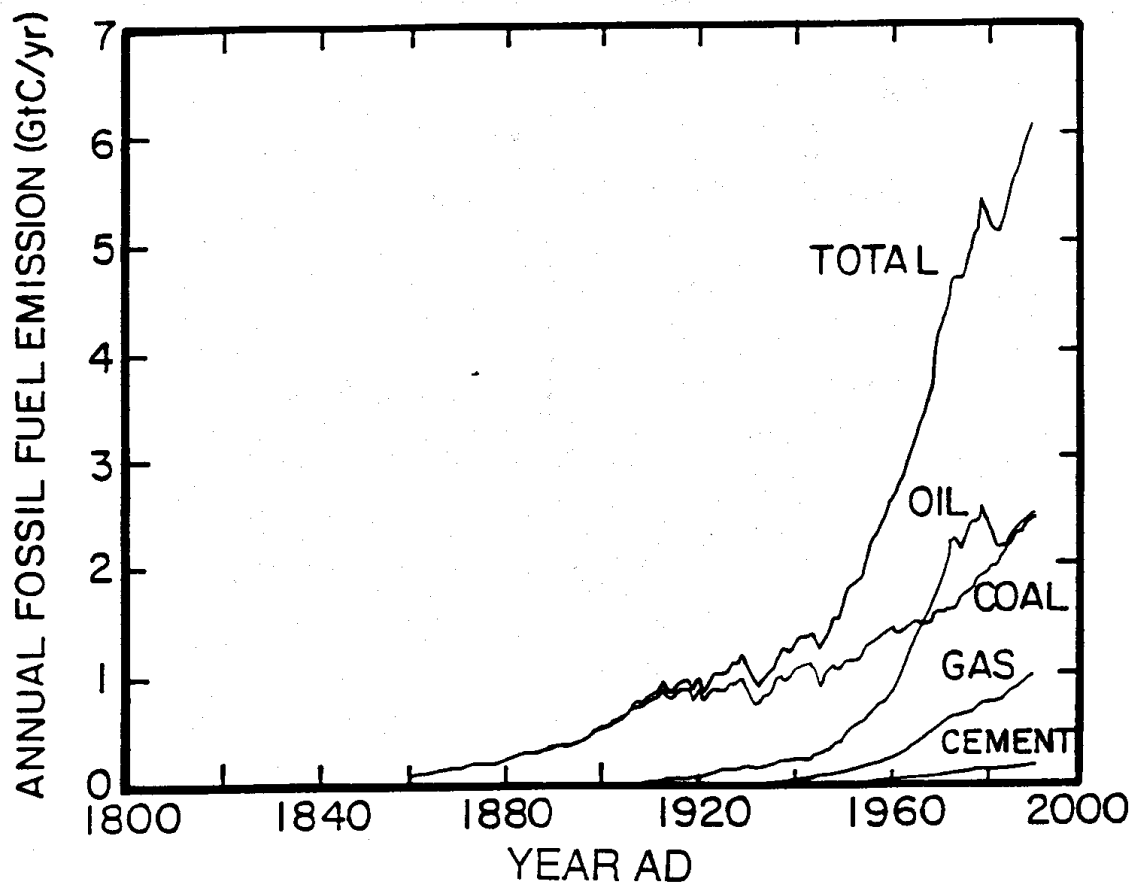
Anthropogenic Influence on Atmospheric Concentration of Greenhouse Gases

Source: IPCC TAR 2001

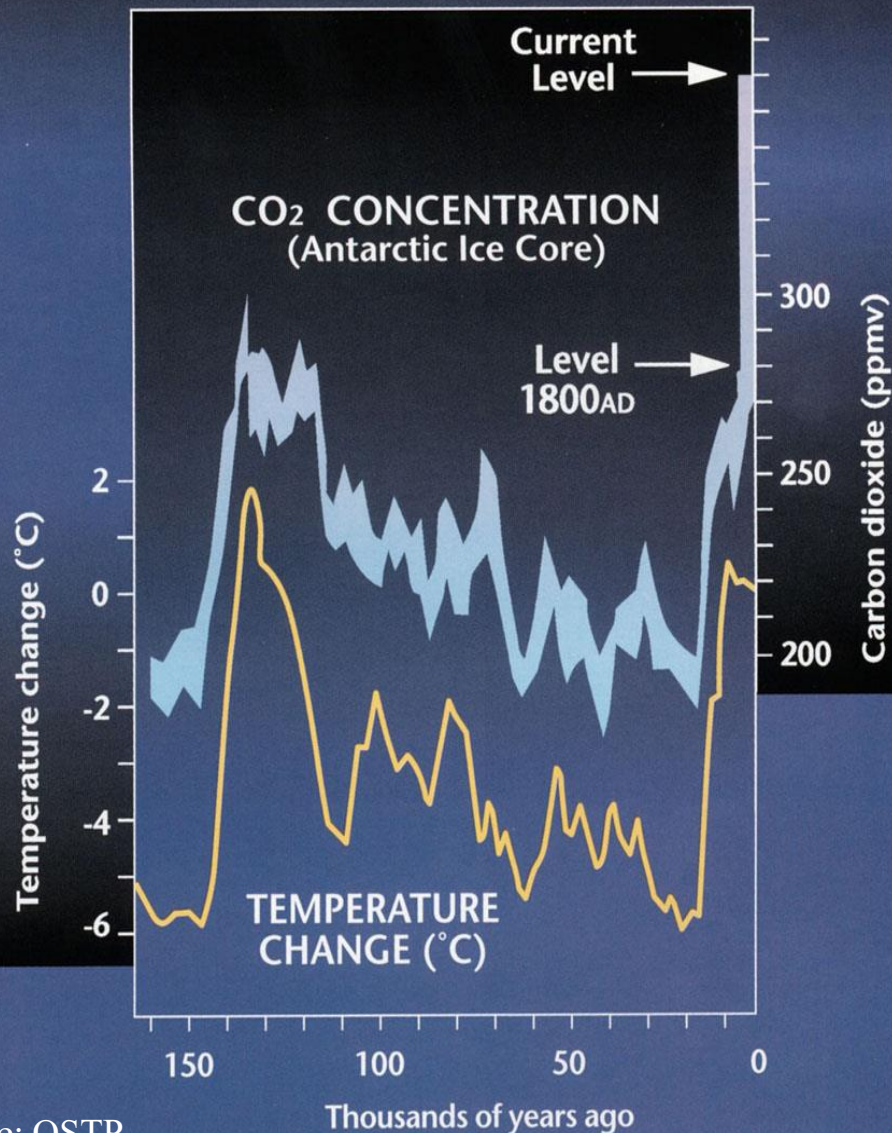


Union of Concerned Scientists

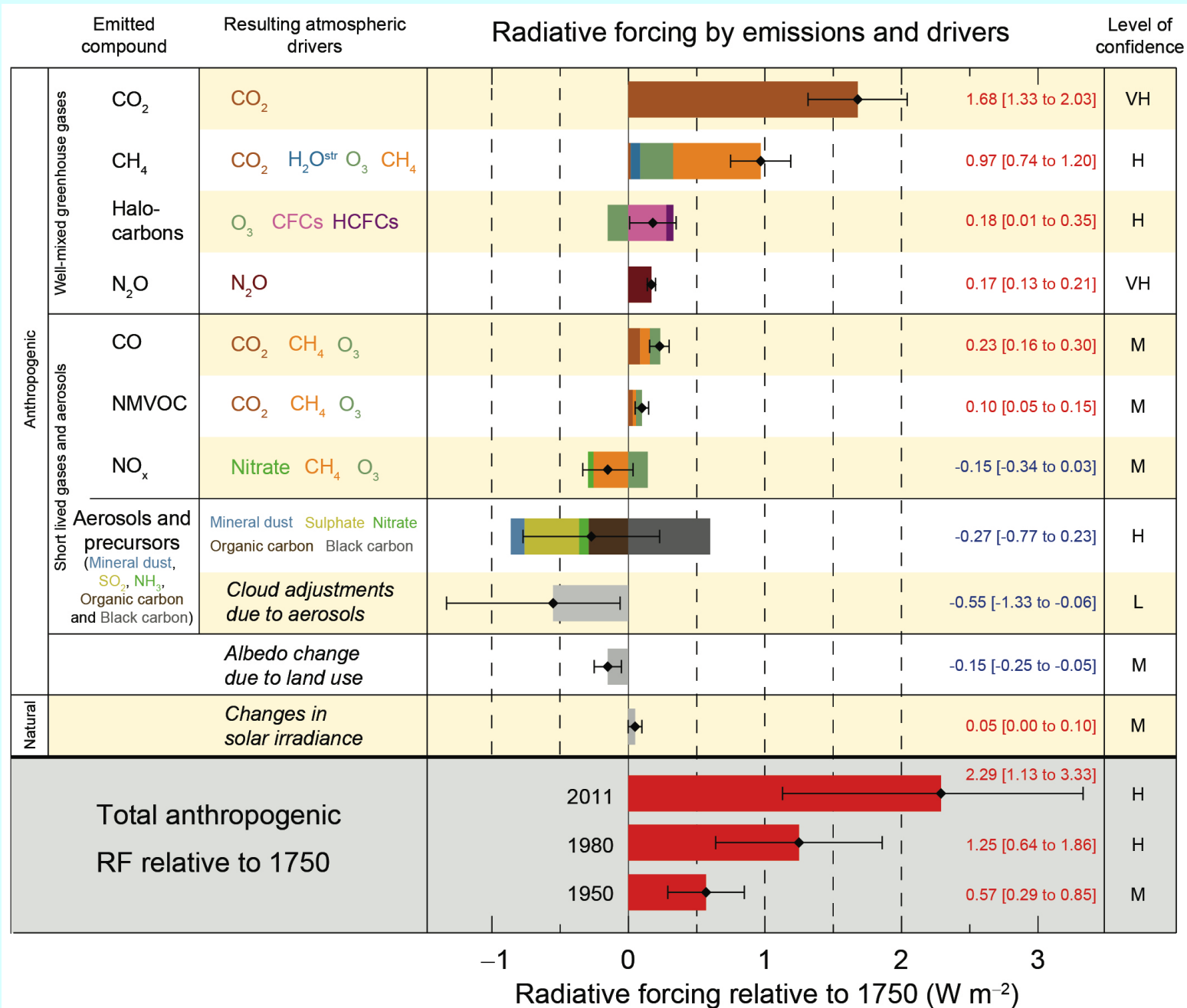
TIME HISTORY OF FOSSIL FUEL CONSUMPTION



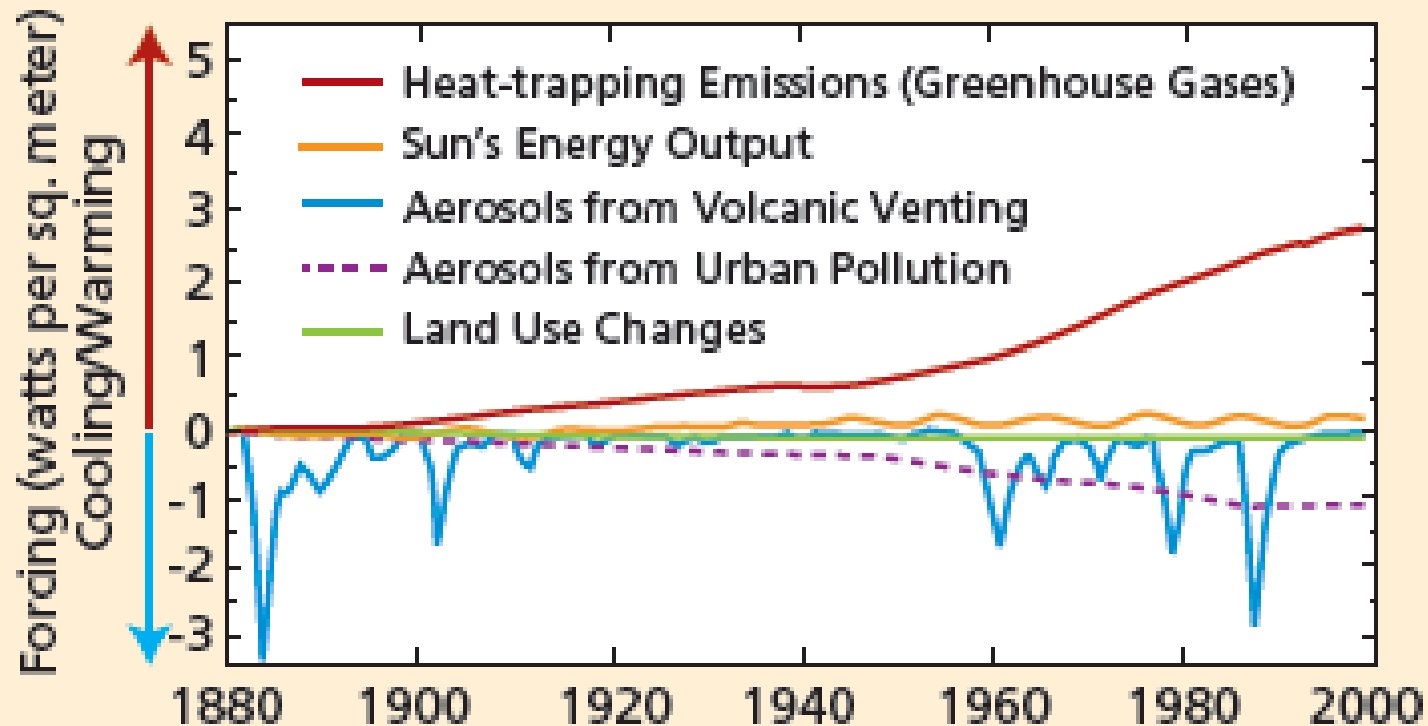
Atmospheric Carbon Dioxide Concentration and Temperature Change



- Clear correlation between atmospheric CO₂ and temperature over last 160,000 years
- Current level of CO₂ is *outside* bounds of natural variability
- *Rate* of change of CO₂ is also unprecedented



Global Climate Drivers

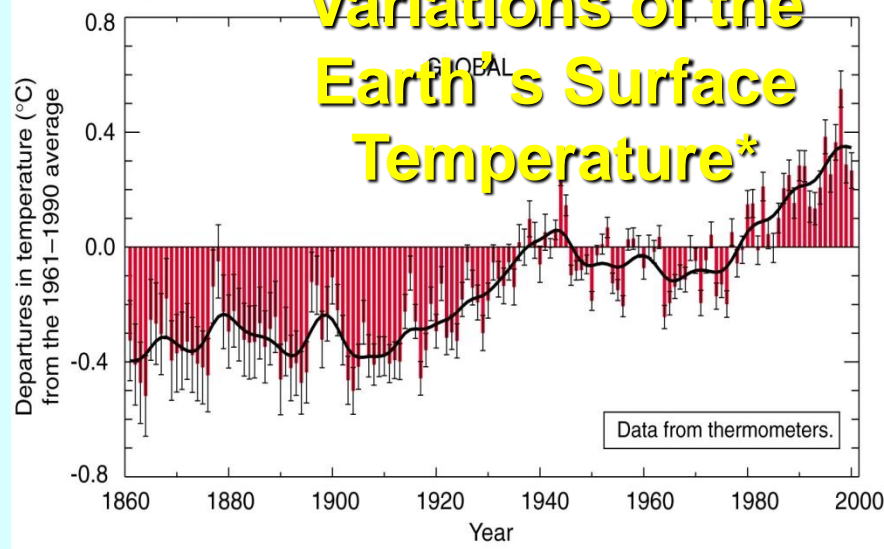


Heat-trapping emissions (greenhouse gases) far outweigh the effects of other drivers acting on Earth's climate.

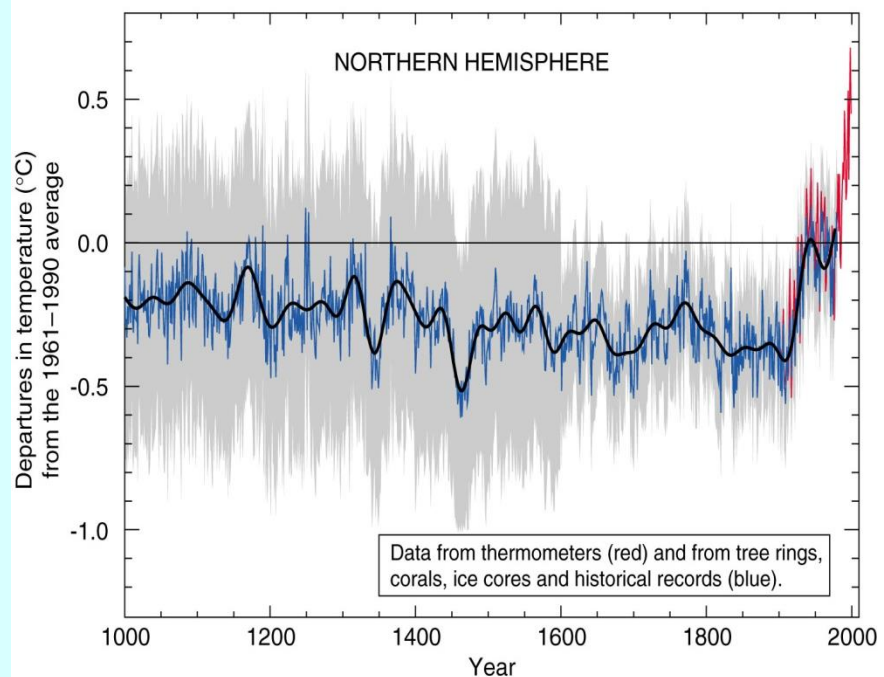
Source: Hansen et al. 2005.

Variations of the Earth's Surface Temperature*

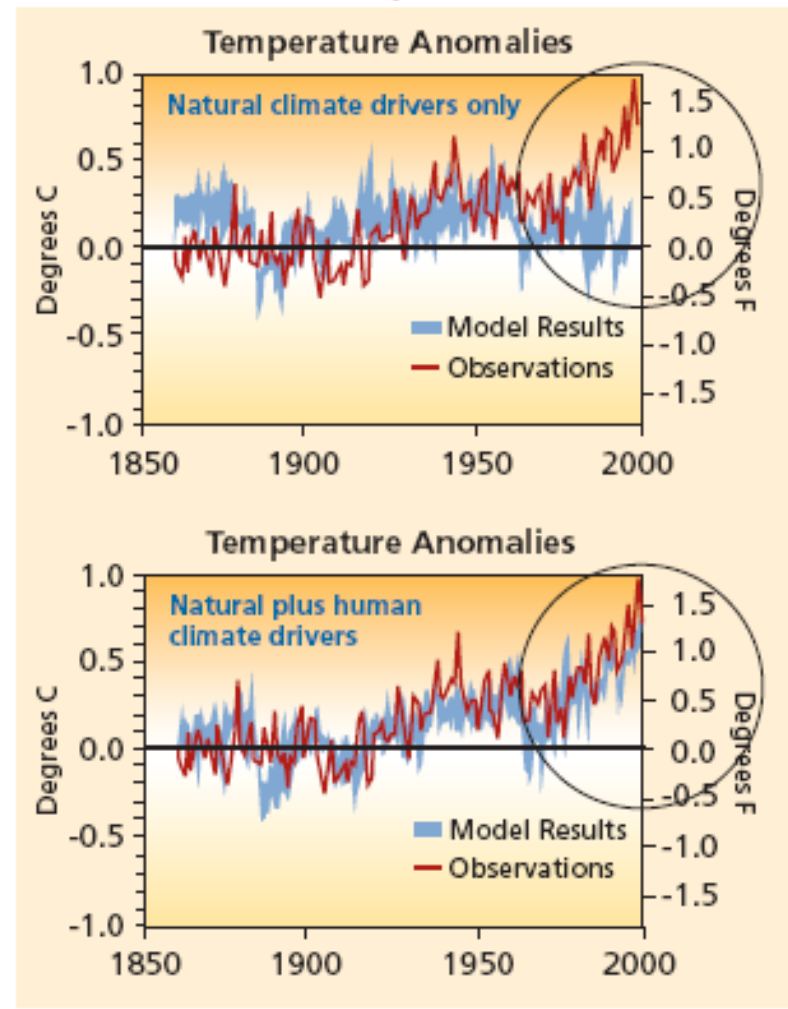
(a) the past 140 years



(b) the past 1000 years

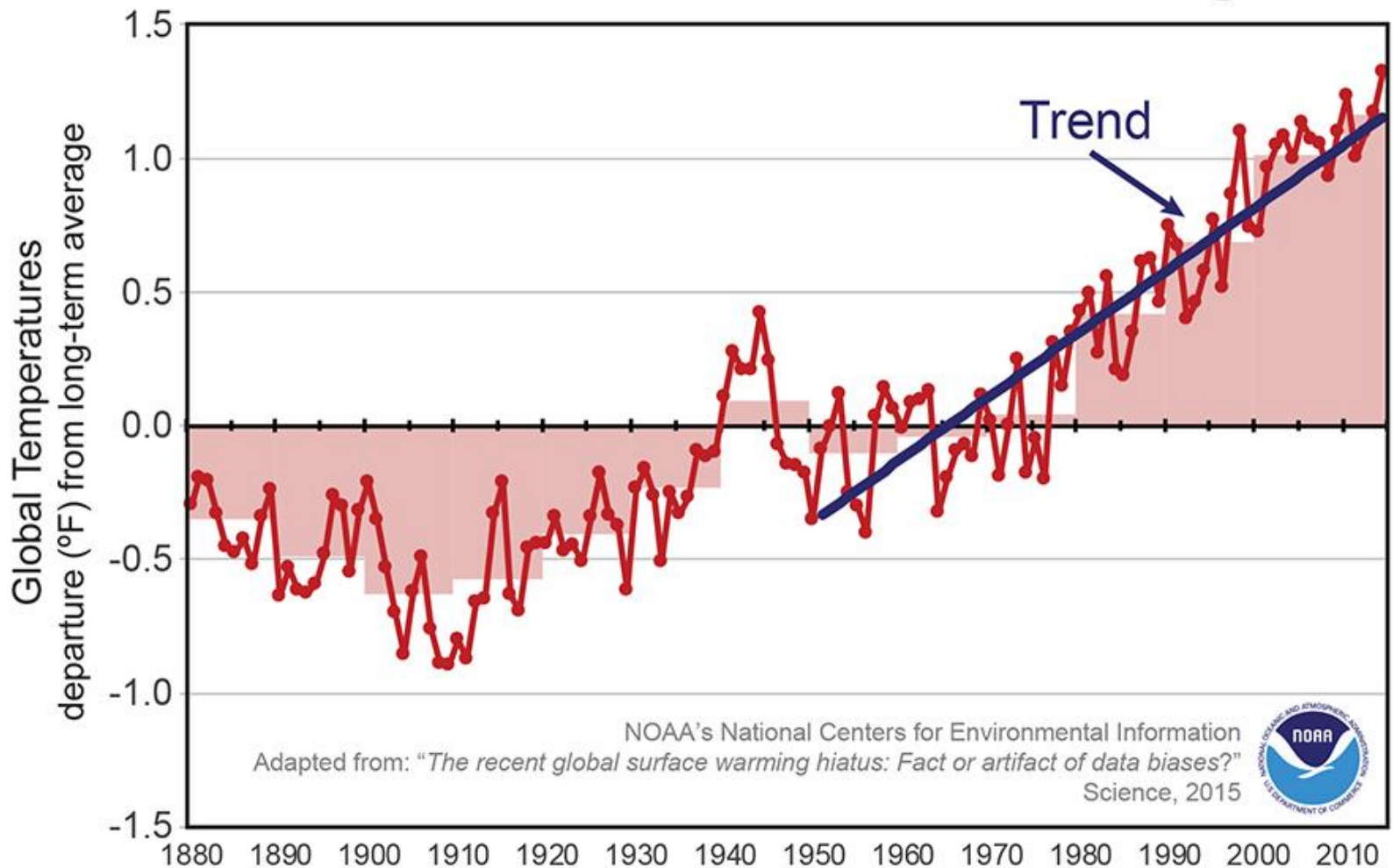


Climate Drivers Compared with Global Surface Temperature

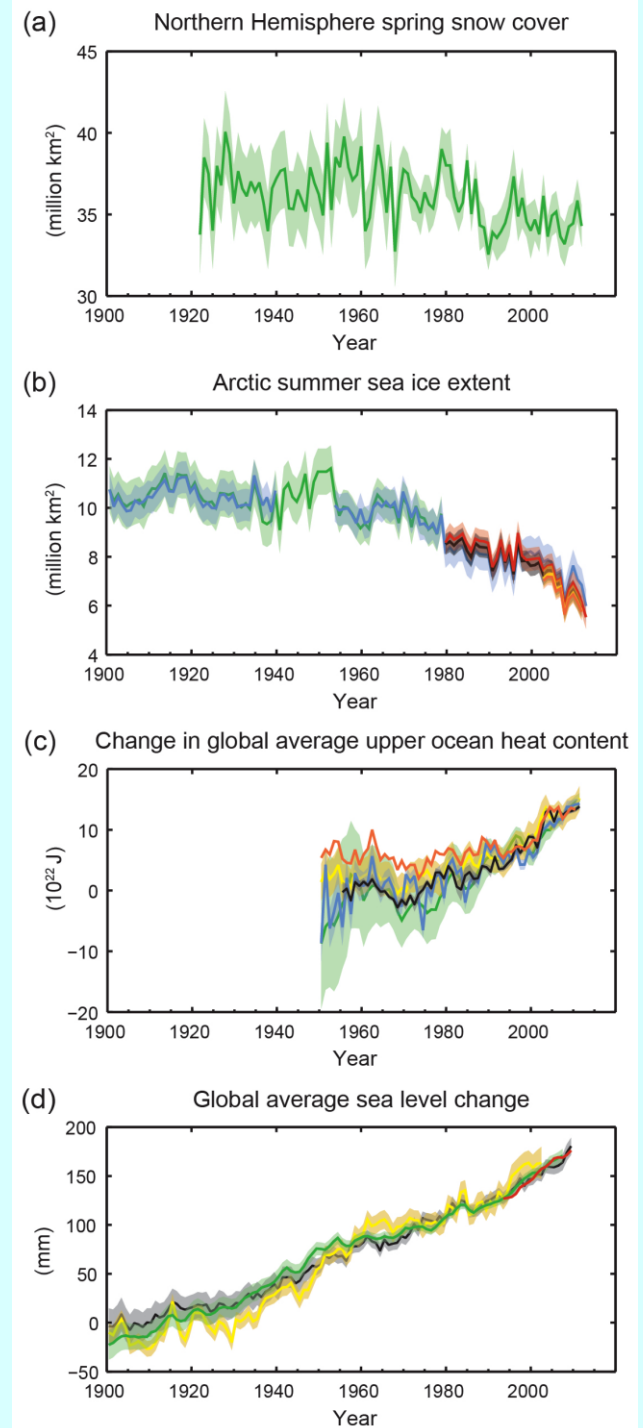
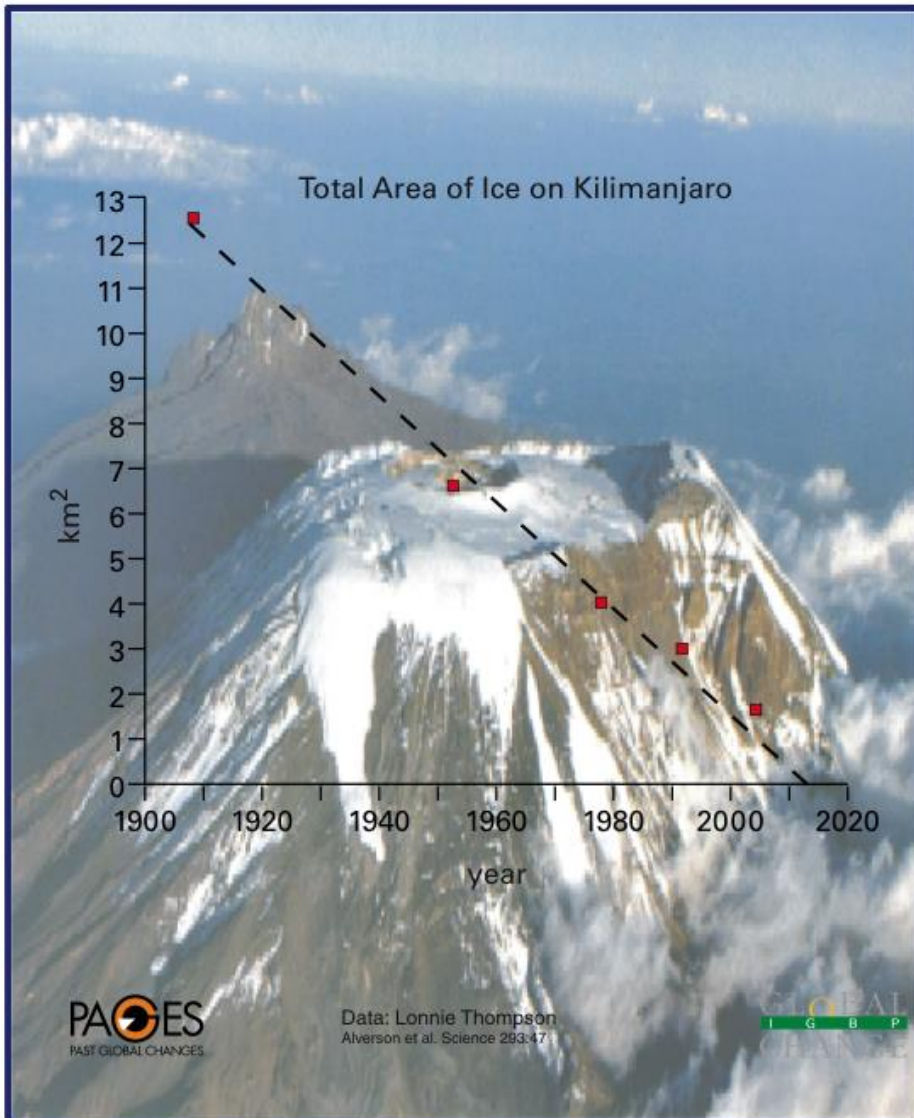


The model output (blue shading) that includes both natural and human-induced drivers (lower graph) gives a better match with the observed temperature response (red line). Source: IPCC TAR 2001.

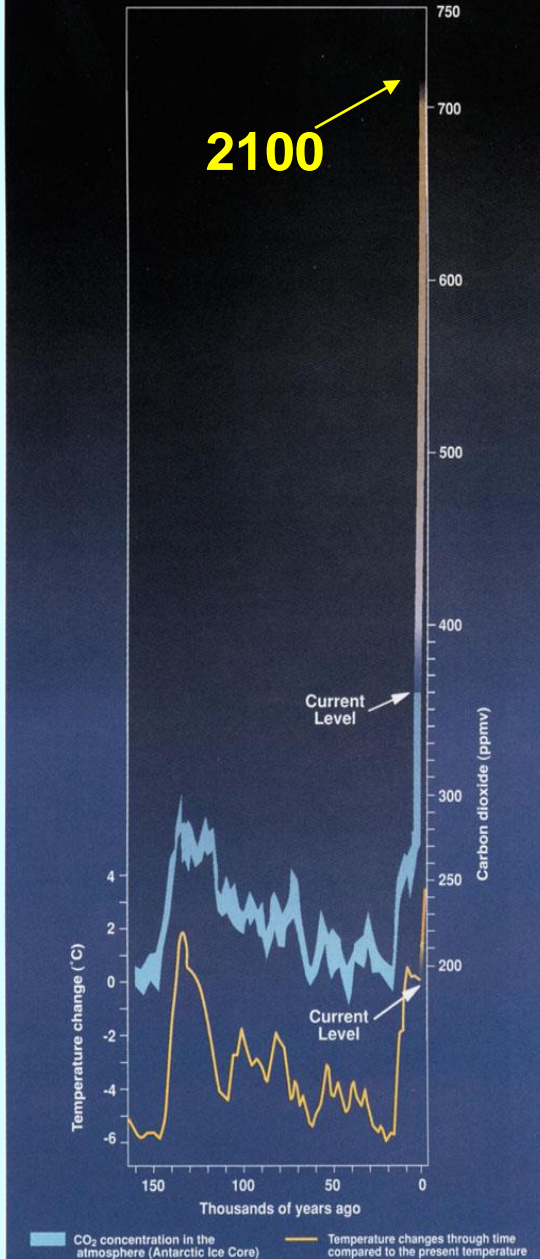
No Slow Down in Global Warming



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.



Atmospheric Carbon Dioxide Concentration and Temperature Change



If business as usual:

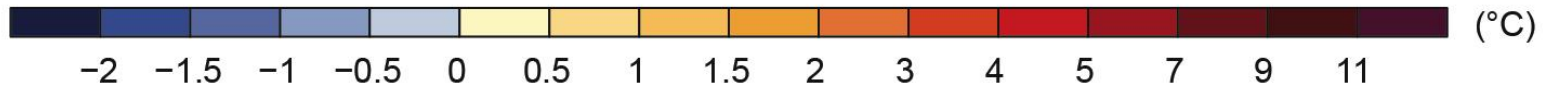
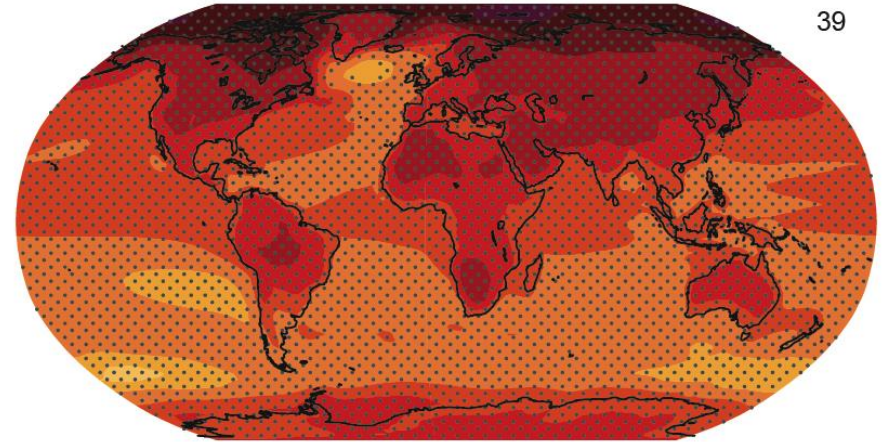
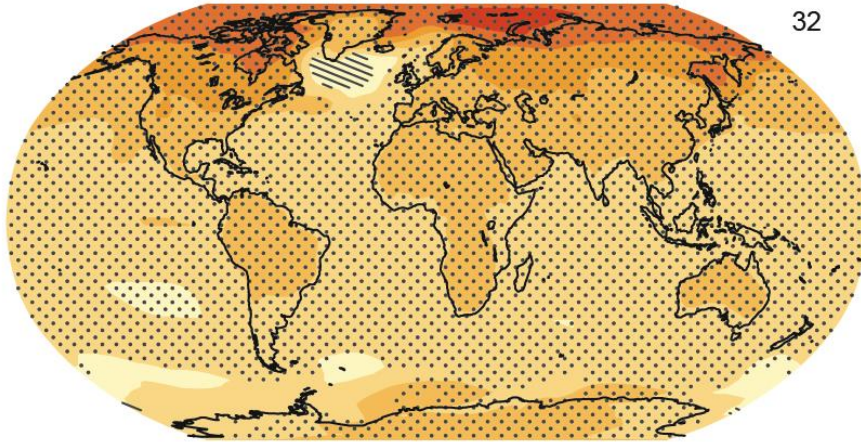
- CO₂ concentrations will likely be more than 700 ppm by 2100
- Global average temperatures projected to increase between 2.5 - 10.4° F

RCP 2.6

RCP 8.5

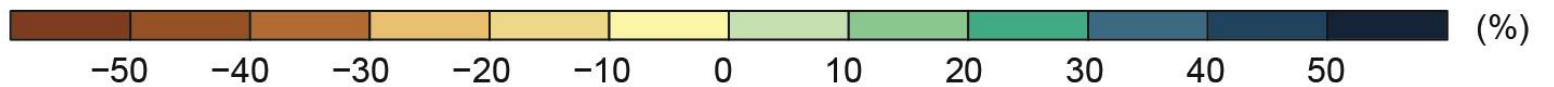
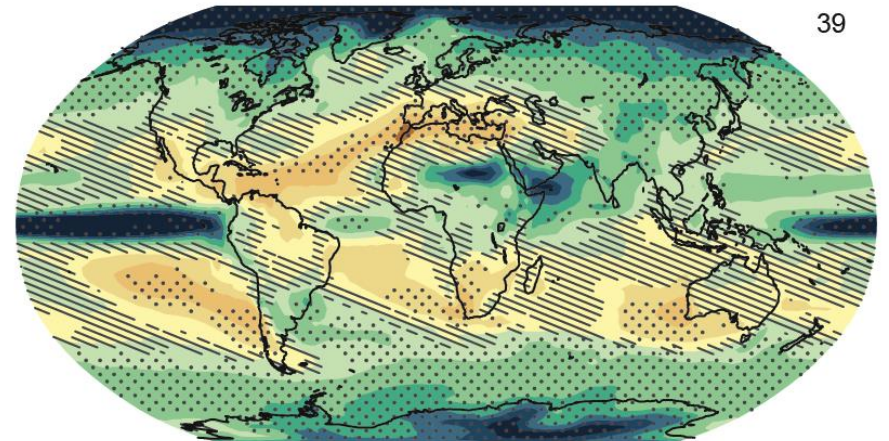
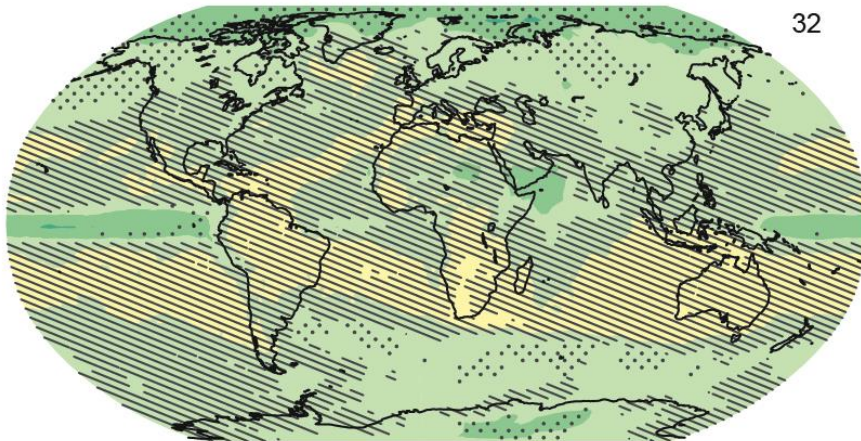
(a)

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

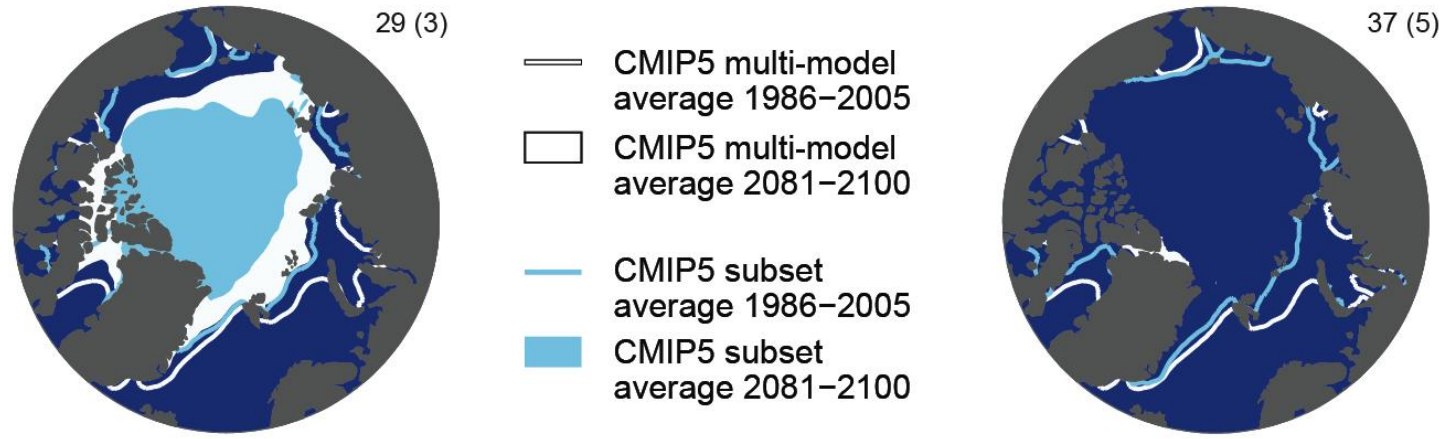


(b)

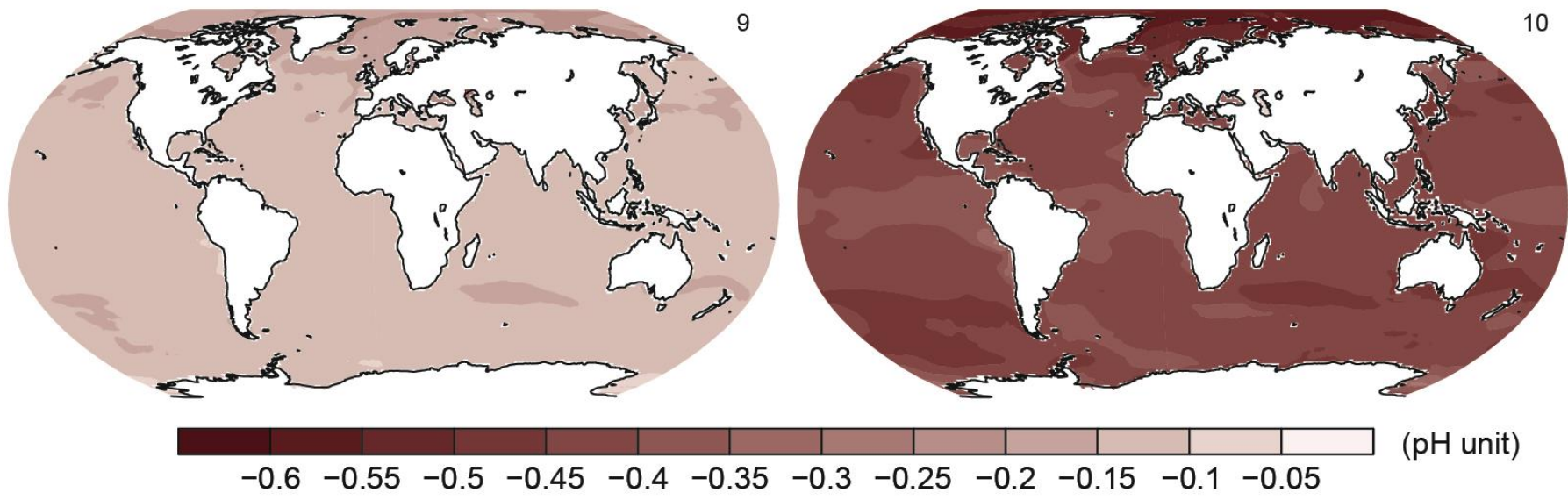
Change in average precipitation (1986–2005 to 2081–2100)



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



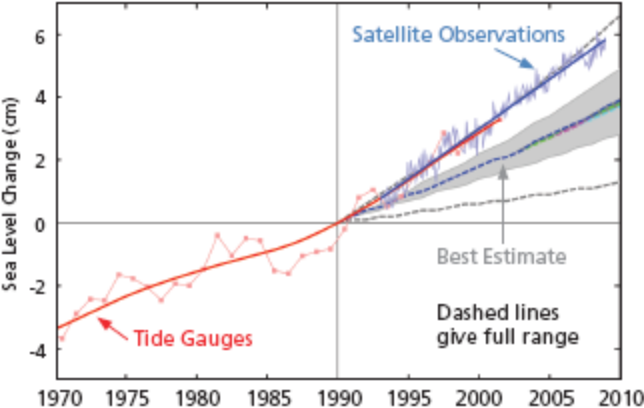
(d) Change in ocean surface pH (1986–2005 to 2081–2100)



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

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).^{4,5}

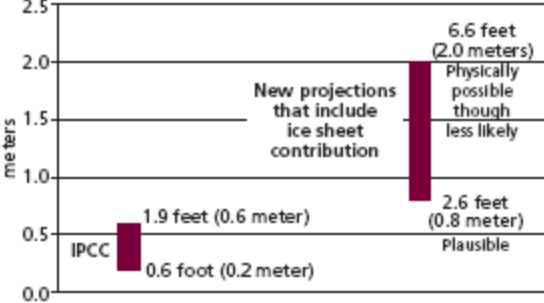
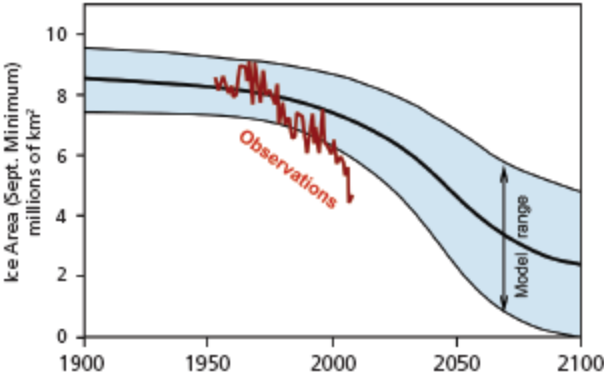


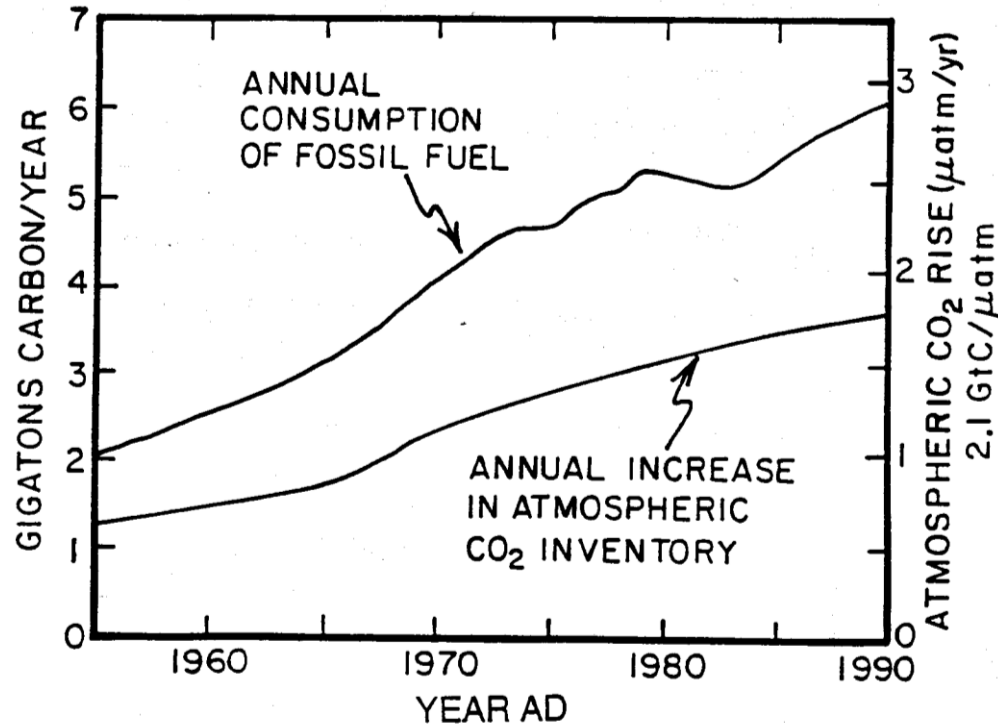
FIGURE 4 Shrinking Summer Arctic Sea Ice Area



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

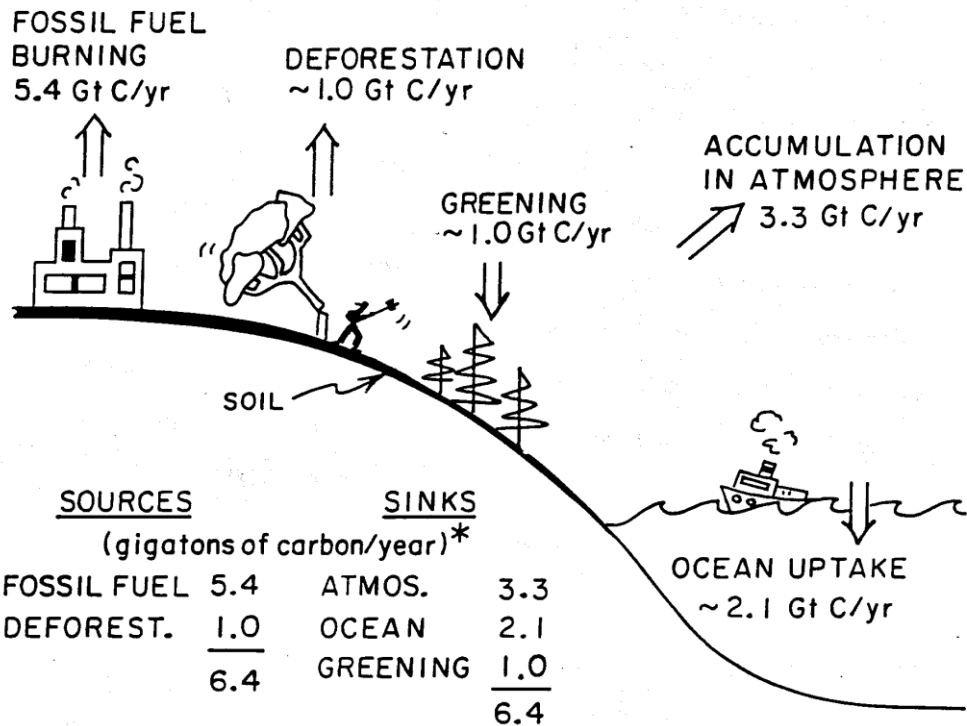
Source: Dirk Notz from Hamburg adapted figures from <http://www.nslc.org/news/images/20070430Figure1.png>.

COMPARISON WITH THE RATE OF ACCUMULATION OF CO₂ IN THE ATMOSPHERE



OVER THE TIME PERIOD DURING WHICH THE ATMOSPHERE HAS BEEN ACCURATELY MONITORED, ITS CO₂ CONTENT HAS BEEN RISING AT A RATE ONLY ABOUT 60% THE RATE EXPECTED IF ALL THE FOSSIL FUEL CO₂ 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

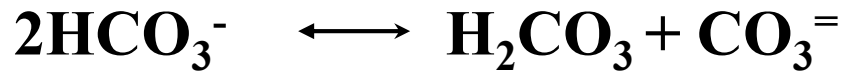
*1 Gt = 1×10^{15} grams
= 1×10^9 tons

Atmosphere

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



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



Surface/deep
exchange primary
brake on net CO_2
transfer

Whole ocean has the capacity to absorb 5/6
of the atm. increase in CO_2 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 CO₂ 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

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

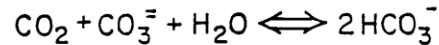
OR

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

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_c'=1445 ALK=2100

pCO ₂ = 280 μatm	pCO ₂ = 360 μatm	Δ
[CO ₂] = 9.6	[CO ₂] = 12.3	+2.6 μmol/kg
[HCO ₃ ⁻] = 1700	[HCO ₃ ⁻] = 1769	+69 μmol/kg
[CO ₃ ⁼] = 200	[CO ₃ ⁼] = 166	-34 μmol/kg
[ALK] = 2100	[ALK] = 2100	0 μmol/kg
[ΣCO ₂] = 1910	[ΣCO ₂] = 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

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

MASS BALANCE BORON

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

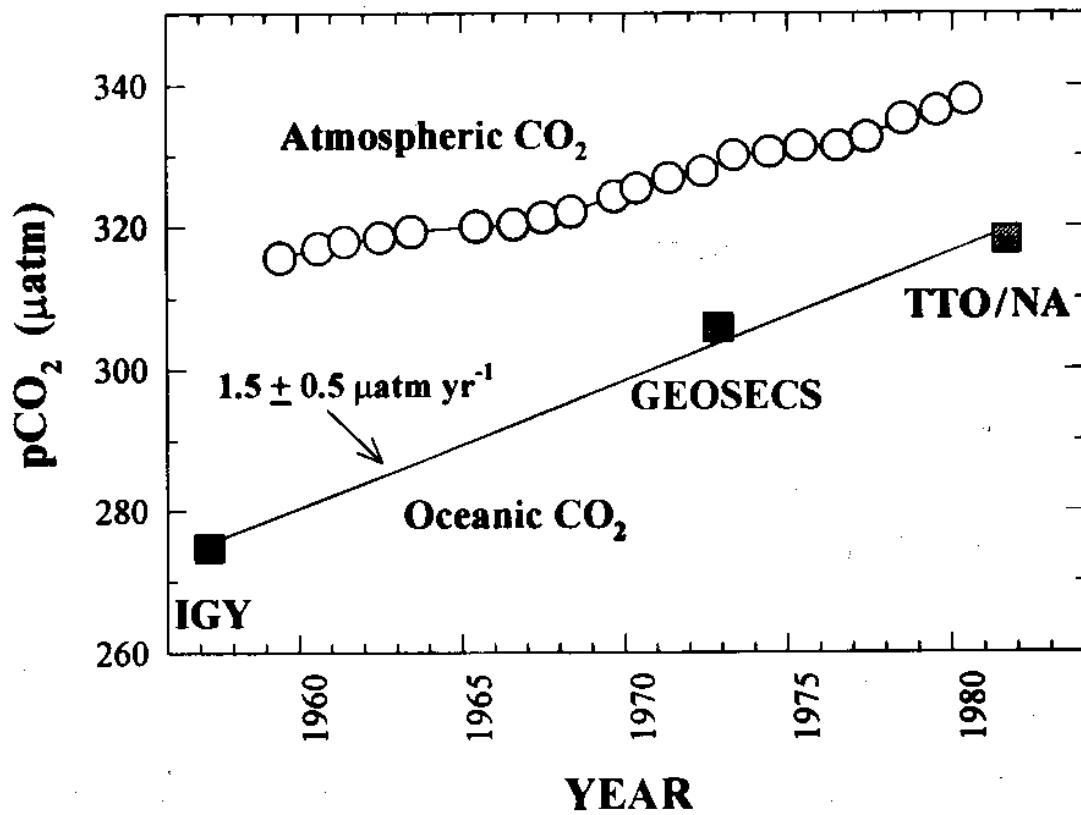
CHEMICAL EQUILIBRIUM

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

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

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

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



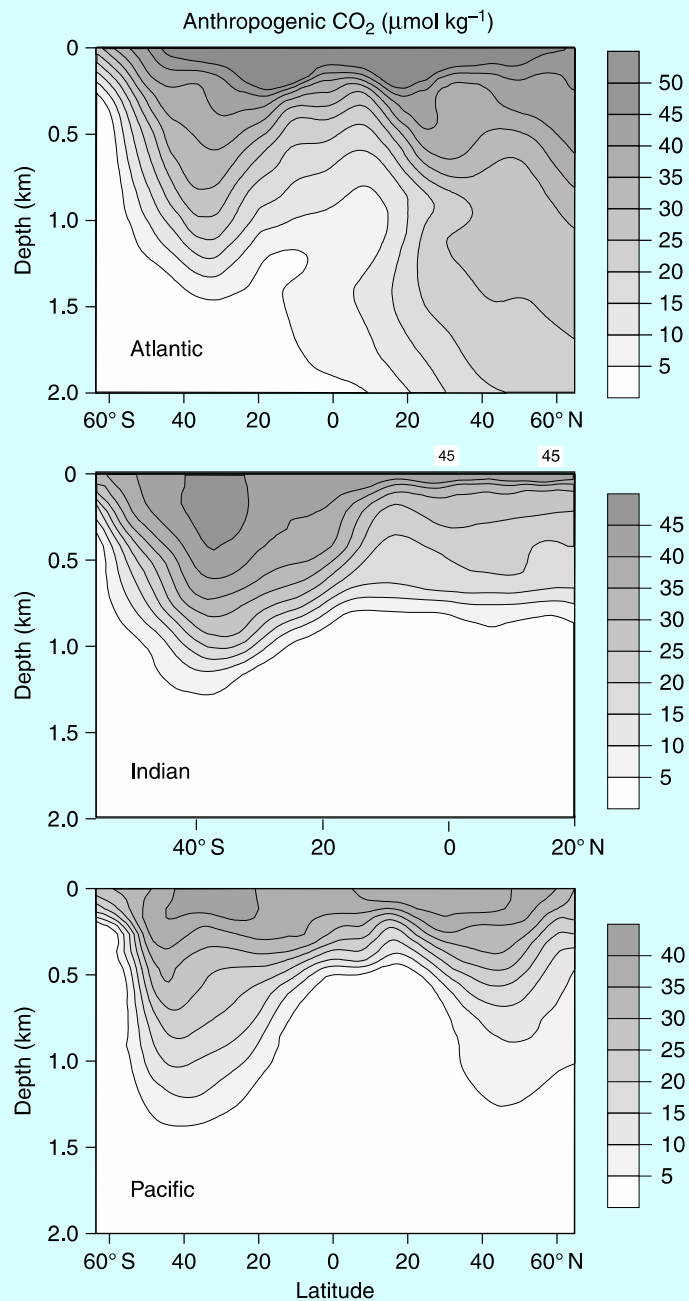


Figure 11.7. A cross section of the anthropogenic CO₂ in the ocean as determined by the C* method. Robert Key, personal communication; Key *et al.* (2004).