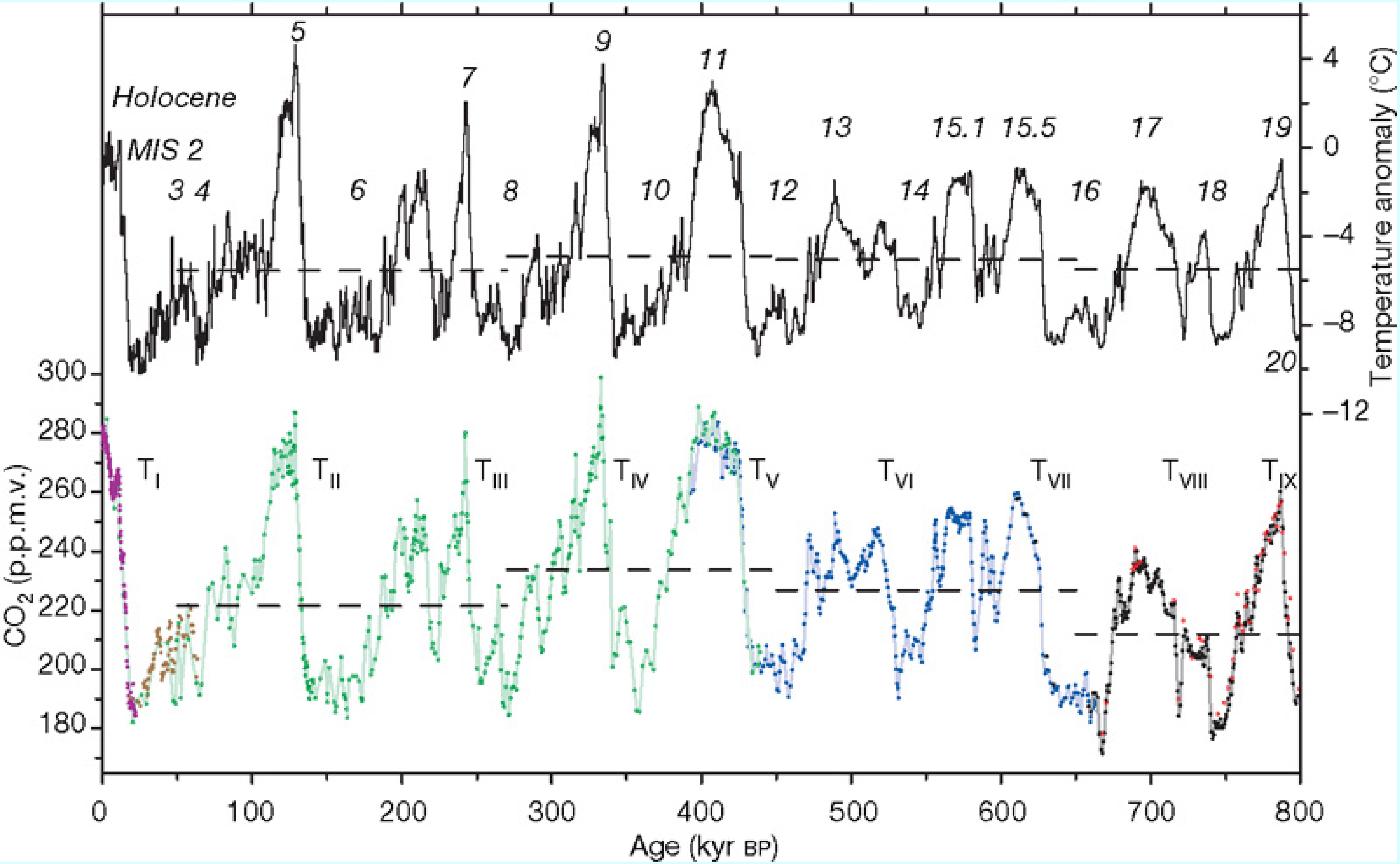
Greenhouse Gases & Global Climate Change



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/nature06949PICA ice core , Antarctica

In 1896, Arrhenius made the connection between atmospheric CO_2 and global climate!

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 Atmospherical 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° 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).

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_2 in ocean than in atmosphere!

Oceanic processes drive glacial to interglacial changes in atm. CO_2

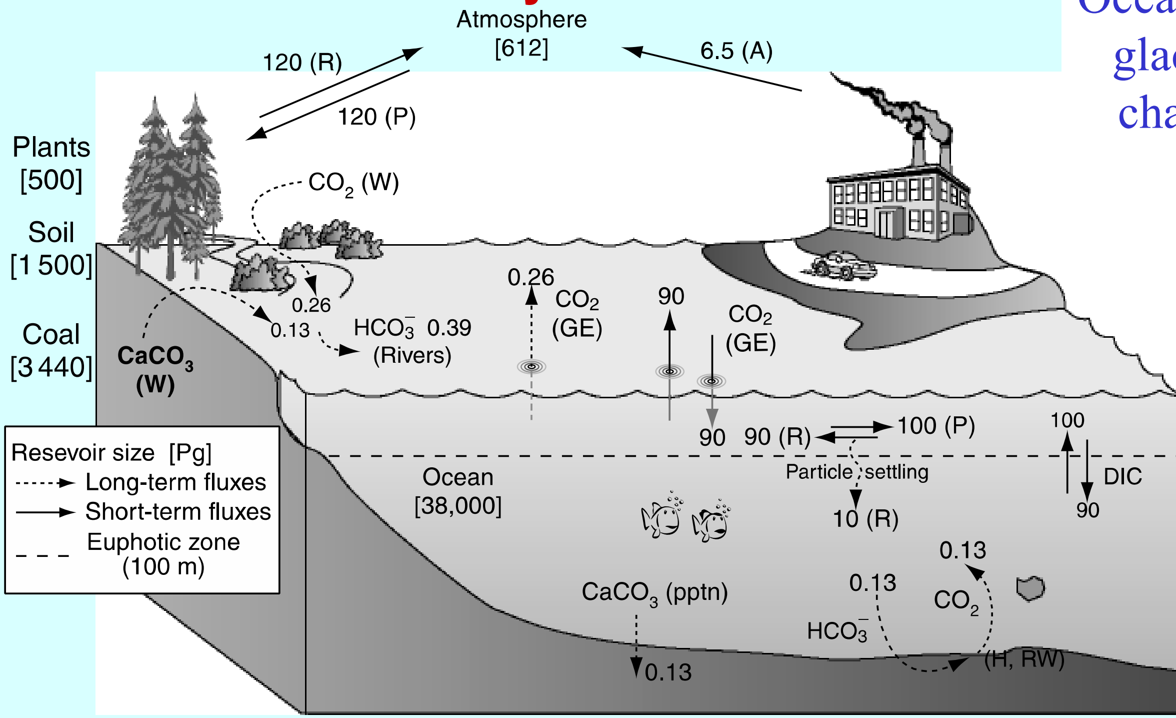


Figure 11.1. The global carbon cycle. Values in brackets are preanthropogenic reservoir sizes in Pg (10^{15} g); values on the arrows are furxes in Pg y^{-1}. Dashed lines represent the long-term carbon cycle determined by weathering. Values are normalized to the flux of DIC from rivers (see Chapter 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 ($CaCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + Ca^{2+}$) and silicates (silicate $+ CO_2 + H_2O \rightarrow$ clay $+ HCO_3^- +$ cations); GE, gas exchange; P, gross photosynthesis ($CO_2 + H_2O \rightarrow CH_2O$ (OM) $+ O_2$); R, respiration (CH_2O (OM) $+ O_2 \rightarrow CO_2 + H_2O$); PPT, calcite precipitation (the reverse of carbonate weathering); H, hydrothermal processes; RW, reverse weathering (the reverse of silicate weathering).

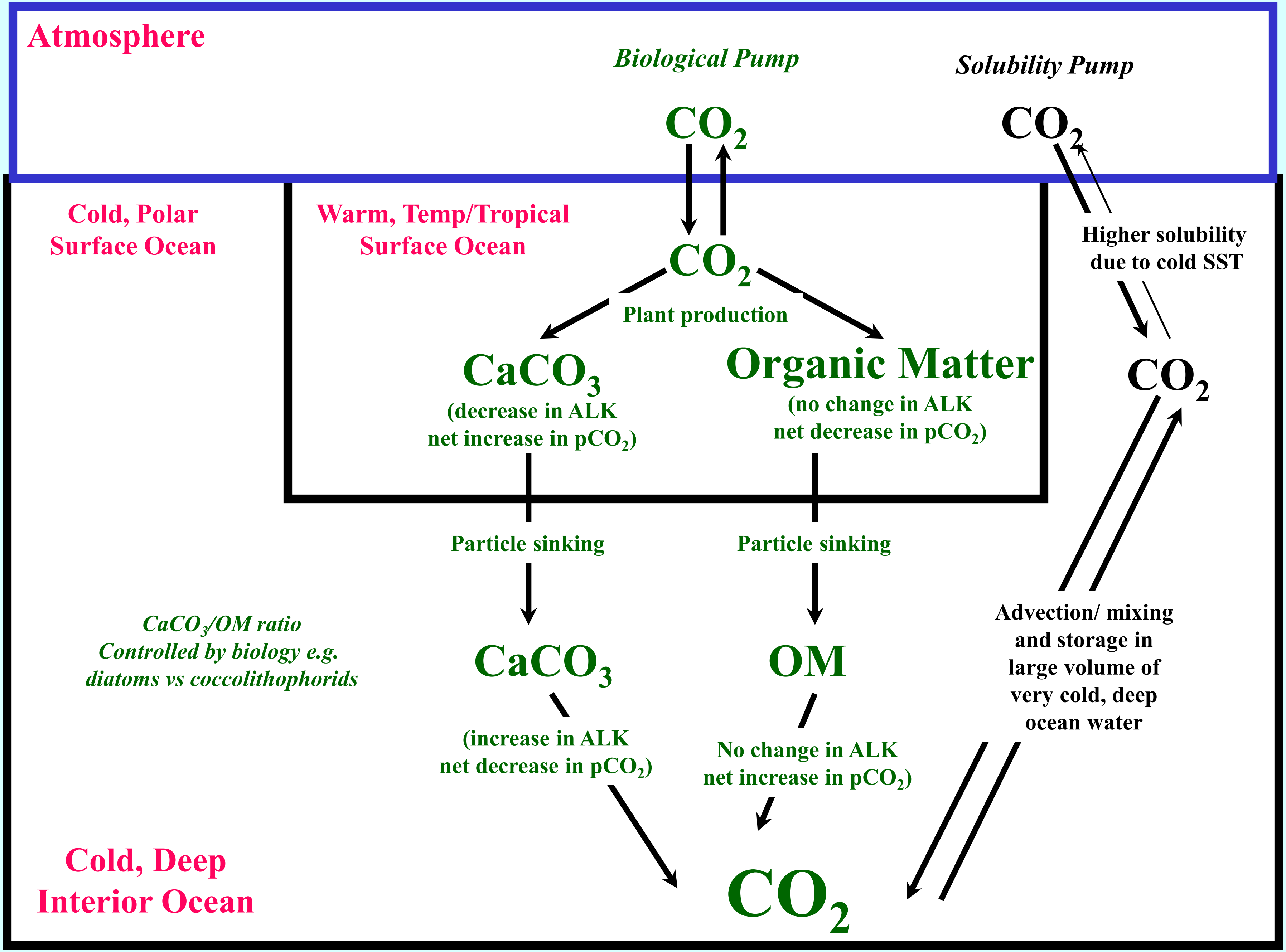
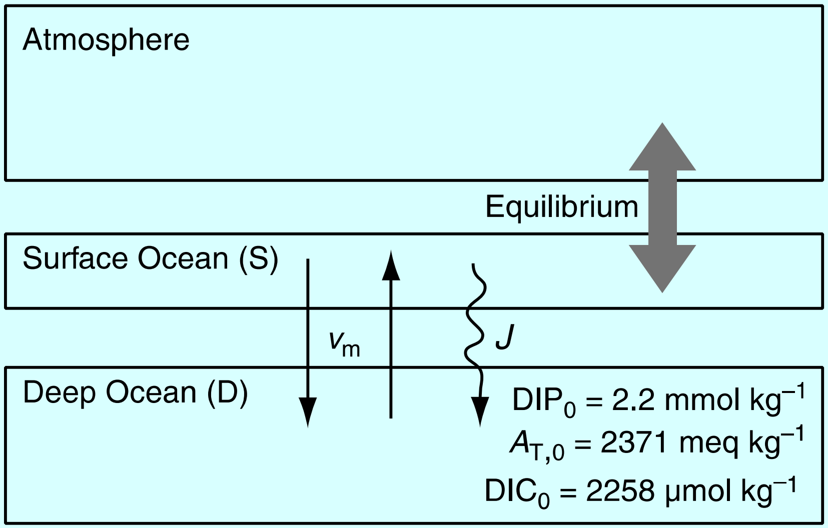

Atmosphere
Biological Pump
Solubility Pump
CO2
CO2
Cold, Polar
Surface Ocean
Warm, Temp/Tropical
Surface Ocean
CO2
Higher solubility
due to cold SST
Plant production
CaCO3
(decrease in ALK
net increase in pCO2)
Organic Matter
(no change in ALK
net decrease in pCO2)
CO2
Particle sinking
Particle sinking
CaCO3/OM ratio
Controlled by biology e.g.
diatoms vs coccolithophorids
CaCO3
OM
Advection/ mixing
and storage in
large volume of
very cold, deep
ocean water
(increase in ALK
net decrease in pCO2)
No change in ALK
net increase in pCO2)
Cold, Deep
Interior Ocean
CO2

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 mol m^{-2} y^{-1}); and chemical equilibria of the carbonate system.



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

Stoichiometry: $\Delta P : \Delta N : \Delta DIC : \Delta A_T : \Delta Ca$

1 : 16 : 136 : 44 : 30

Equilibrium:

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2]$$

$$A_{C\&B} = [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-]$$

$$B_T = B(OH)_3 + B(OH_4^-)$$

$$K_{H,CO_2} = \frac{[CO_2]}{f^a_{CO_2}} \qquad K'_2 = \frac{[CO_3^{2-}]\,[H^+]}{[HCO_3^-]}$$

$$K'_1 = \frac{[HCO_3^-]\,[H^+]}{[CO_2]} \qquad K'_B = \frac{[B(OH)_4^-]\,[H^+]}{[B(OH)_3]}$$

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 : $CaCO_3$.

Case	Temp °C	$[DIP]_S$ μmol kg^{-1}	τ_{mix} y	$R_{OC:CA}$	DIC_S μmol kg^{-1}	$A_{T,S}$ μeq kg^{-1}	f_{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:$CaCO_3$		0.5	1000	10:1	2059	2361	337
(P:OC = 106)							
				1.5:1	1957	2157	485

SOFEX Fe Fertilization Study in Southern Ocean

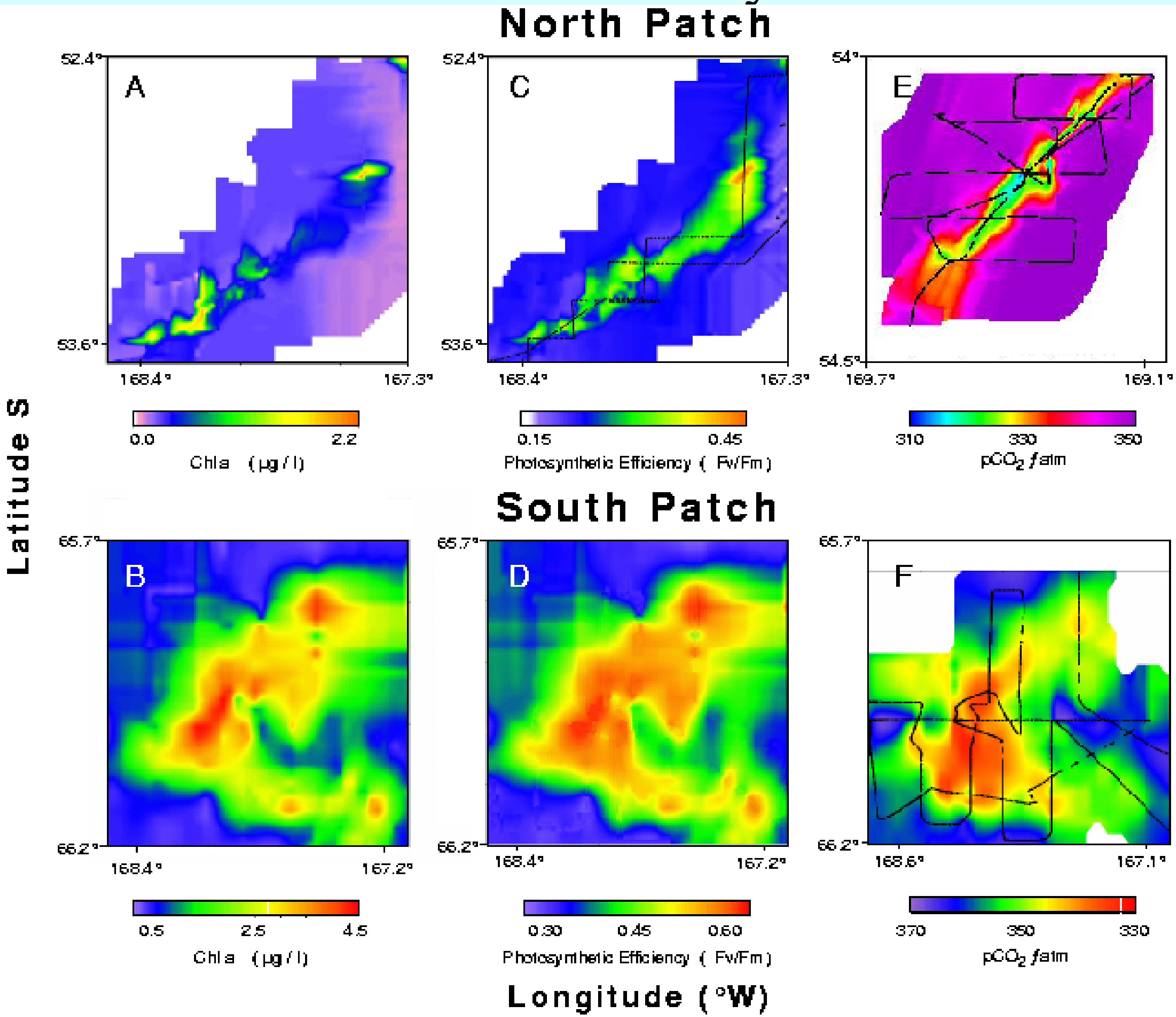
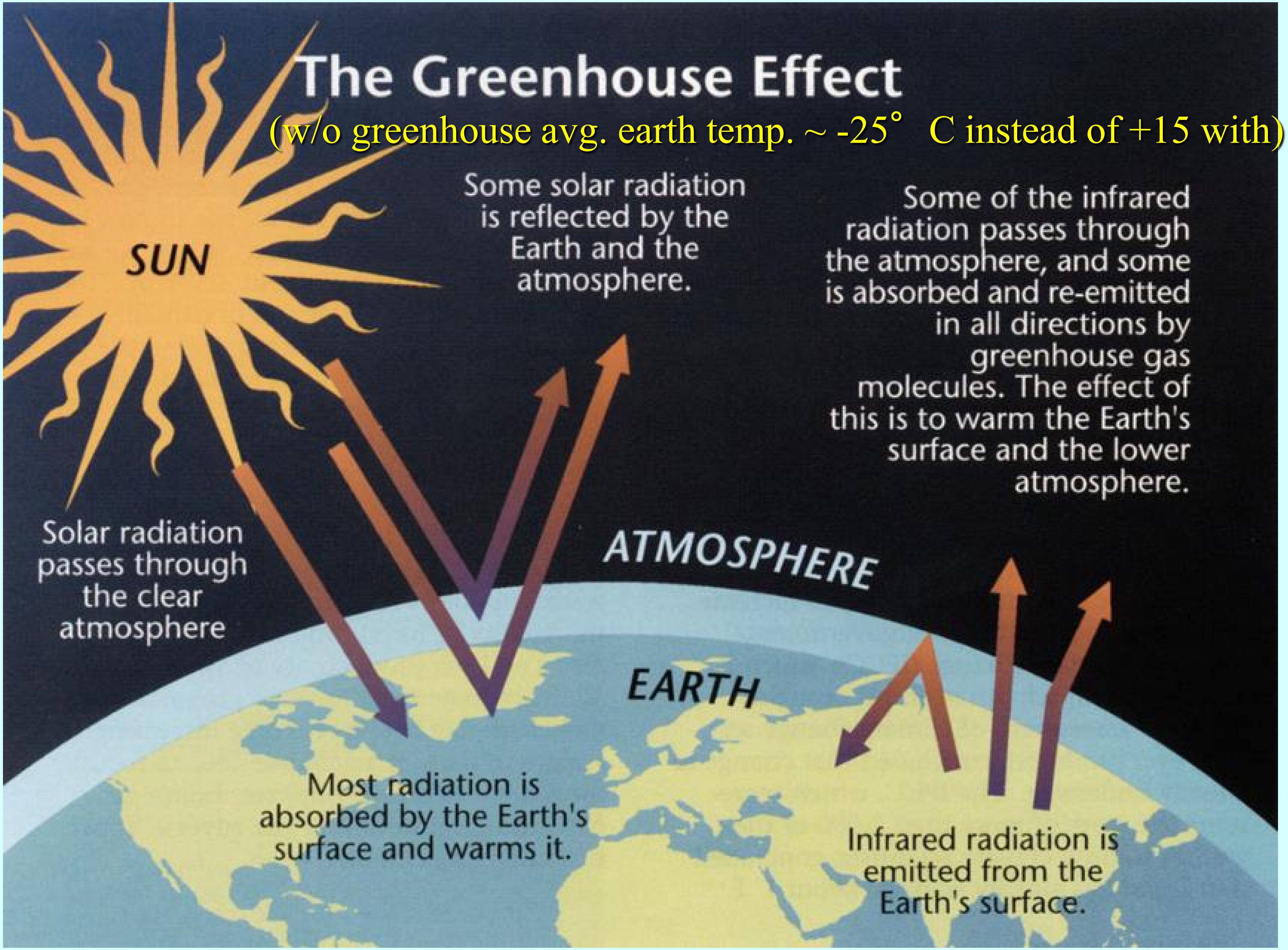
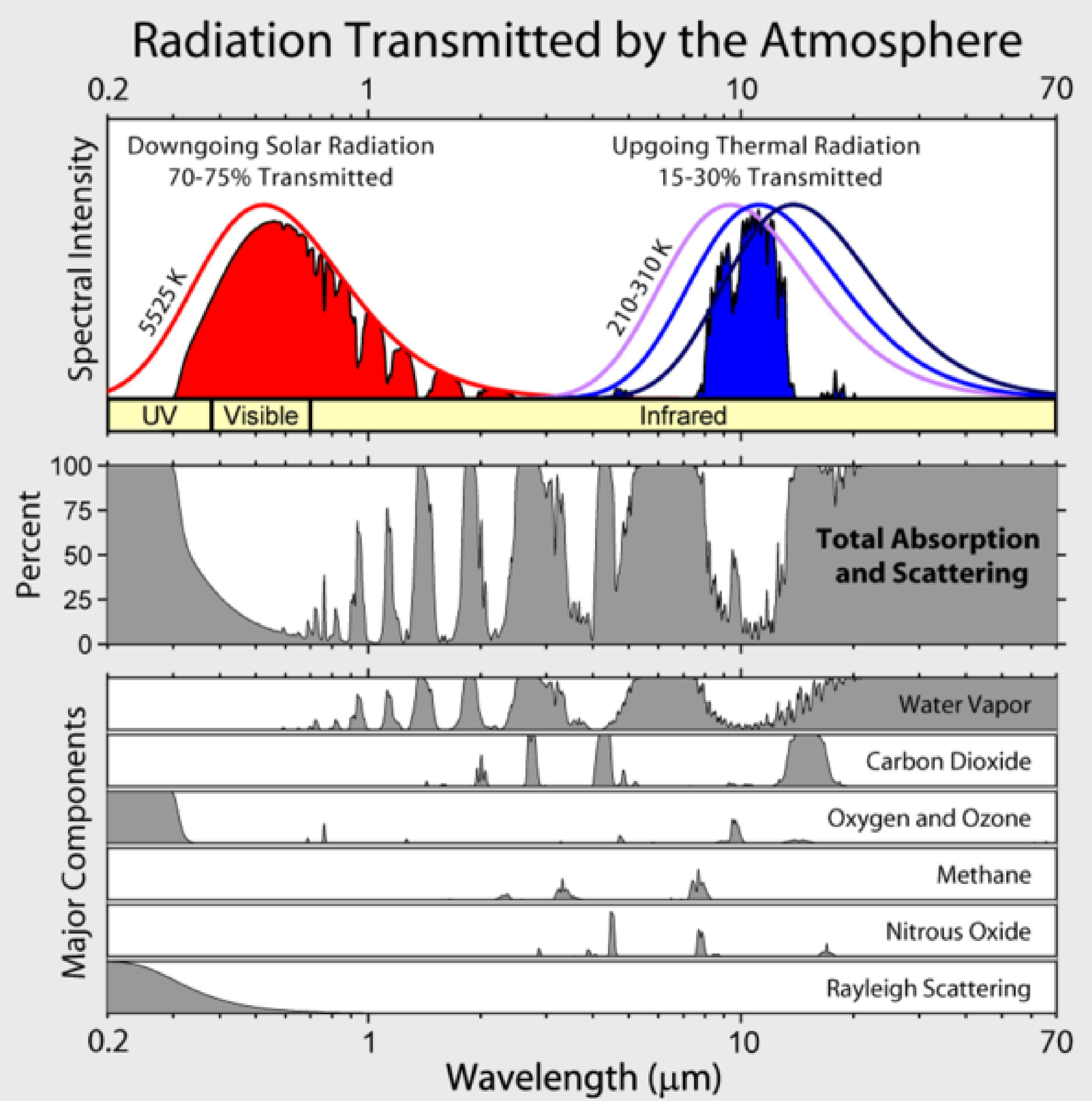


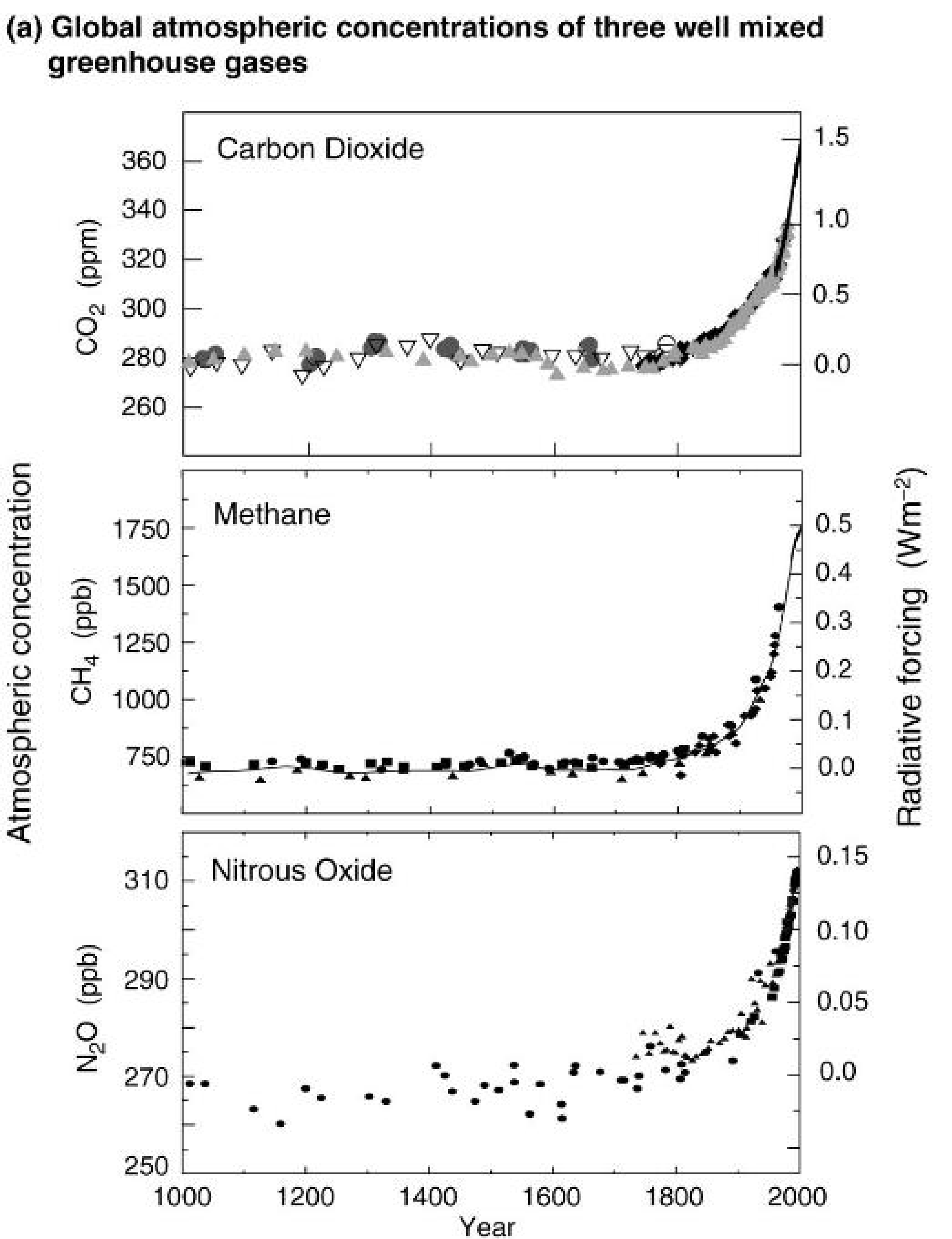
Fig. S3


The Greenhouse Effect
(w/o greenhouse avg. earth temp. ~ -25° C instead of +15 with)
SUN
Some solar radiation is reflected by the Earth and the atmosphere.
Some of the infrared radiation passes through the atmosphere, and some is absorbed and re-emitted in all directions by greenhouse gas molecules. The effect of this is to warm the Earth's surface and the lower atmosphere.
Solar radiation passes through the clear atmosphere
ATMOSPHERE
EARTH
Most radiation is absorbed by the Earth's surface and warms it.
Infrared radiation is emitted from the Earth's surface.

Source: OSTP

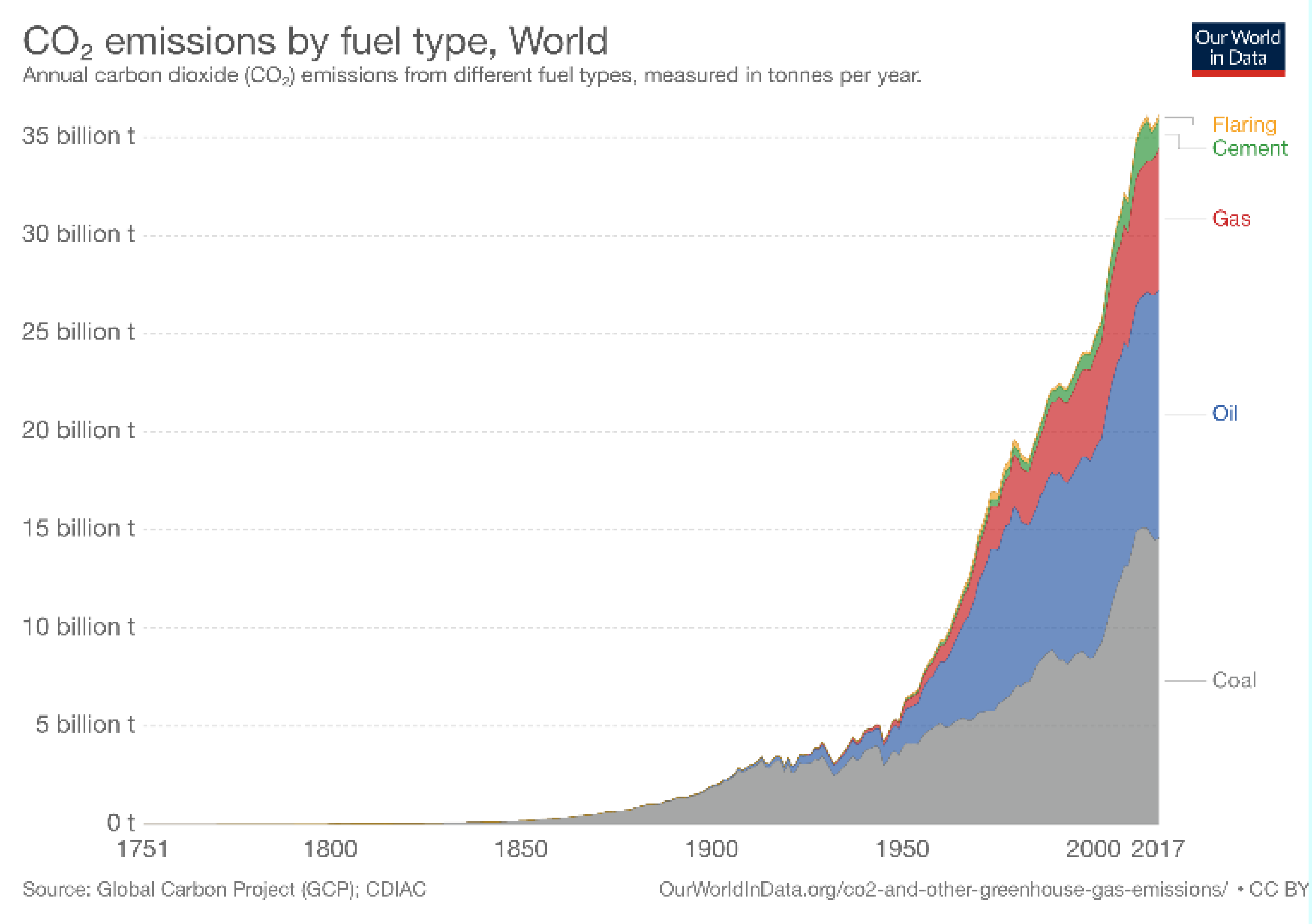

Radiation Transmitted by the Atmosphere
0.2
1
10
70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
UV
Visible
Infrared
Percent
100
75
50
25
0
Total Absorption
and Scattering
Major Components
Water Vapor
Carbon Dioxide
Oxygen and Ozone
Methane
Nitrous Oxide
Rayleigh Scattering
0.2
1
10
70
Wavelength (μm)

Anthropogenic Influence on Atmospheric Concentration of Greenhouse Gases

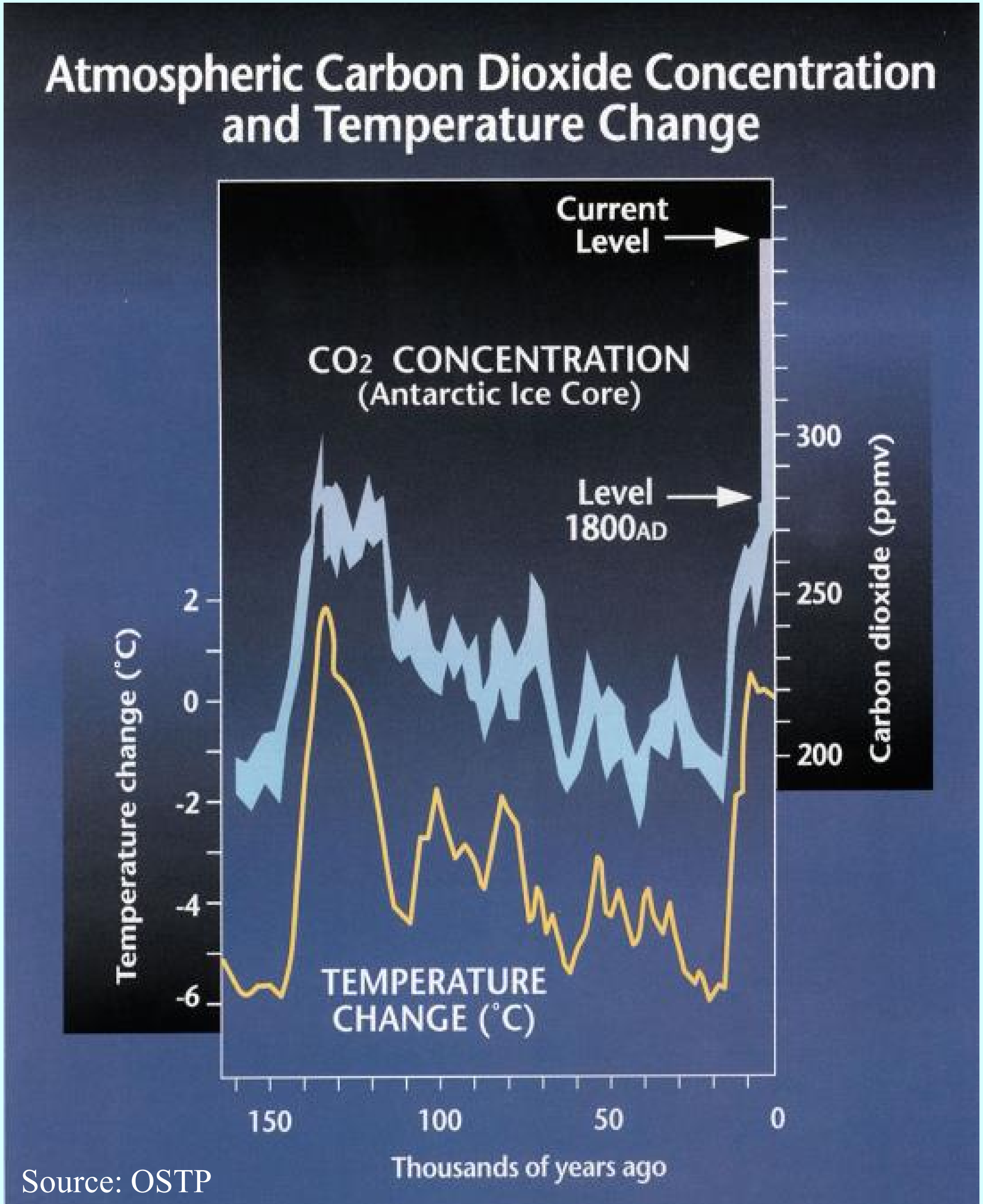


Source: IPCC TAR 2001

Union of Concerned Scientists



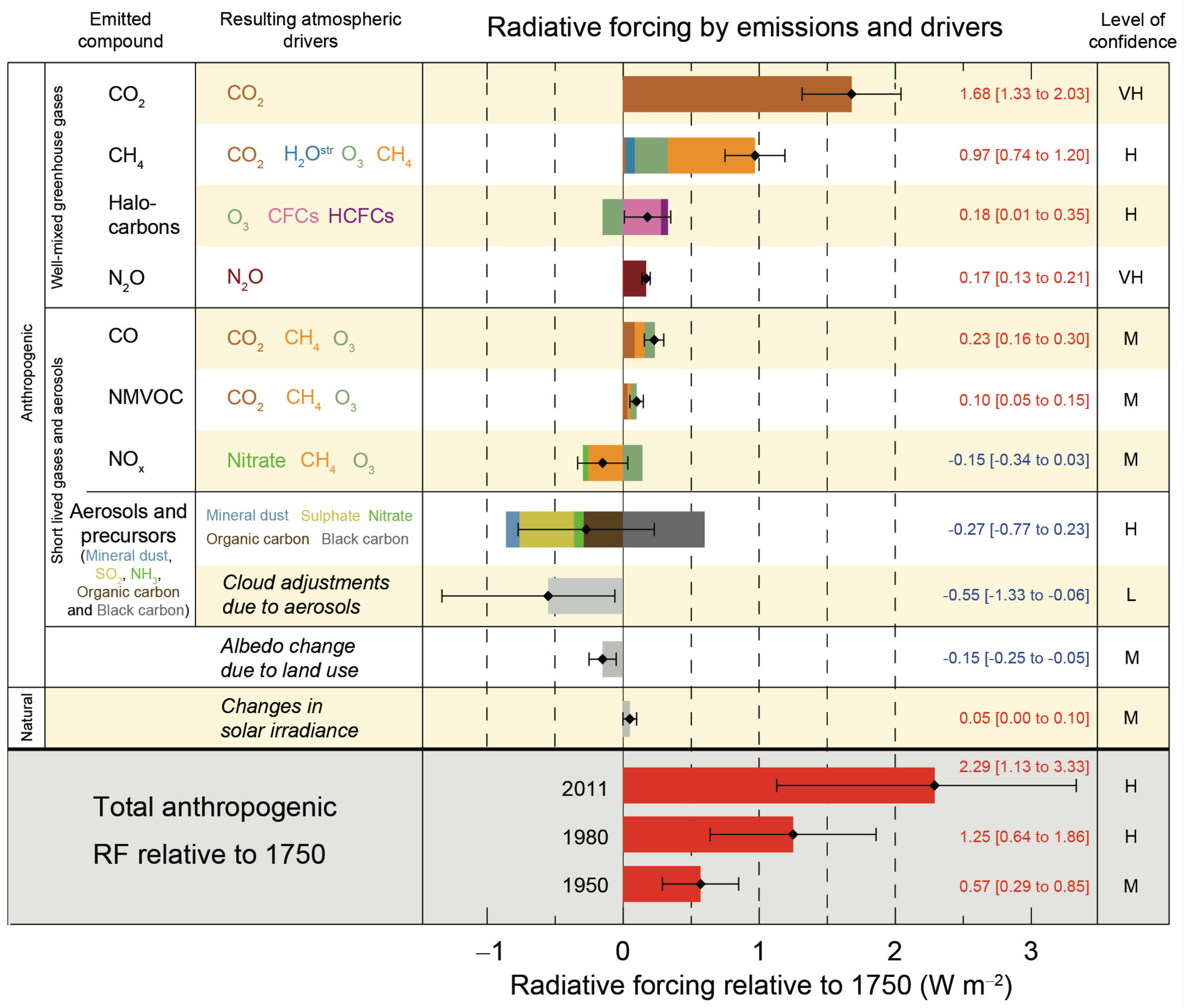
CO_2 emissions by fuel type, World
Annual carbon dioxide (CO_2) emissions from different fuel types, measured in tonnes per year.
Our World in Data
35 billion t
30 billion t
25 billion t
20 billion t
15 billion t
10 billion t
5 billion t
0 t
1751
1800
1850
1900
1950
2000
2017
Flaring
Cement
Gas
Oil
Coal
Source: Global Carbon Project (GCP); CDIAC
OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/ • CC BY



- Clear correlation between atmospheric CO_2 and temperature over last 160,000 years

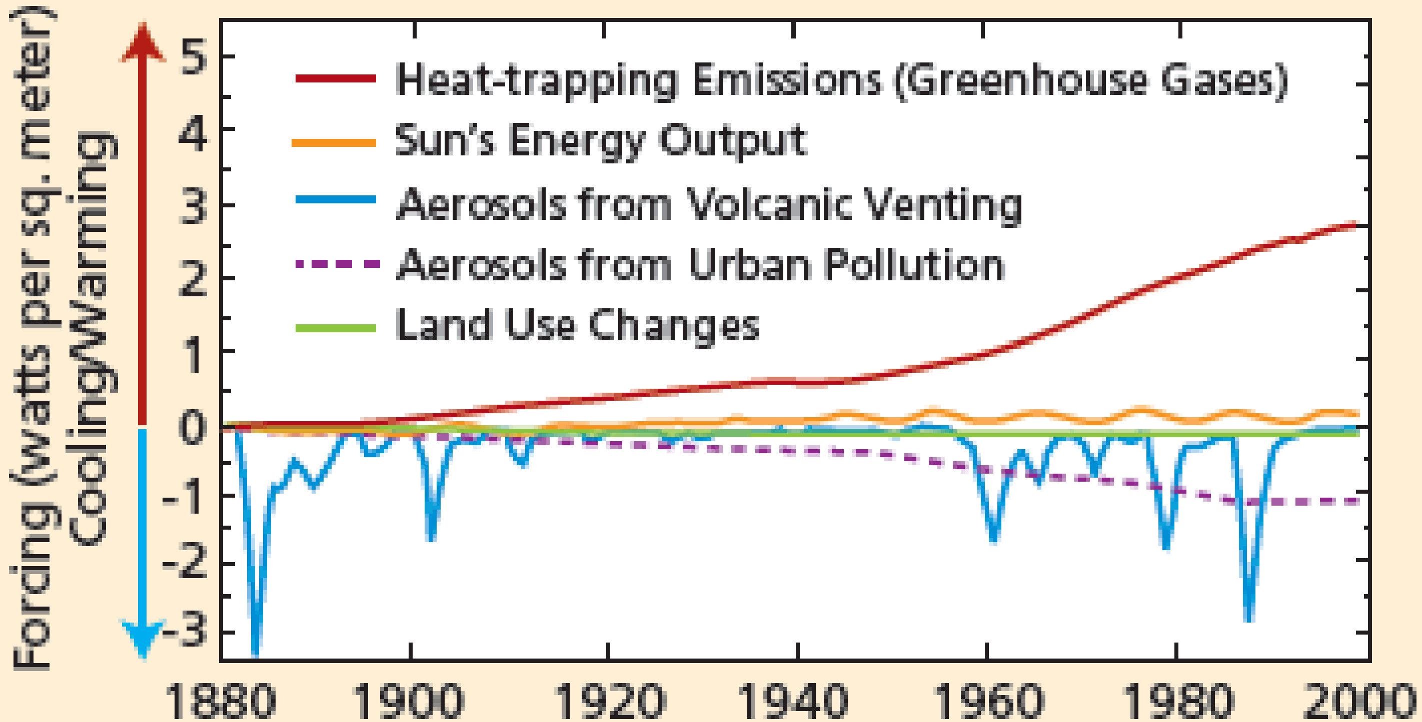
- Current level of CO_2 is *outside* bounds of natural variability

- *Rate* of change of CO_2 is also unprecedented



Emitted compound
Resulting atmospheric drivers
Radiative forcing by emissions and drivers
Level of confidence
Anthropogenic
Well-mixed greenhouse gases
CO2 | CO2 | 1.68 [1.33 to 2.03] | VH
CH4 | CO2 H2Ostr O3 CH4 | 0.97 [0.74 to 1.20] | H
Halo-carbons | O3 CFCs HCFCs | 0.18 [0.01 to 0.35] | H
N2O | N2O | 0.17 [0.13 to 0.21] | VH
Short lived gases and aerosols
CO | CO2 CH4 O3 | 0.23 [0.16 to 0.30] | M
NMVOC | CO2 CH4 O3 | 0.10 [0.05 to 0.15] | M
NOx | Nitrate CH4 O3 | -0.15 [-0.34 to 0.03] | M
Aerosols and precursors (Mineral dust, SO2, NH3, Organic carbon and Black carbon)
Mineral dust Sulphate Nitrate Organic carbon Black carbon | -0.27 [-0.77 to 0.23] | H
Cloud adjustments due to aerosols | -0.55 [-1.33 to -0.06] | L
Albedo change due to land use | -0.15 [-0.25 to -0.05] | M
Natural
Changes in solar irradiance | 0.05 [0.00 to 0.10] | M
Total anthropogenic RF relative to 1750
2011 | 2.29 [1.13 to 3.33] | H
1980 | 1.25 [0.64 to 1.86] | H
1950 | 0.57 [0.29 to 0.85] | M
–1 0 1 2 3
Radiative forcing relative to 1750 (W m–2)

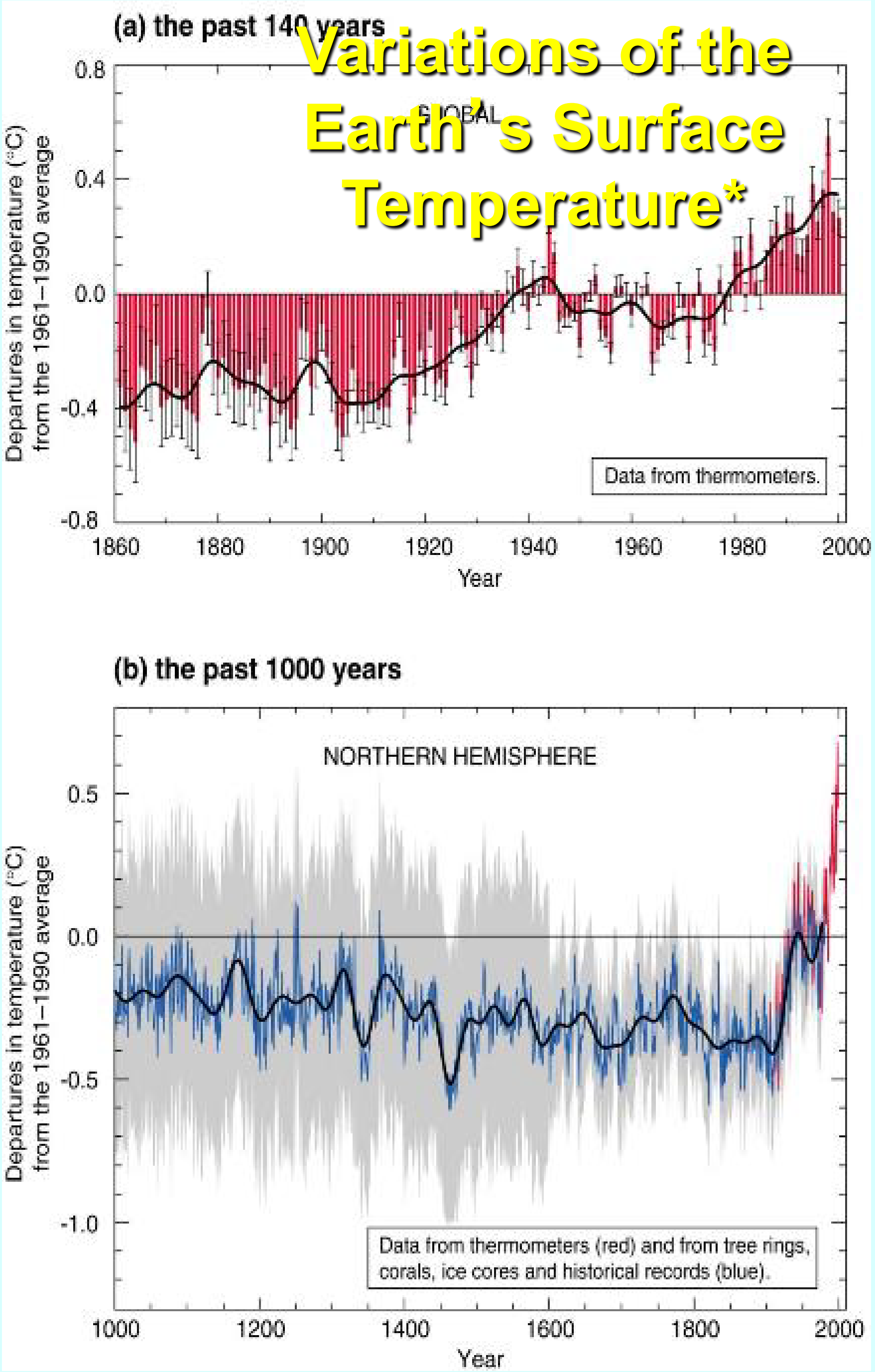
Global Climate Drivers



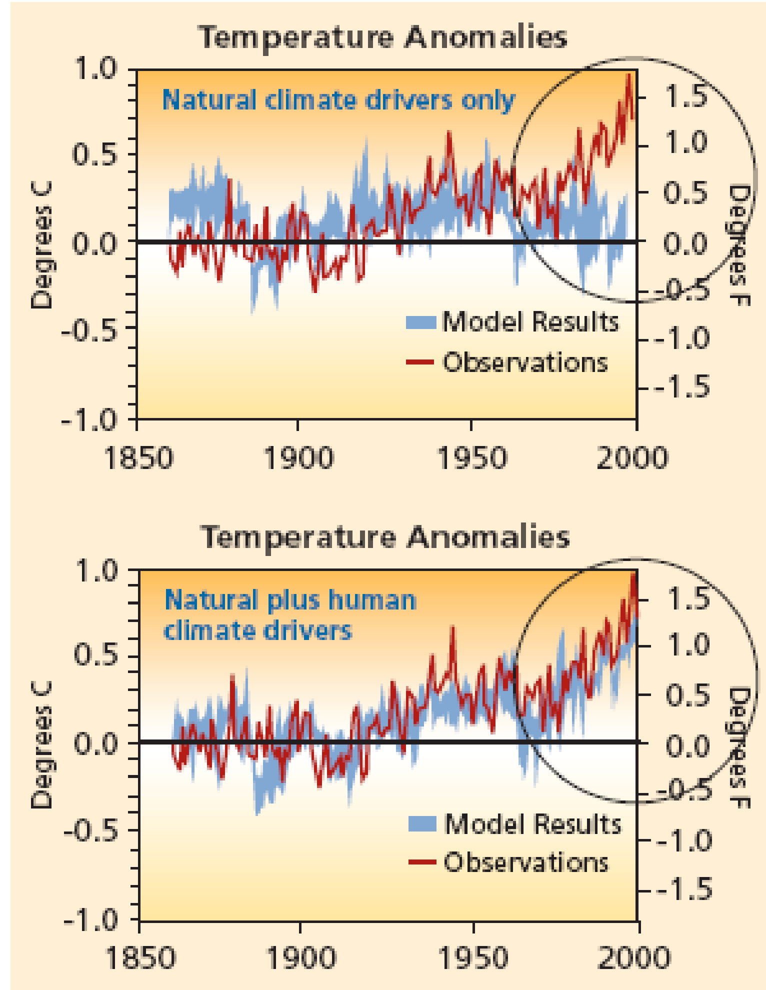
Heat-trapping emissions (greenhouse gases) far outweigh the effects of other drivers acting on Earth's climate.

Source: Hansen et al. 2005.

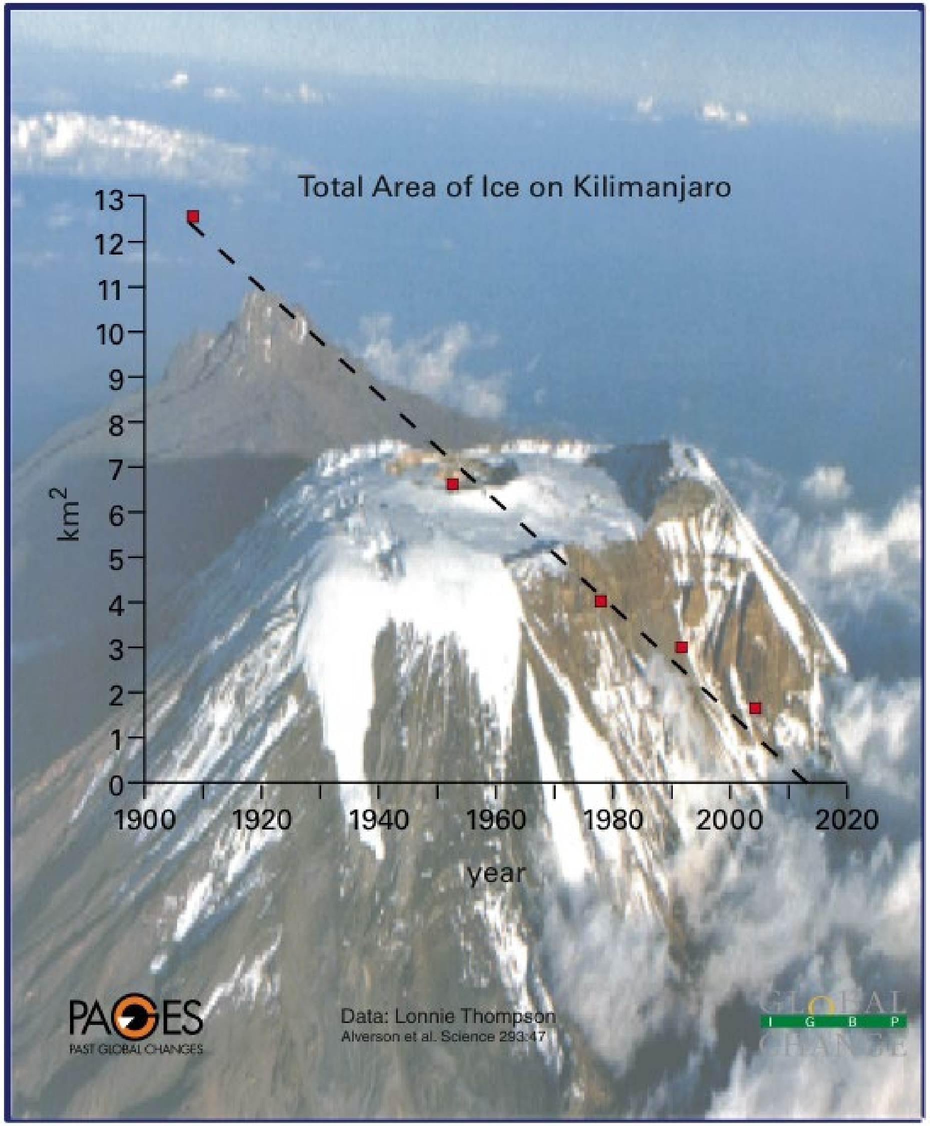
Variations of the Earth's Surface Temperature*



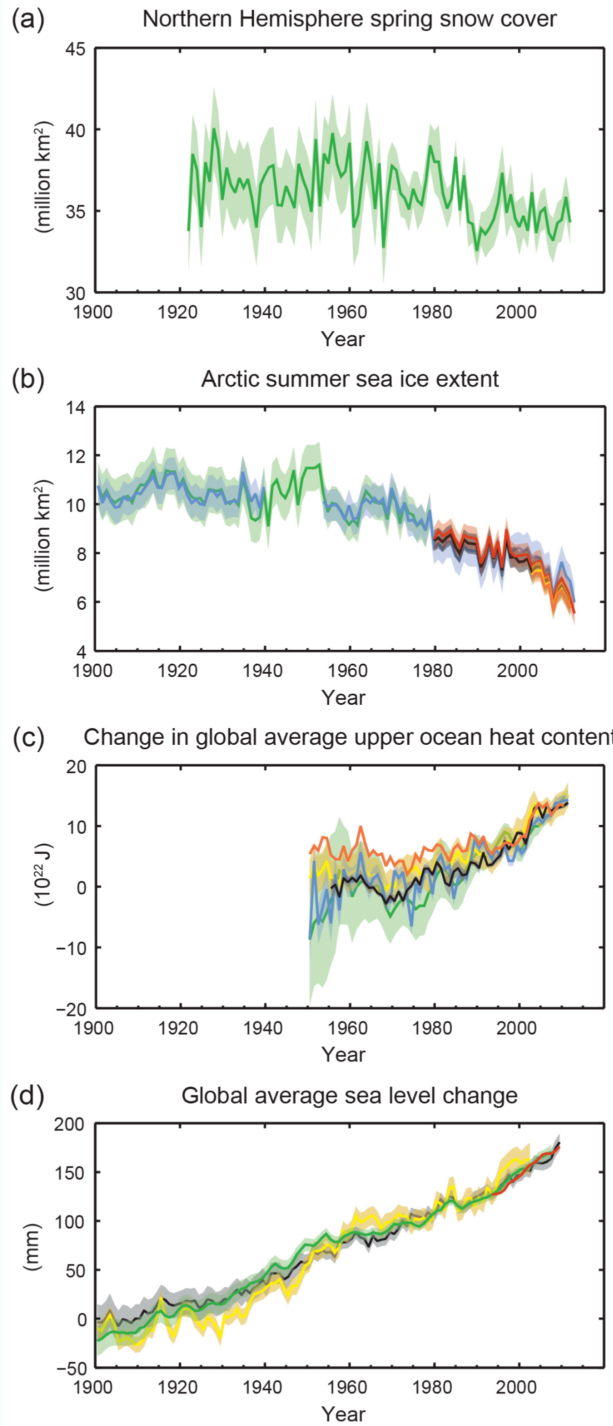
Climate Drivers Compared with Global Surface Temperature



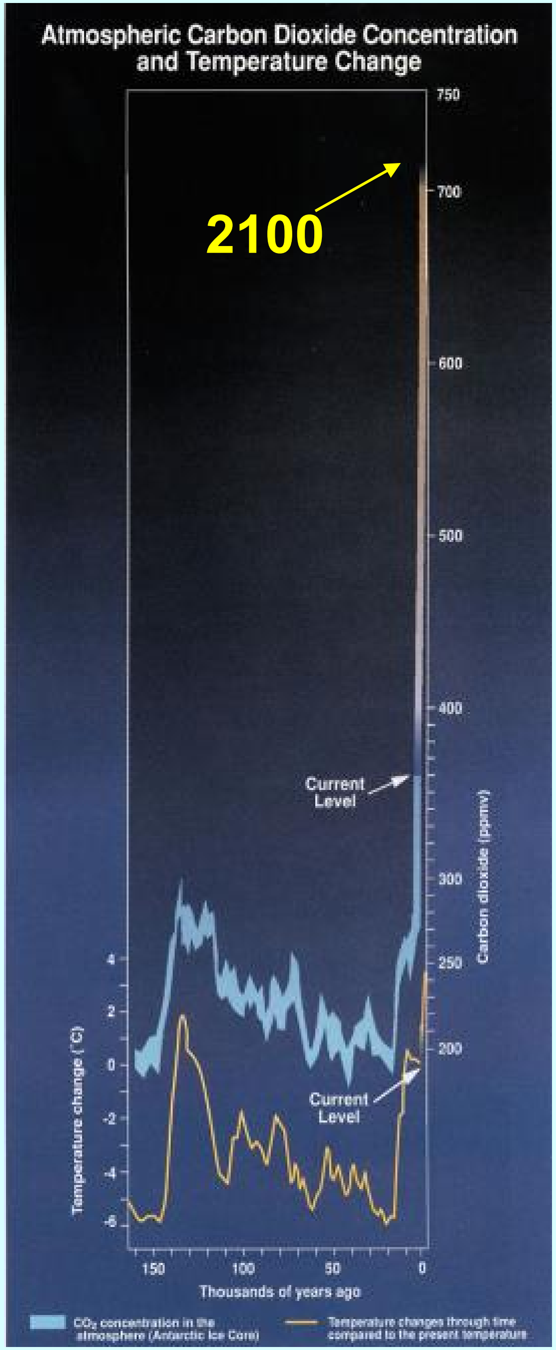
The model output (blue shading) that includes both natural and human-induced drivers (lower graph) gives a better match with the observed temperature response (red line). Source: IPCC TAR 2001.



Total Area of Ice on Kilimanjaro
km2
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1900
1920
1940
1960
1980
2000
2020
year
PAGES
PAST GLOBAL CHANGES
Data: Lonnie Thompson
Alverson et al. Science 293:47
I G B P



(a)
Northern Hemisphere spring snow cover
(million km²)
Year
(b)
Arctic summer sea ice extent
(million km²)
Year
(c)
Change in global average upper ocean heat content
(10²² J)
Year
(d)
Global average sea level change
(mm)
Year

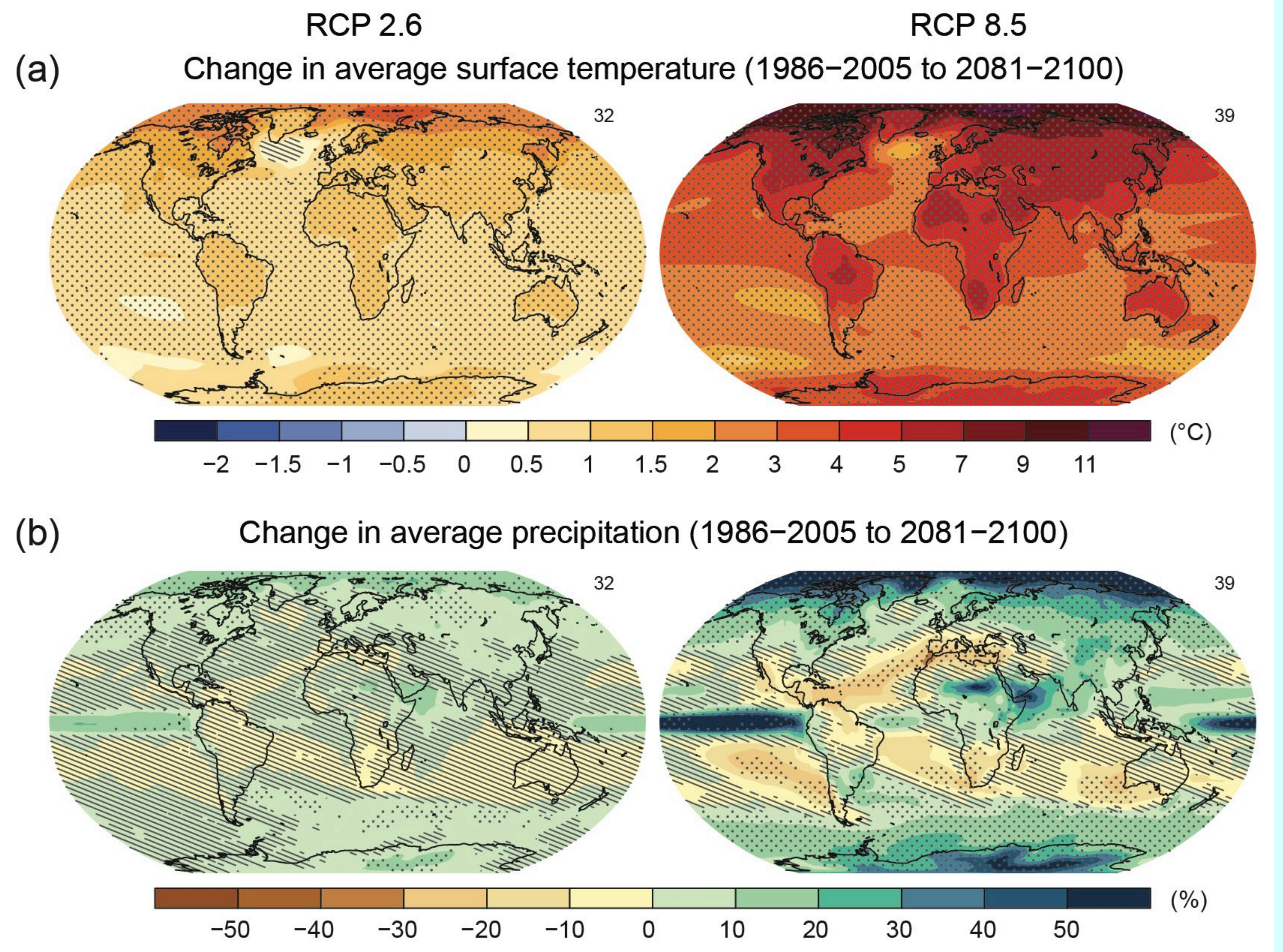


If business as usual:

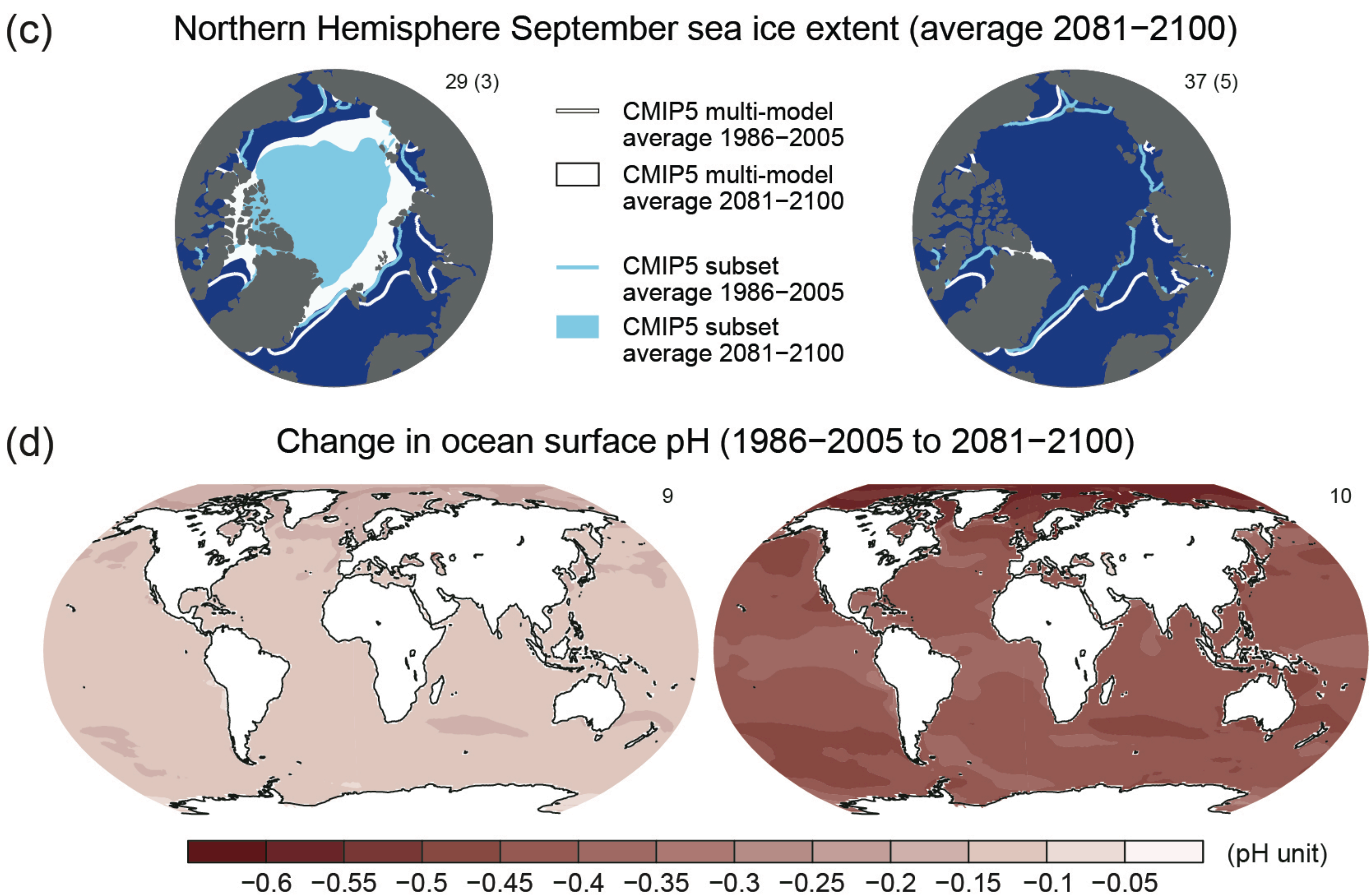
- CO_2 concentrations will likely be more than 700 ppm by 2100

- Global average temperatures projected to increase between 2.5 - 10.4° F

Source: OSTP

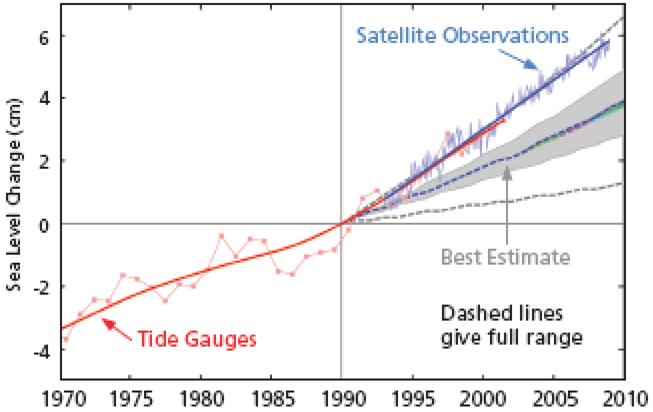


RCP 2.6
RCP 8.5
(a)
Change in average surface temperature (1986−2005 to 2081−2100)
32
39
−2 −1.5 −1 −0.5 0 0.5 1 1.5 2 3 4 5 7 9 11
(°C)
(b)
Change in average precipitation (1986−2005 to 2081−2100)
32
39
−50 −40 −30 −20 −10 0 10 20 30 40 50
(%)


(c)
Northern Hemisphere September sea ice extent (average 2081−2100)
29 (3)
37 (5)
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)
9
10
−0.6 −0.55 −0.5 −0.45 −0.4 −0.35 −0.3 −0.25 −0.2 −0.15 −0.1 −0.05
(pH unit)

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]

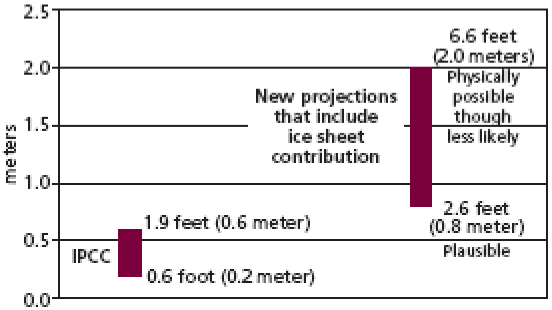
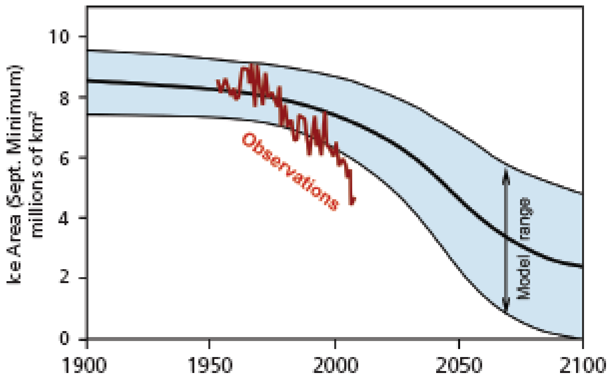
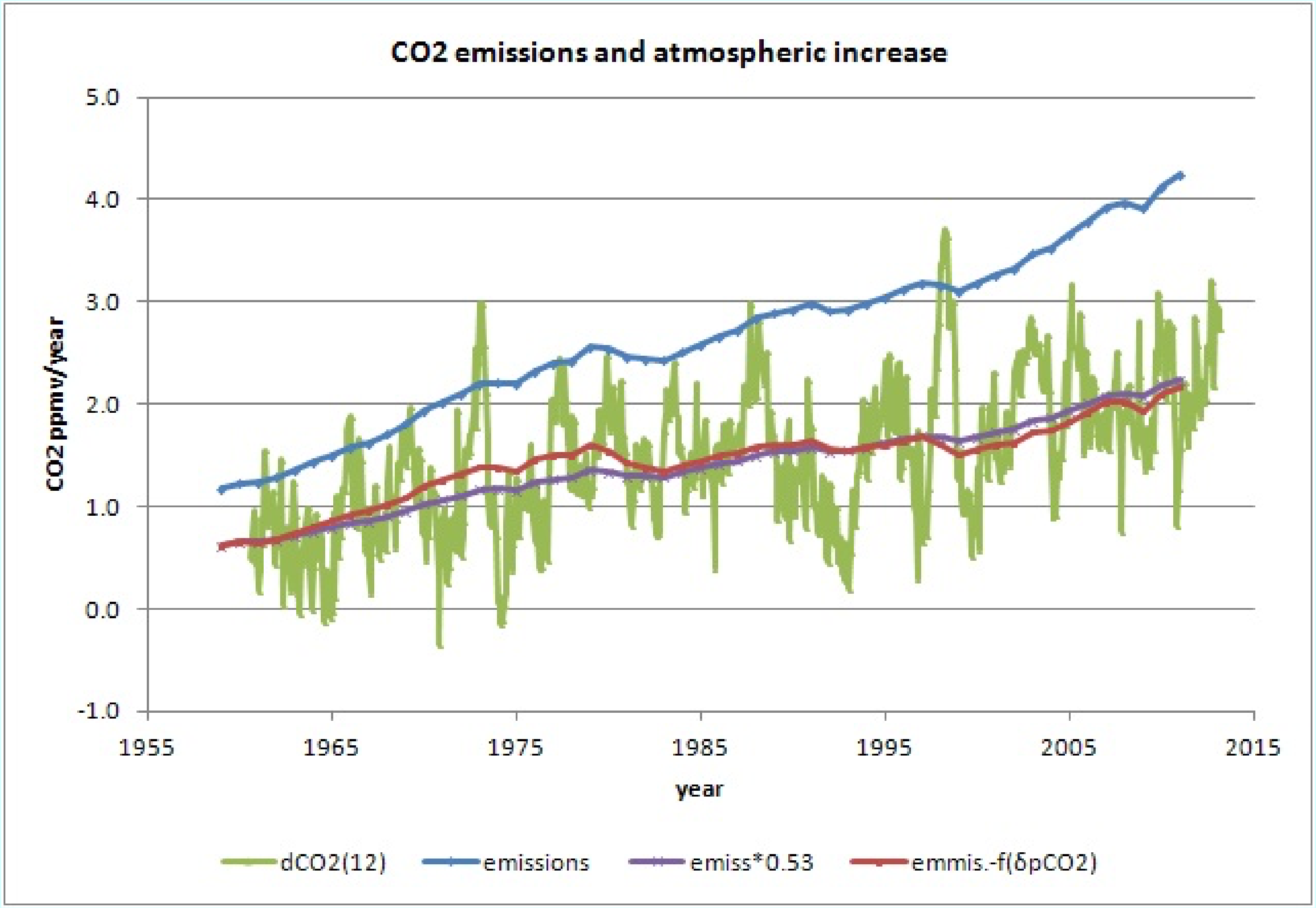


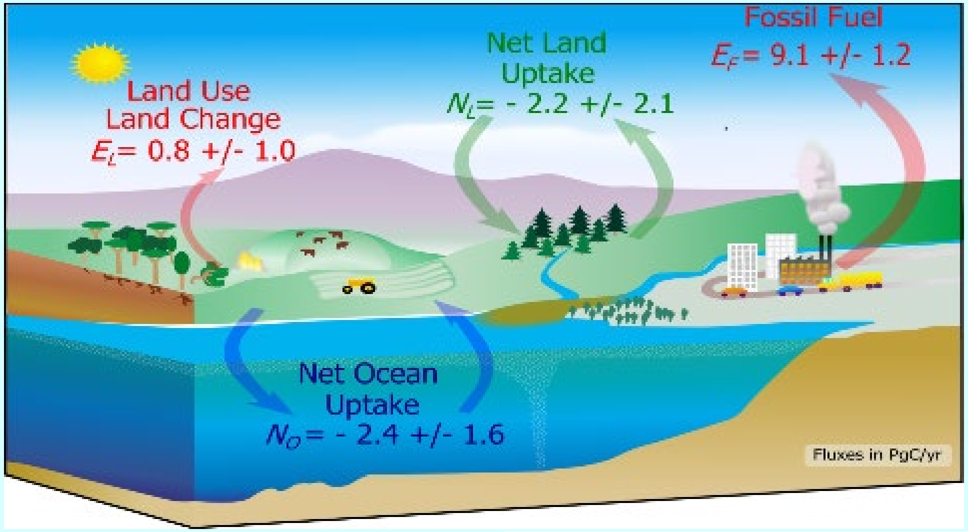
FIGURE 4 **Shrinking Summer Arctic Sea Ice Area**

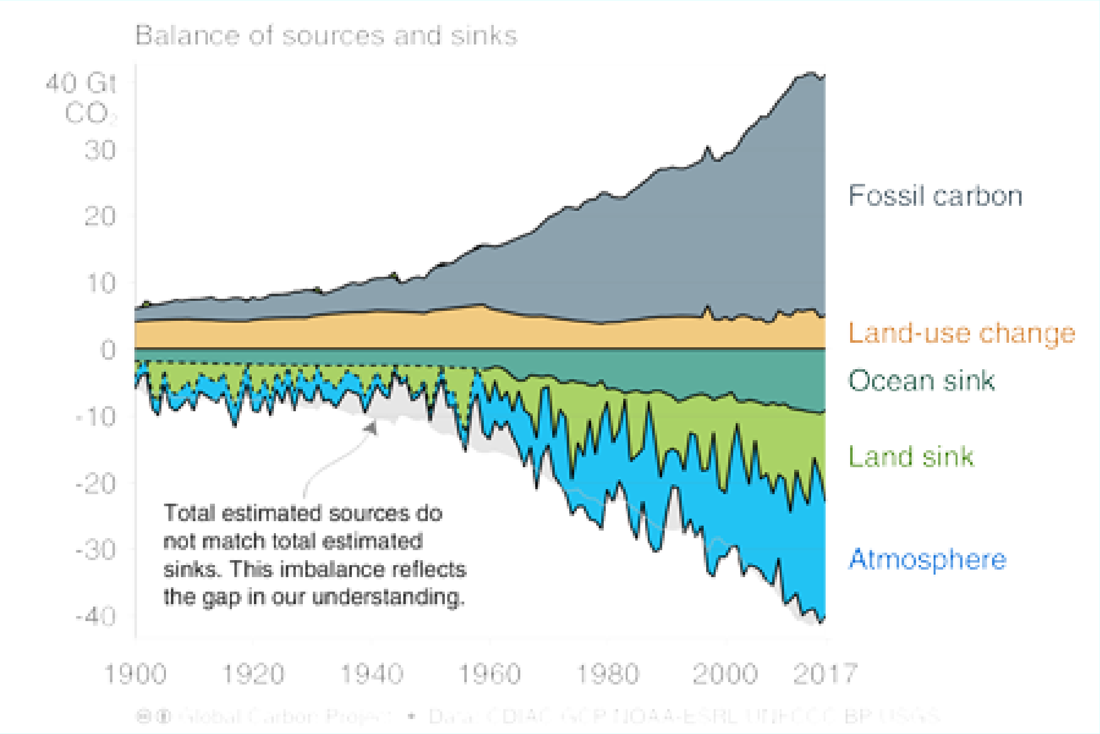


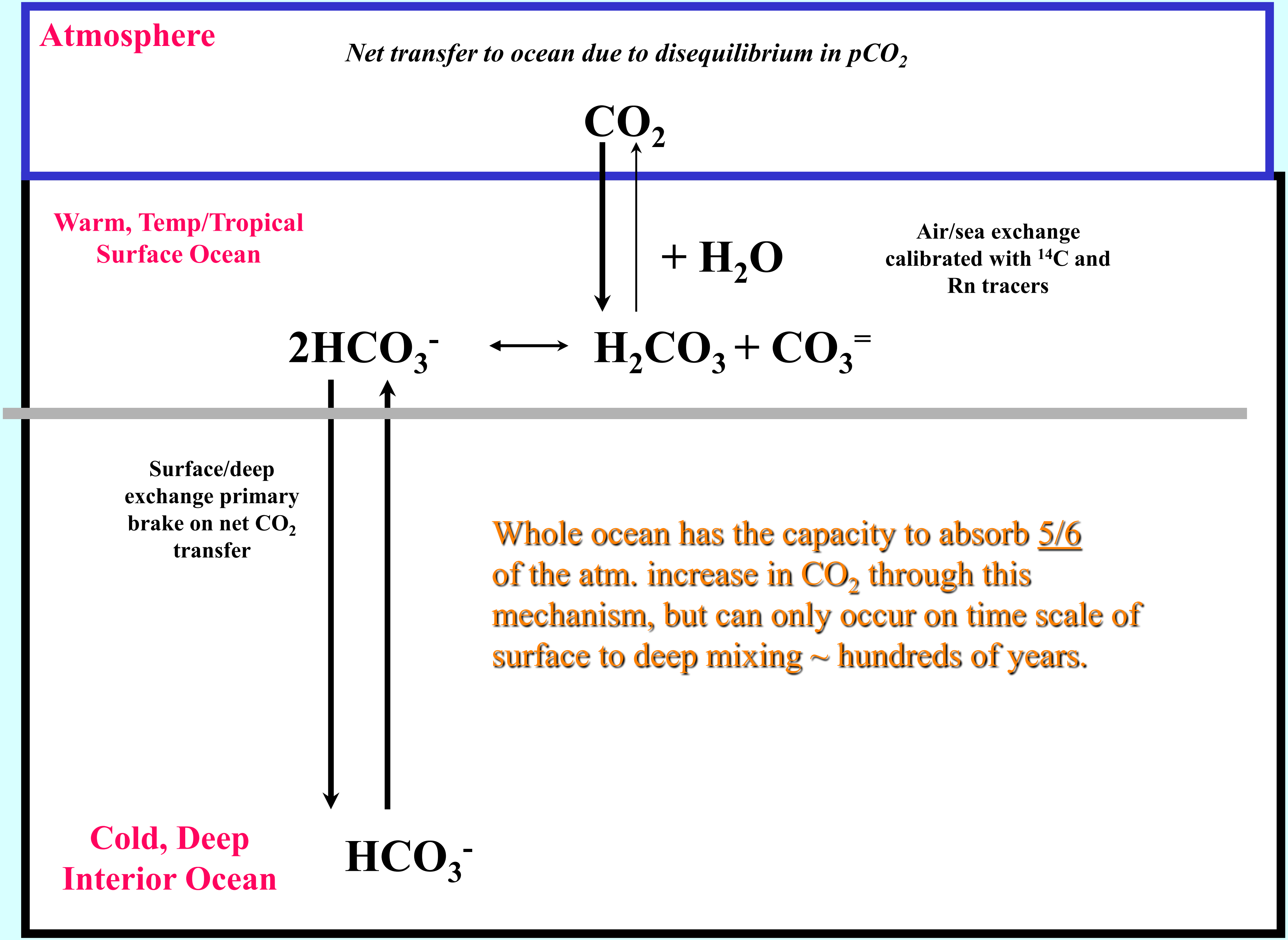
Arctic models of September sea ice area underestimate the rate of observed sea ice retreat. Based on Stroeve et al. 2007.

Source: Dirk Notz from Hamburg adapted figure from *http://www.nsidc.org/news/images/20070430Figure1.png*.


CO2 emissions and atmospheric increase
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
CO2 ppmv/year
1955
1965
1975
1985
1995
2005
2015
year
dCO2(12)
emissions
emiss*0.53
emmis.-f(δpCO2)


Fossil Fuel
E_F = 9.1 +/- 1.2
Net Land Uptake
N_L = - 2.2 +/- 2.1
Land Use Land Change
E_L = 0.8 +/- 1.0
Net Ocean Uptake
N_O = - 2.4 +/- 1.6
Fluxes in PgC/yr


Balance of sources and sinks
40 Gt CO_2
30
20
10
0
-10
-20
-30
-40
Fossil carbon
Land-use change
Ocean sink
Land sink
Atmosphere
Total estimated sources do not match total estimated sinks. This imbalance reflects the gap in our understanding.
1900
1920
1940
1960
1980
2000
2017
Global Carbon Project • Data: CDIAC GCP NOAA-ESRL UNFCCC BP USGS


Atmosphere
Net transfer to ocean due to disequilibrium in pCO2
CO2
+ H2O
Air/sea exchange calibrated with 14C and Rn tracers
Warm, Temp/Tropical Surface Ocean
2HCO3-
H2CO3 + CO3=
Surface/deep exchange primary brake on net CO2 transfer
Whole ocean has the capacity to absorb 5/6 of the atm. increase in CO2 through this mechanism, but can only occur on time scale of surface to deep mixing ~ hundreds of years.
Cold, Deep Interior Ocean
HCO3-

THERMODYNAMIC CAPACITY FOR CO_2 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

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

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

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
$[\Sigma CO_2]$ = 1910	$[\Sigma CO_2]$ = 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

$$[ALKALINITY] = [HCO_2^-] + 2[CO_3^=] + [H_4BO_4^-]$$

MASS BALANCE BORON

$$[\Sigma B] = [H_3BO_3^0] + [H_4BO_4^-] = 410.6 \frac{S}{35} \mu mol/kg$$

CHEMICAL EQUILIBRIUM

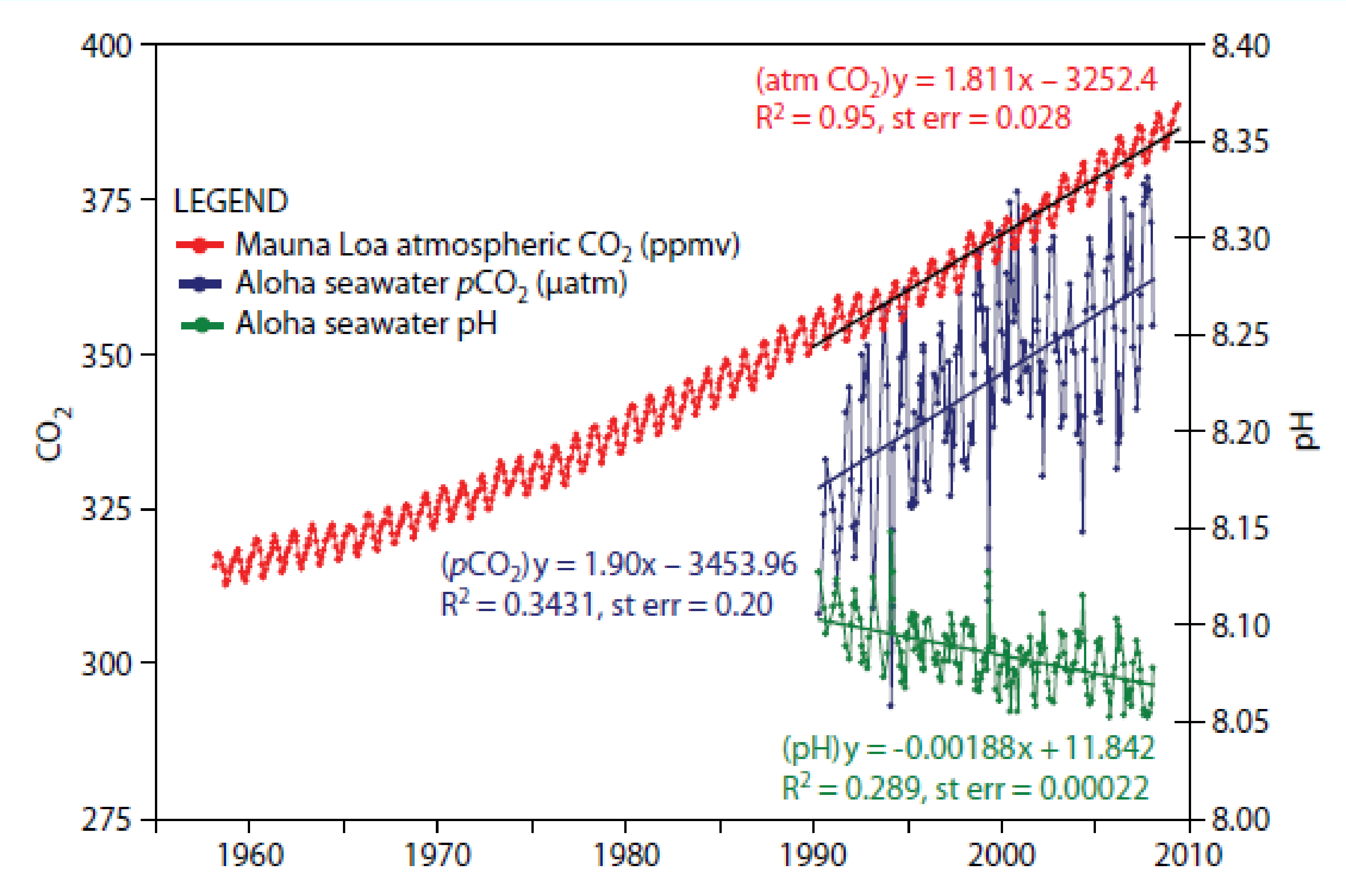
$$K_B' = \frac{[H_4BO_4^-][HCO_3^-]}{[H_3BO_3^0][CO_3^=]}$$

EXAMPLE $T = 18°C$ $S = 35‰$ $K_C' = 1482$ $K_B' = 2.75$

$ALK = 2216$ $SiO_2 = 0$ $NO_3 = 0$ $PO_4 = 0$

$pCO_2 = 280 \mu atm$		$pCO_2 = 360 \mu atm$		Δ
$[CO_2]$	= 9.6	$[CO_2]$	= 12.3	+2.6 µmol/kg
$[HCO_3^-]$	= 1702.5	$[HCO_3^-]$	= 1779.5	+77.0 µmol/kg
$[CO_3^=]$	= 203.7	$[CO_3^=]$	= 173.1	−30.6 µmol/kg
$[\Sigma CO_2]$	= 1915.8	$[\Sigma CO_2]$	= 1964.9	+49.1 µmol/kg
$[H_3BO_3^0]$	= 308.9	$[H_3BO_3^0]$	= 323.9	+15.0 µmol/kg
$[H_4BO_4^-]$	= 101.7	$[H_4BO_4^-]$	= 86.7	−15.0 µmol/kg
$[\Sigma B]$	= 410.6	$[\Sigma B]$	= 410.6	0.0 µmol/kg
$[OH^-]$	= 4.4	$[OH^-]$	= 3.6	−0.8 µmol/kg
$[ALK]$	= 2216.0	$[ALK]$	= 2216.0	0.0 µmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2 / pCO_2}{\Delta \Sigma CO_2 / \Sigma CO_2} = \frac{80/280}{49.1/1915.8} = 11.1$$


(atm CO2)y = 1.811x – 3252.4
R2 = 0.95, st err = 0.028
LEGEND
Mauna Loa atmospheric CO2 (ppmv)
Aloha seawater pCO2 (μatm)
Aloha seawater pH
(pCO2)y = 1.90x – 3453.96
R2 = 0.3431, st err = 0.20
(pH)y = -0.00188x + 11.842
R2 = 0.289, st err = 0.00022
CO2
pH
400
375
350
325
300
275
8.40
8.35
8.30
8.25
8.20
8.15
8.10
8.05
8.00
1960
1970
1980
1990
2000
2010

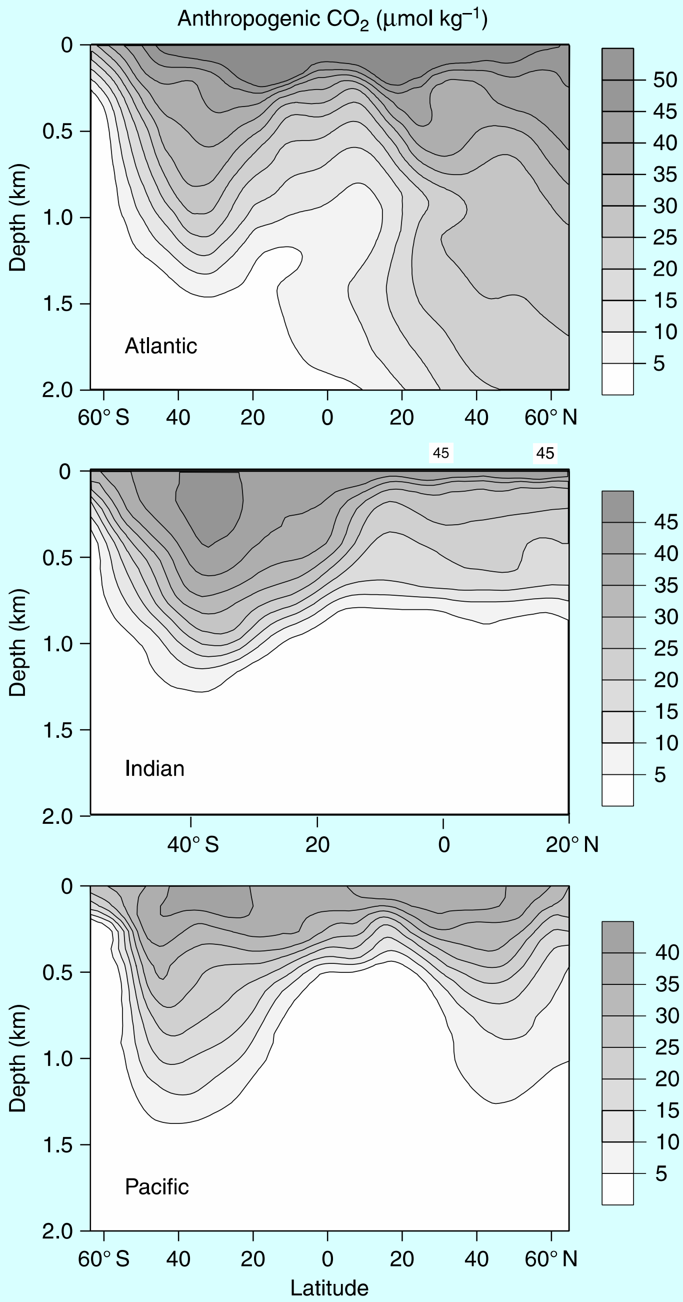


Figure 11.7. A cross section of the anthropogenic CO_2 in the ocean as determined by the C* method. Robert Key, personal communication; Key *et al.* (2004).