

# Global Carbon Cycle

## AOSC 433/633 & CHEM 433

Ross Salawitch

**Class Web Site:** <http://www.atmos.umd.edu/~rjs/class/spr2017>

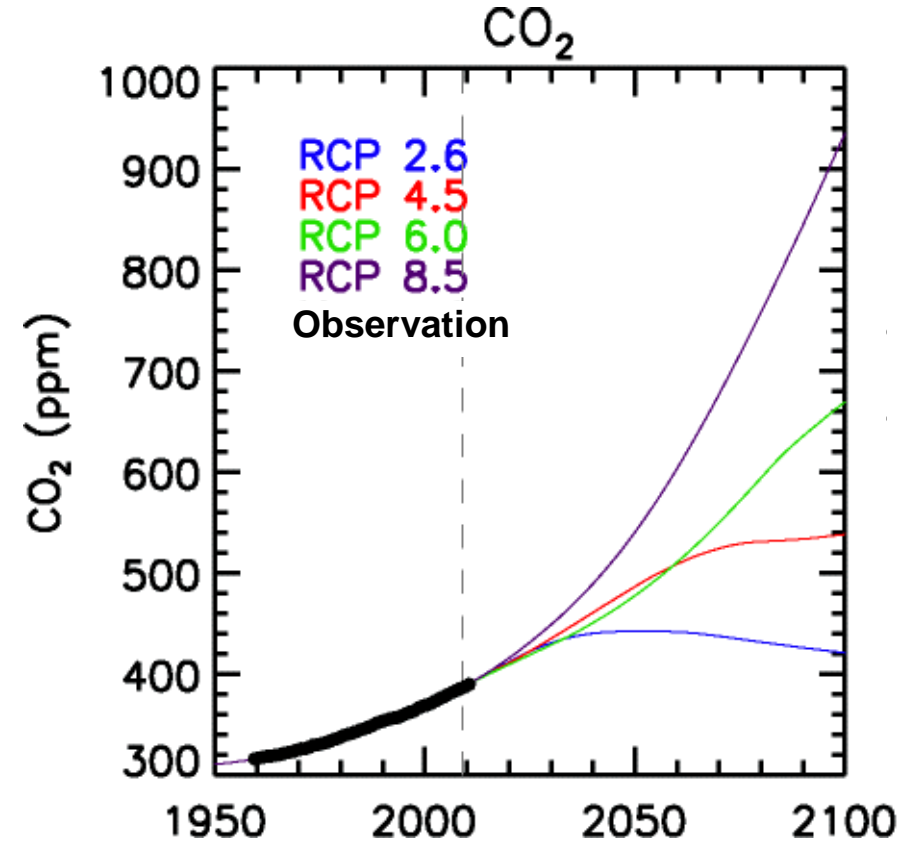
### Goals for today:

- **Overview of the Global Carbon Cycle “scratching below the surface”**
- **Ocean and land uptake of CO<sub>2</sub>**
- **Connect to prior lecture (glacial CO<sub>2</sub> draw down), policy, and long-term climate change**

**Lecture 5**

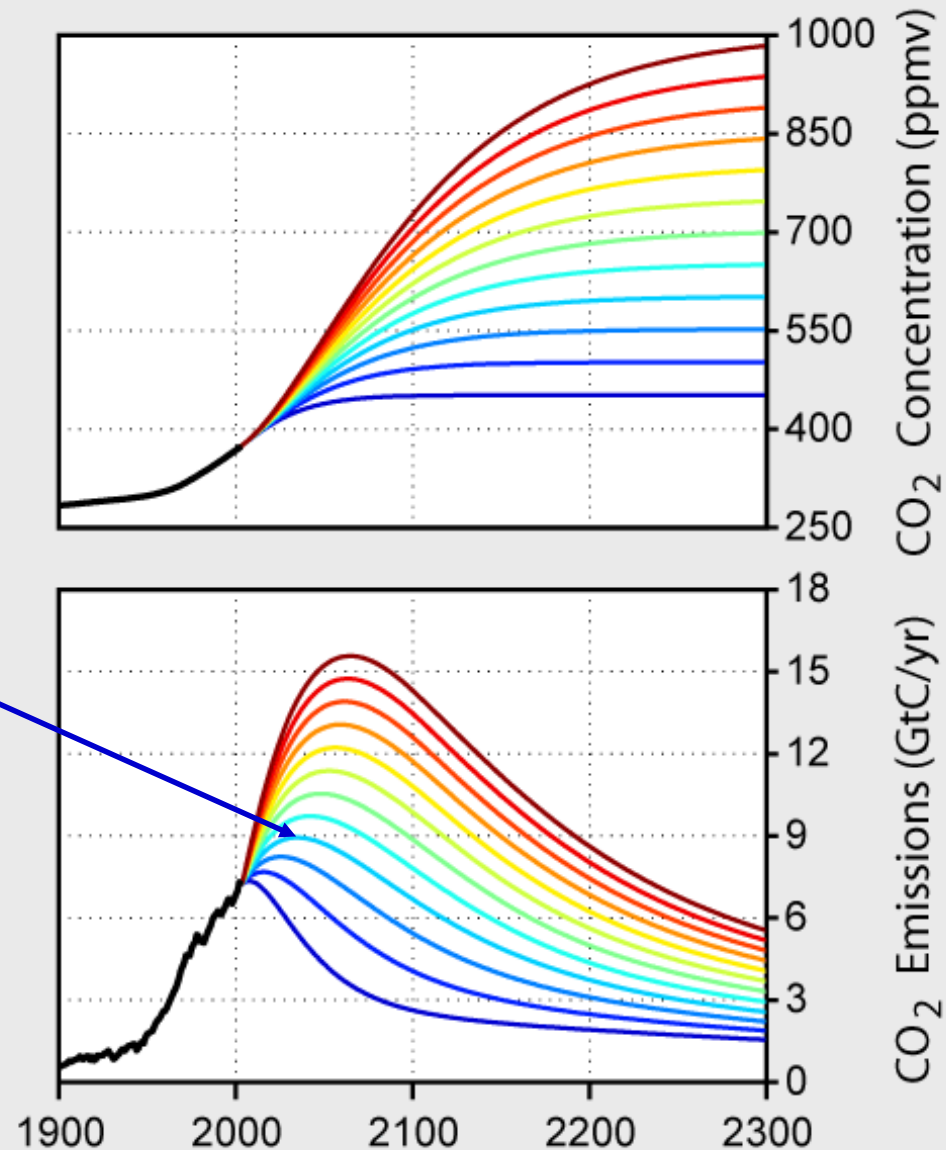
**9 February 2017**

# Motivation 1



- RCP: Representative Concentration Pathway  
Number represents RF of climate, units  $W m^{-2}$ , at the end of this century
- GHG mixing ratio time series for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, as well as CFCs, HCFCs, and HFCs provided to climate model groups
- What is the utility of “command central” providing GHG scenarios to the climate model groups?
- How do you think these various scenarios are devised?

# Carbon Dioxide Stabilization

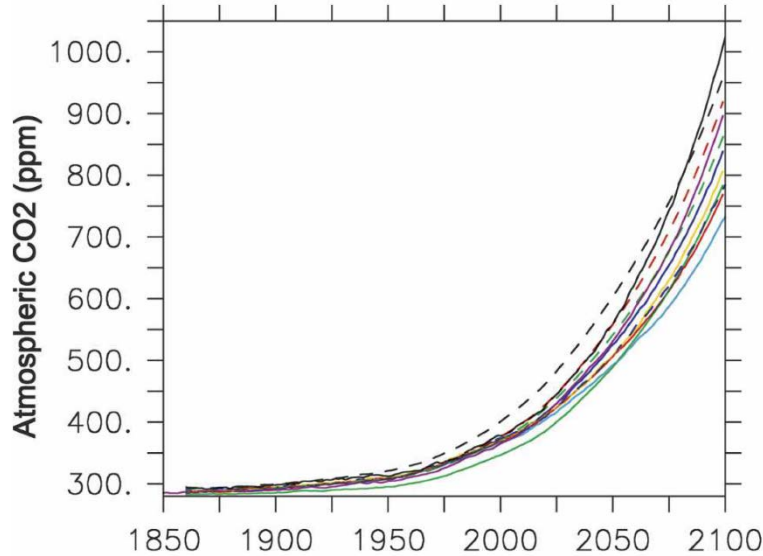


**CO<sub>2</sub> is long lived: society must reduce emissions soon or we will be committed to dramatic, future increases**

**Curve that levels off at ~560 ppm has emissions peaking ~2030**  
**Less than 20 years from now !**

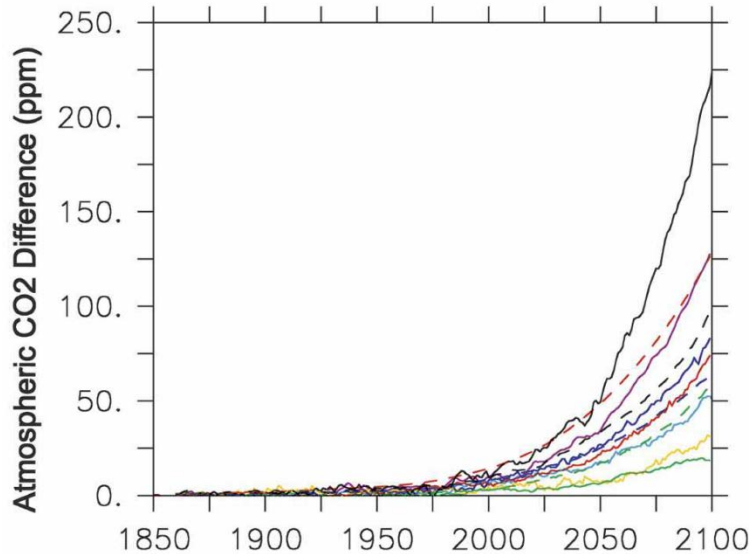
Image: "Global Warming Art" : <http://archive.is/JT5rO>

# Motivation 2



- Prior slide examined atmospheric  $\text{CO}_2$  from a single model of the global carbon cycle
- Friedlingstein et al. (2006) compared  $\text{CO}_2$  from **11** different coupled climate-carbon cycle models, each constrained by the same specified time series of anthropogenic  $\text{CO}_2$  emission and found:

- 1) future climate change will reduce the efficiency of the *Earth system* to absorb the anthropogenic carbon perturbation
- 2) difference in  $\text{CO}_2$  between a simulation using an interactive carbon-cycle and another run with a non-interactive carbon-cycle varies from 20 to 200 ppm among these **11** models (yikes!)



# Modern CO<sub>2</sub> Record

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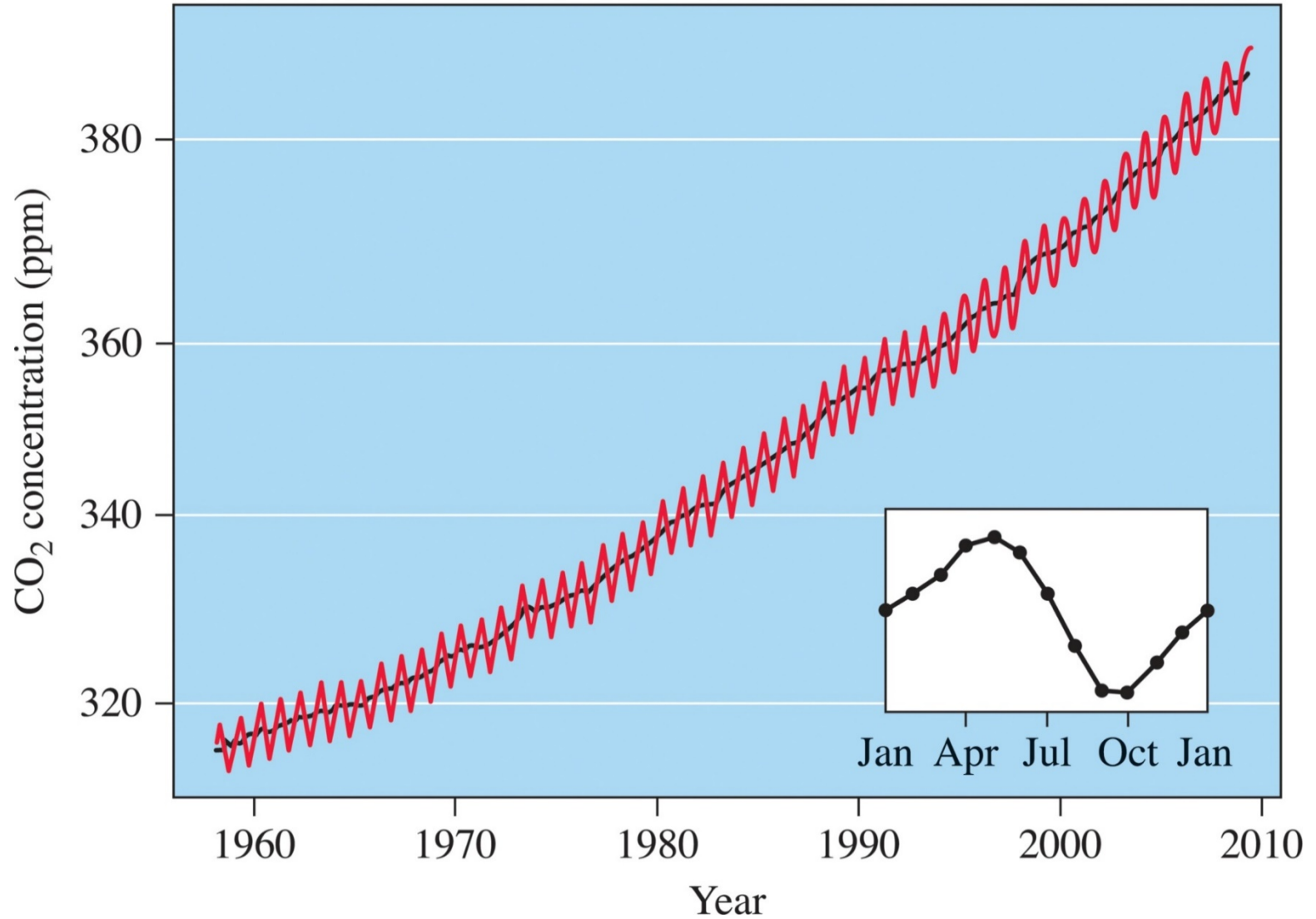
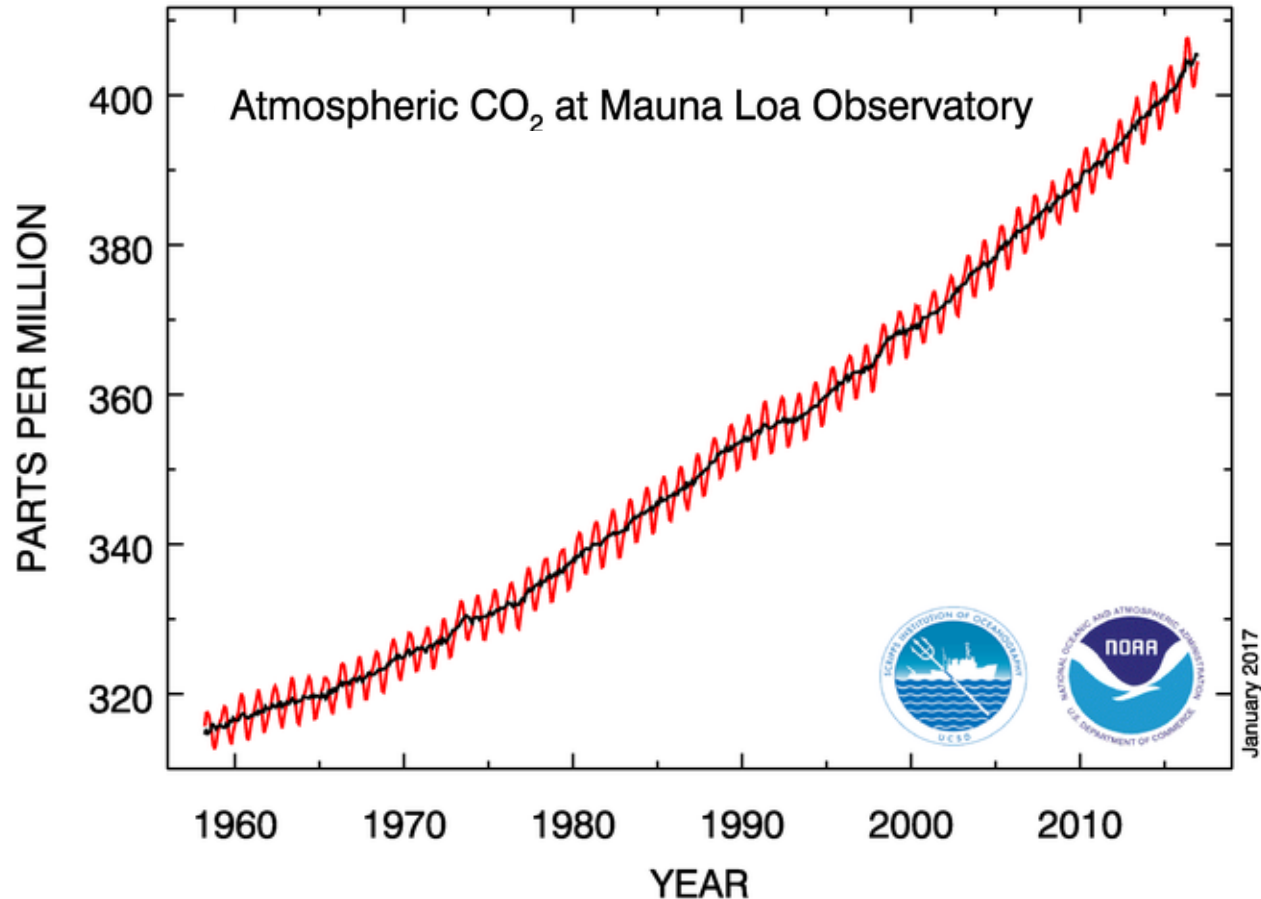


Figure 3.3, Chemistry in Context

# Modern CO<sub>2</sub> Record

CO<sub>2</sub> at MLO on 7 Feb 2017: 406.7 parts per million (ppm) and rising !

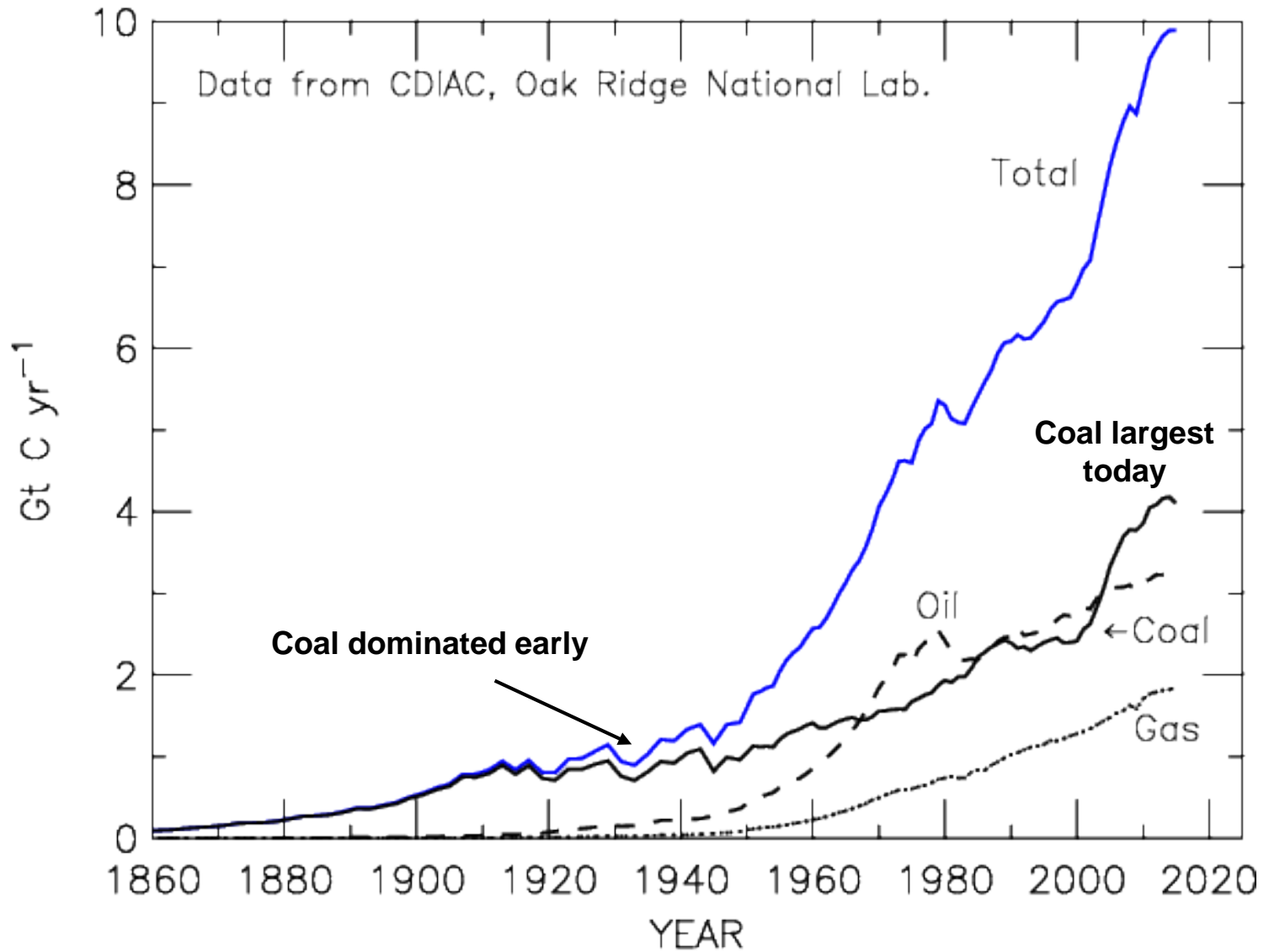


Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA

<https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html>

See also <https://www.co2.earth/daily-co2>

# Fossil Fuel Emissions 1860 to Present



**Coal dominated early**

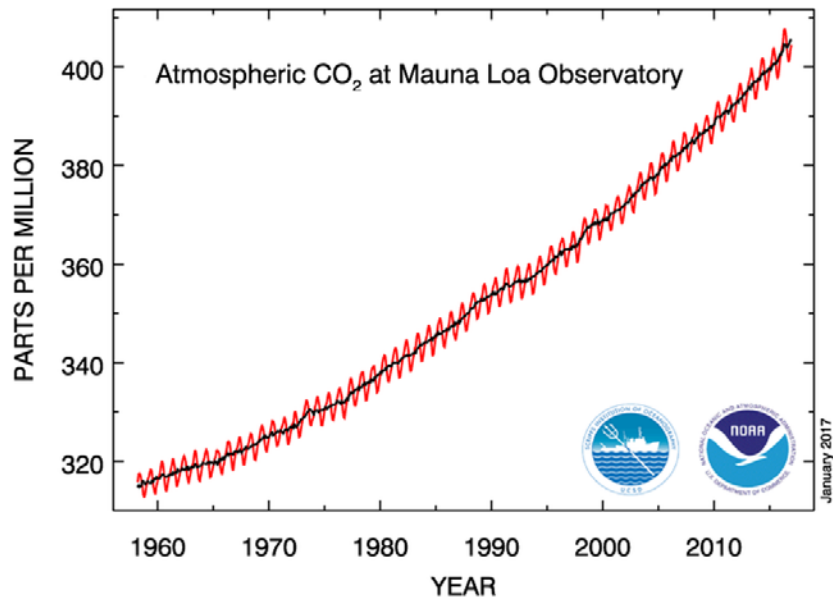
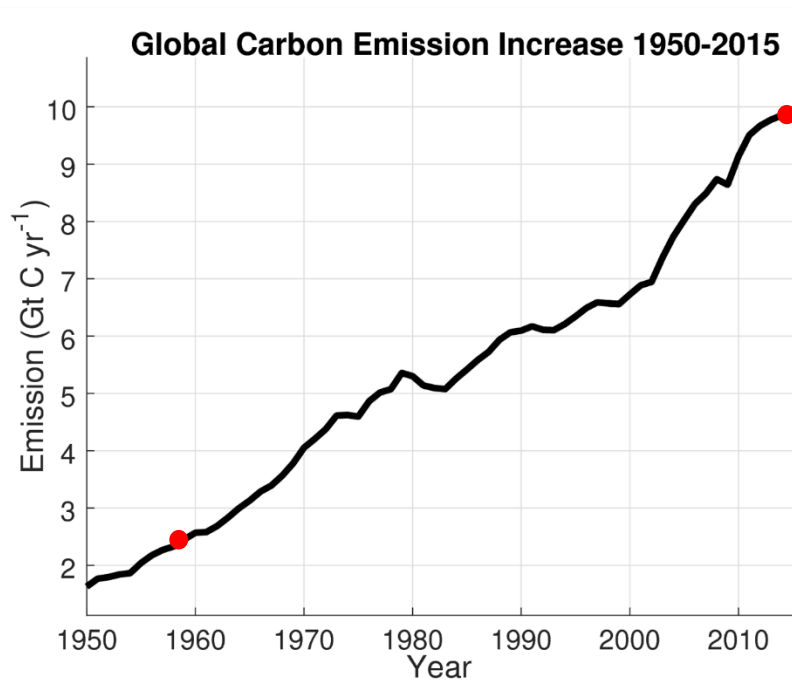
**Coal largest today**

Oil

Coal

Gas

# Fossil Fuel Emissions





20 June 2007

# World Carbon Emissions

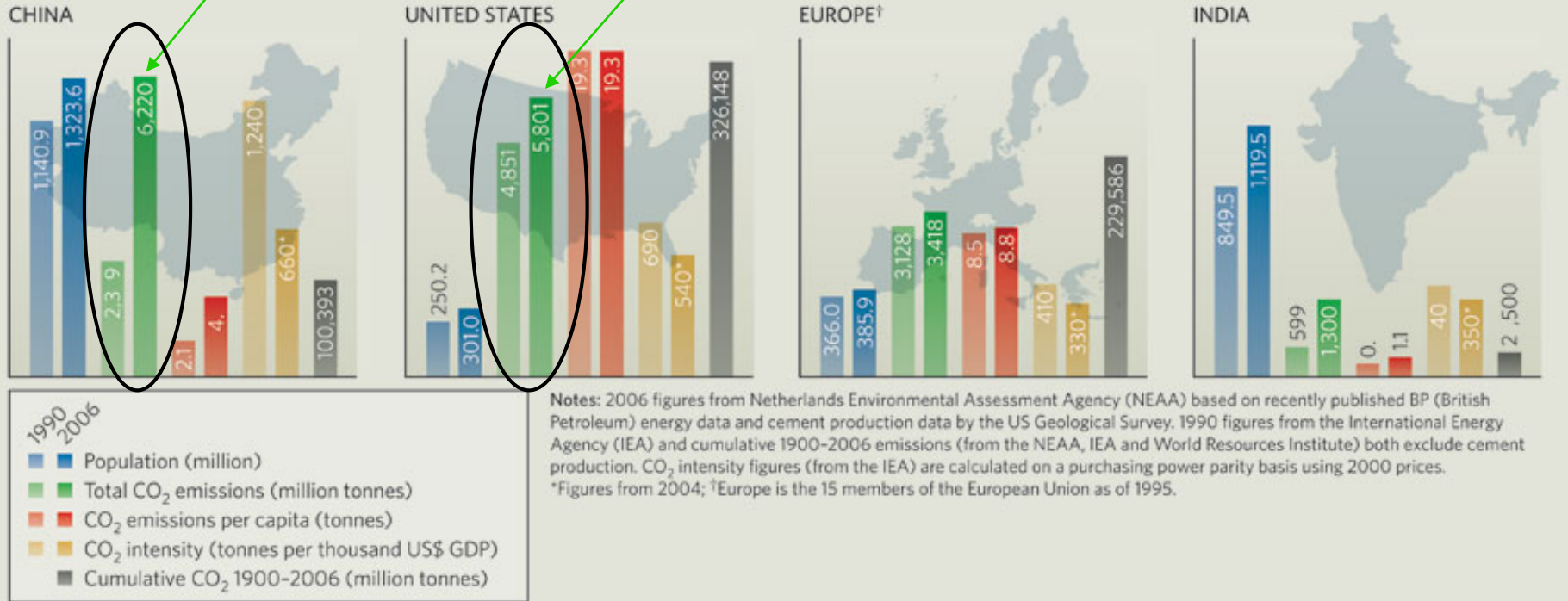
China: 1.70 Gt C per year

US: 1.58 Gt C per year

Last week, the Netherlands Environmental Assessment Agency produced a preliminary report showing that China had overtaken the United States as the world's largest emitter of carbon dioxide from the burning of fossil fuels and the manufacture of cement (44% of the world's new cement is currently being laid in China).

Here's how the world's big emitters stacked up. In per capita terms, the United States is still easily the most carbon-profligate economy, and it has made by far the largest historical contribution to the stock of atmospheric CO<sub>2</sub>. In terms of the emissions it takes to provide a given amount of gross domestic product

(GDP), the carbon intensity, China is in the worst position. The carbon intensity has dropped in all four economies since 1990, most impressively in China. But given economic growth, overall global CO<sub>2</sub> emissions rose by more than 35% between 1990 and 2006.



Source: [http://www.nature.com/nature/journal/v447/n7148/fig\\_tab/4471038a\\_F1.html](http://www.nature.com/nature/journal/v447/n7148/fig_tab/4471038a_F1.html)

# US / China Announcement $\Rightarrow$ Paris Climate Agreement



Nov 2014, Presidents Obama & Xi announced that the U.S. would reduce C emissions 27% below 2005 level by 2025 & China would peak by 2030 with best effort to peak early



## Paris Climate Agreement:

Article 2, Section 1, Part a):

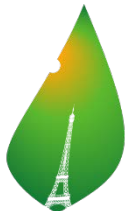
Objective to hold “increase in GMST to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5°C above pre-industrial levels”

**INDC:** Intended **N**ationally **D**etermined **C**ontributions to reduce GHG emissions

- Submitted prior to Dec 2015, COP21-UNFCCC meeting in Paris
- Consist of either unconditional (promise) or conditional (contingent) pledges
- Generally extend from present to year 2030

COP: Conference of the Parties

UNFCCC: United Nations Framework Convention on Climate Change



PARIS2015  
UN CLIMATE CHANGE CONFERENCE  
COP21·CMP11

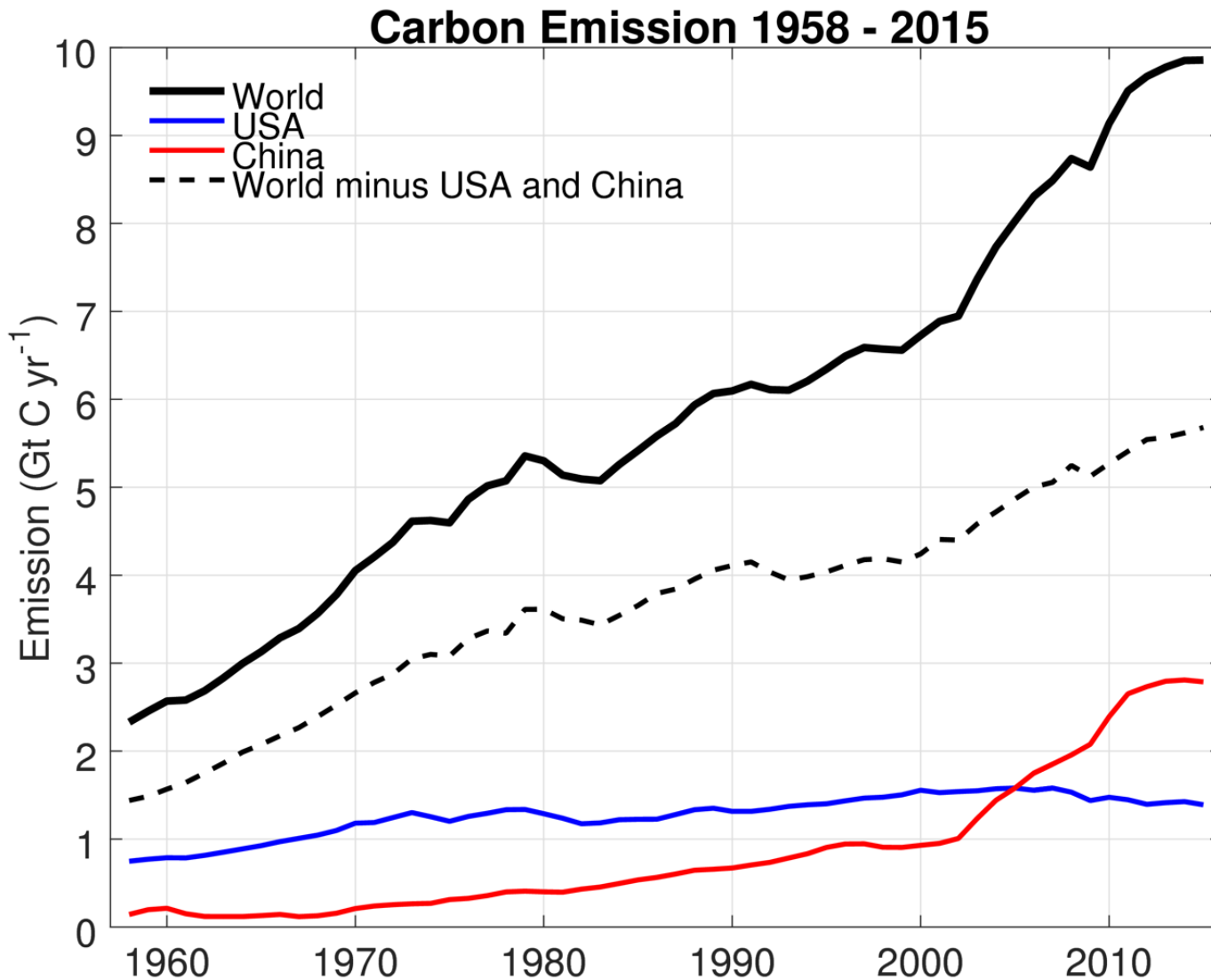


Figure courtesy Walt Tribett

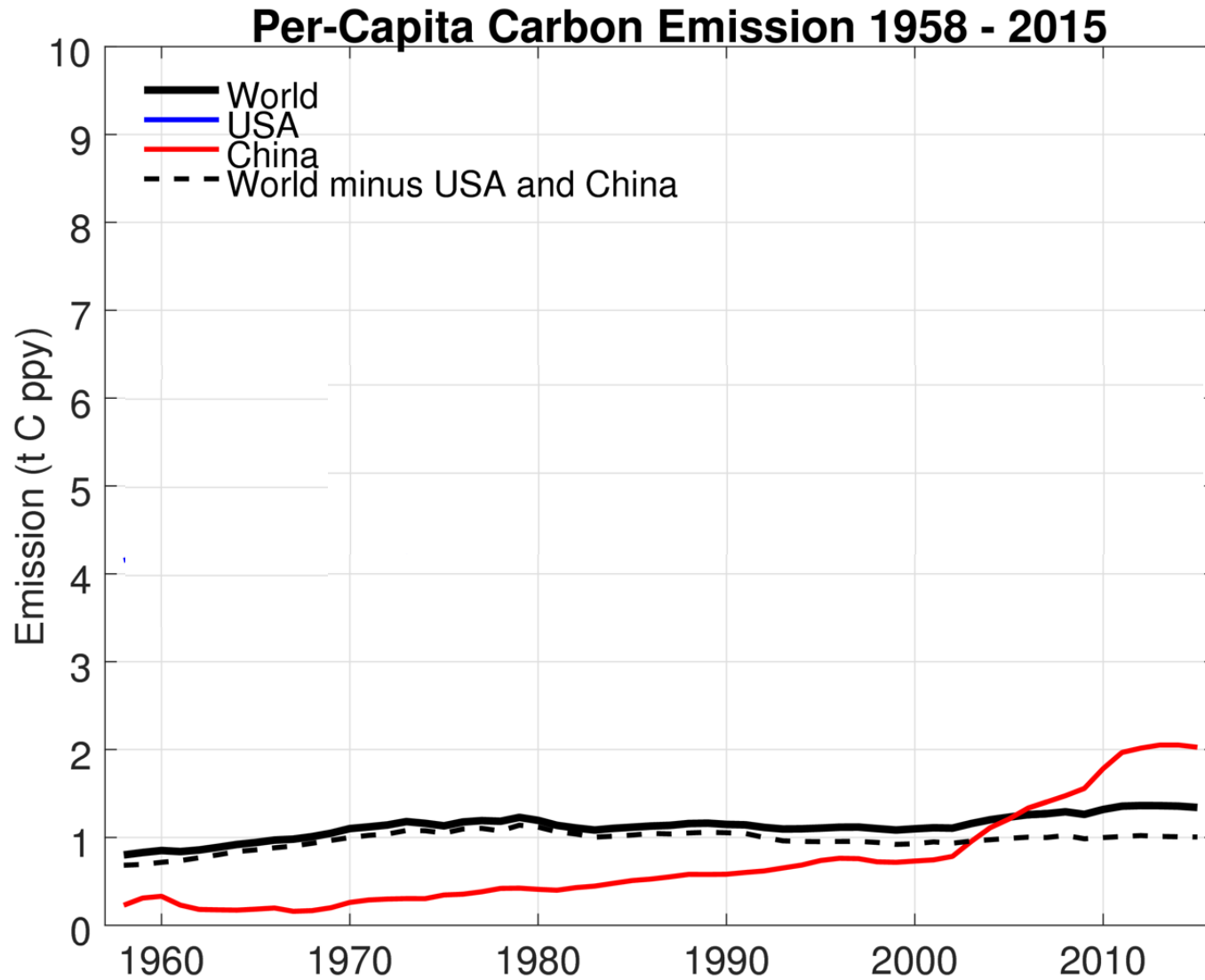


Figure courtesy Walt Tribett

Note, here we use Gt C, whereas in the book, we used GT CO<sub>2</sub>

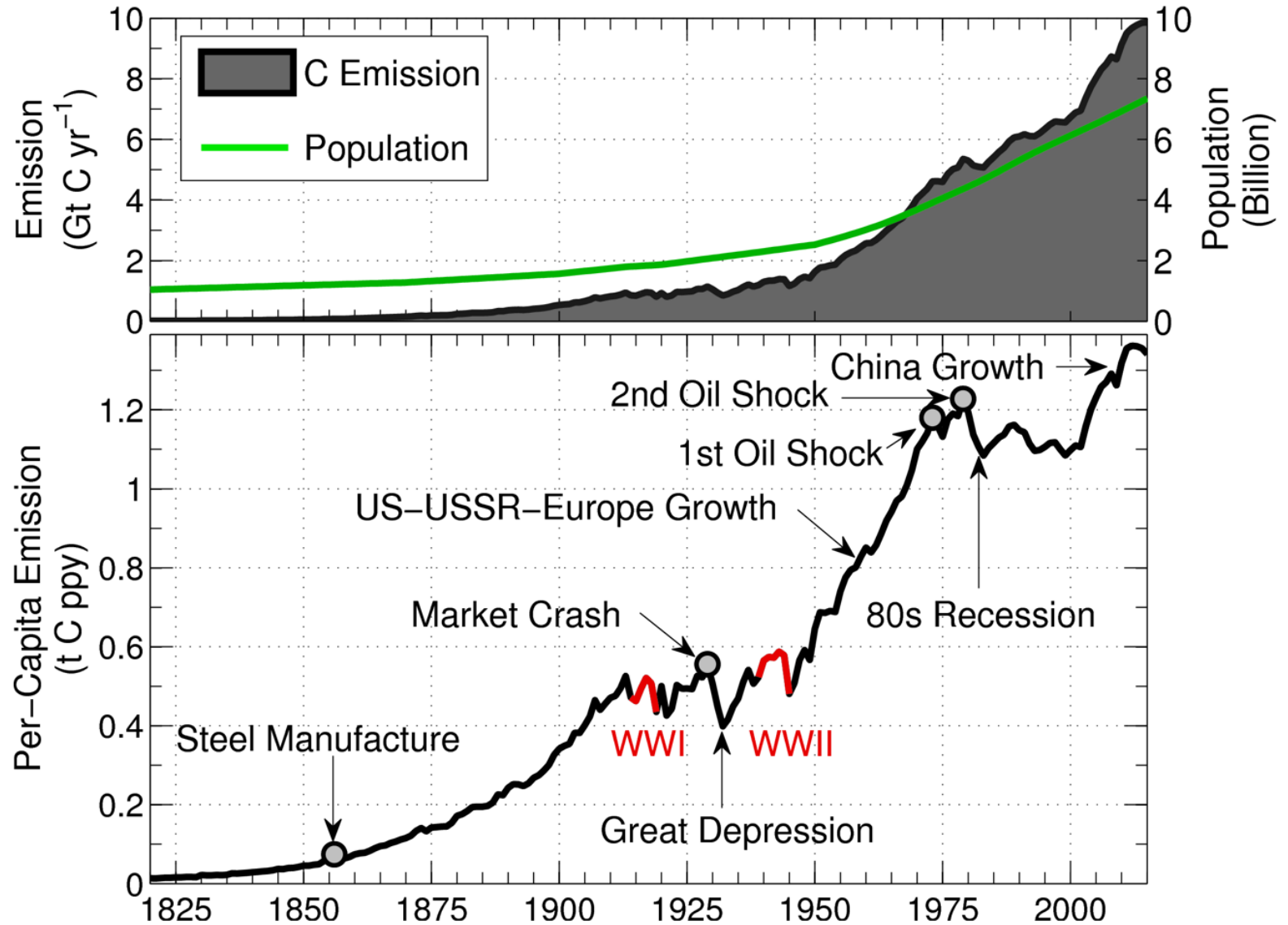


Figure courtesy Walt Tribett

After Fig 3.1 *Paris Beacon of Hope*



# Atmospheric CO<sub>2</sub> since ~1860

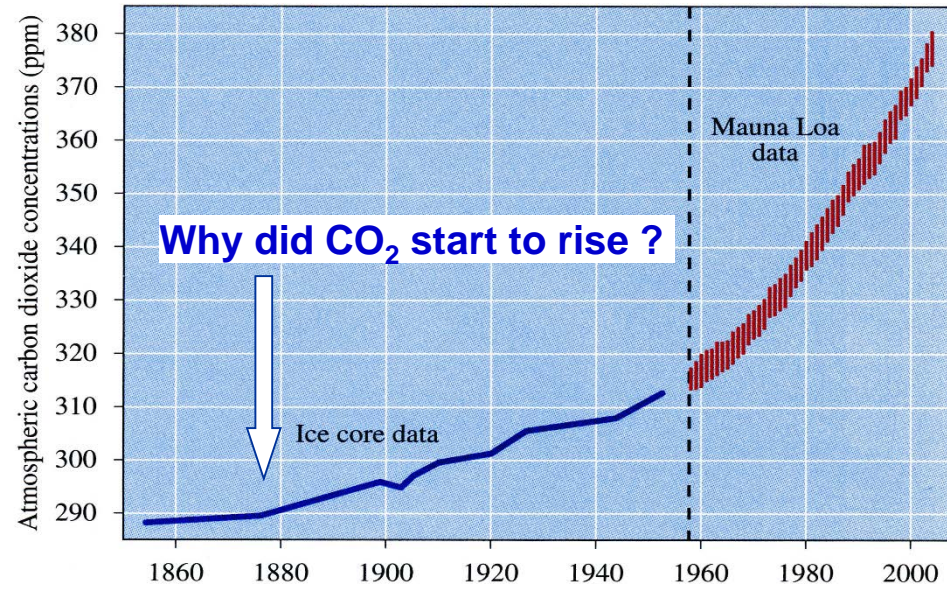
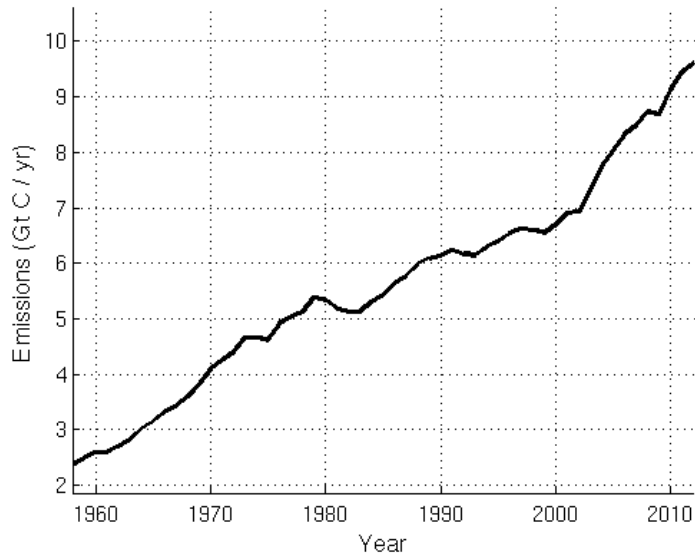


Figure 3.5, *Chemistry in Context*  
6<sup>th</sup> Edition

# Fossil Fuel Emissions

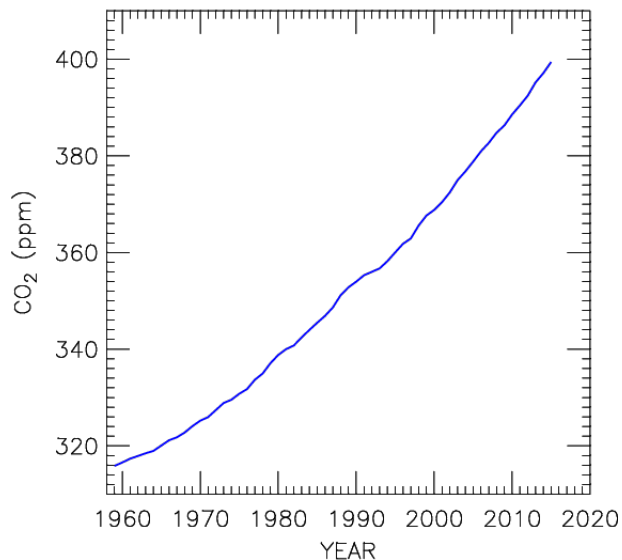
Global Carbon Emission Increase 1958-2012



Fossil fuel emissions, 1959 to 2015 = **336 Gt C**

$\Delta$  (CO<sub>2</sub>) years 1959 to 2015 = **83.6 ppm**

CO<sub>2</sub> Global Average Mixing Ratio vs Time



# Global Carbon Cycle

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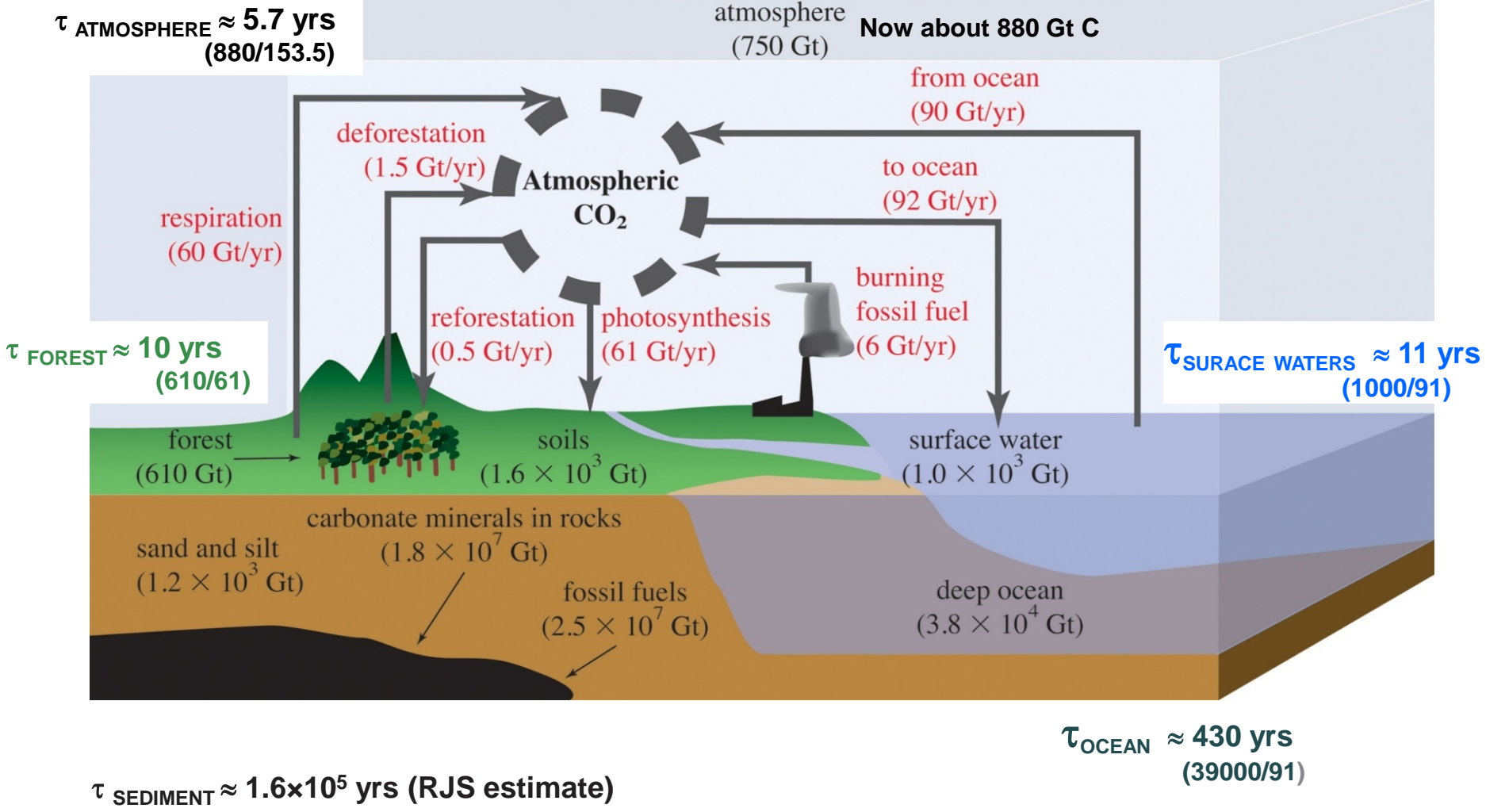
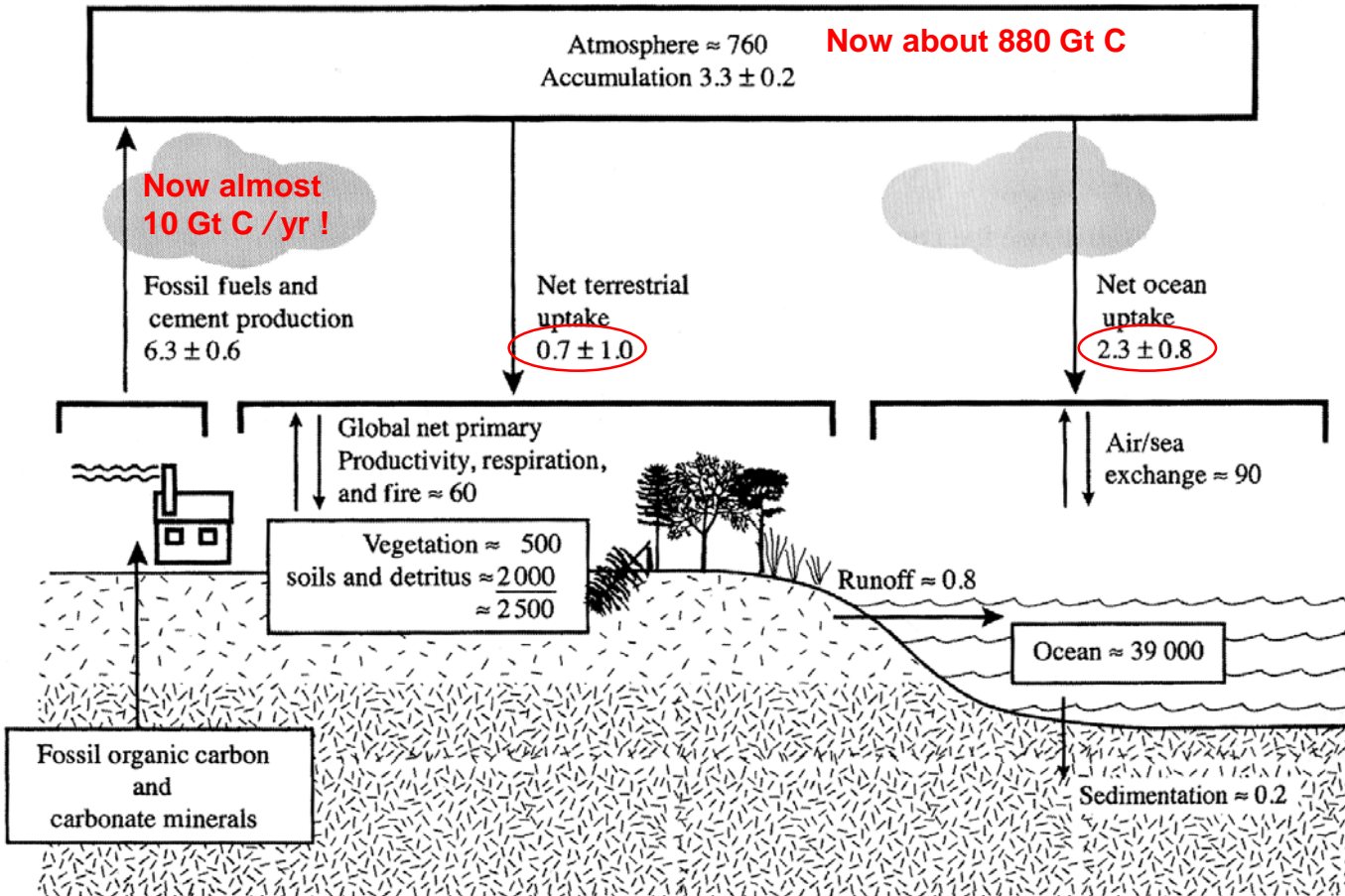


Fig 3.2, Chemistry in Context



# Global Carbon Cycle



**Figure 3.1** The global carbon cycle, showing the carbon stocks in reservoirs (in Gt) and carbon flows (in Gt year<sup>-1</sup>) relevant to the anthropogenic perturbation as annual averages over the decade from 1989 to 1998. Net ocean uptake of the anthropogenic perturbation equals the net air/sea input plus run-off minus sediment. The units are thousand millions of tonnes or gigatonnes (Gt).

# CO<sub>2</sub> Is Long Lived

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH<sub>4</sub>) global warming potentials (GWP) relative to CO<sub>2</sub>. {Table 2.14}

Industrial Designation or Common Name (years)	Chemical Formula	Lifetime (years)	Radiative Efficiency (W m <sup>-2</sup> ppb <sup>-1</sup> )	Global Warming Potential for Given Time Horizon			
				SAR <sup>†</sup> (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO <sub>2</sub>	See below <sup>a</sup>	<sup>b</sup> 1.4x10 <sup>-5</sup>	1	1	1	1
Methane <sup>c</sup>	CH <sub>4</sub>	12 <sup>c</sup>	3.7x10 <sup>-4</sup>	21	72	25	7.6
Nitrous oxide	N <sub>2</sub> O	114	3.03x10 <sup>-3</sup>	310	289	298	153

Notes:

<sup>†</sup> SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

<sup>a</sup> The CO<sub>2</sub> response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO<sub>2</sub> concentration value of 378 ppm. The decay of a pulse of CO<sub>2</sub> with time t is given by

$$a_0 + \sum_{i=1}^3 a_i \cdot e^{-t/\tau_i} \quad \text{where } a_0 = 0.217, a_1 = 0.259, a_2 = 0.338, a_3 = 0.186, \tau_1 = 172.9 \text{ years}, \tau_2 = 18.51 \text{ years}, \text{ and } \tau_3 = 1.186 \text{ years, for } t < 1,000 \text{ years.}$$

<sup>b</sup> The radiative efficiency of CO<sub>2</sub> is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

<sup>c</sup> The perturbation lifetime for CH<sub>4</sub> is 12 years as in the TAR (see also Section 7.4). The GWP for CH<sub>4</sub> includes indirect effects from enhancements of ozone and stratospheric water vapour (see Section 2.10) .

from IPCC 2007 “Physical Science Basis”

CO<sub>2</sub> has multiple time constants

Longest decay of IPCC formula is close to 200 years, which represents time for surface waters to equilibrate with the intermediate ocean

Note: IPCC formula should only be used for t < 1000 years

# Global Carbon Cycle, 1959 to present

Fossil Fuel and Land Use Change Emissions of CO<sub>2</sub> and Atmospheric Growth, 1959 to 2015

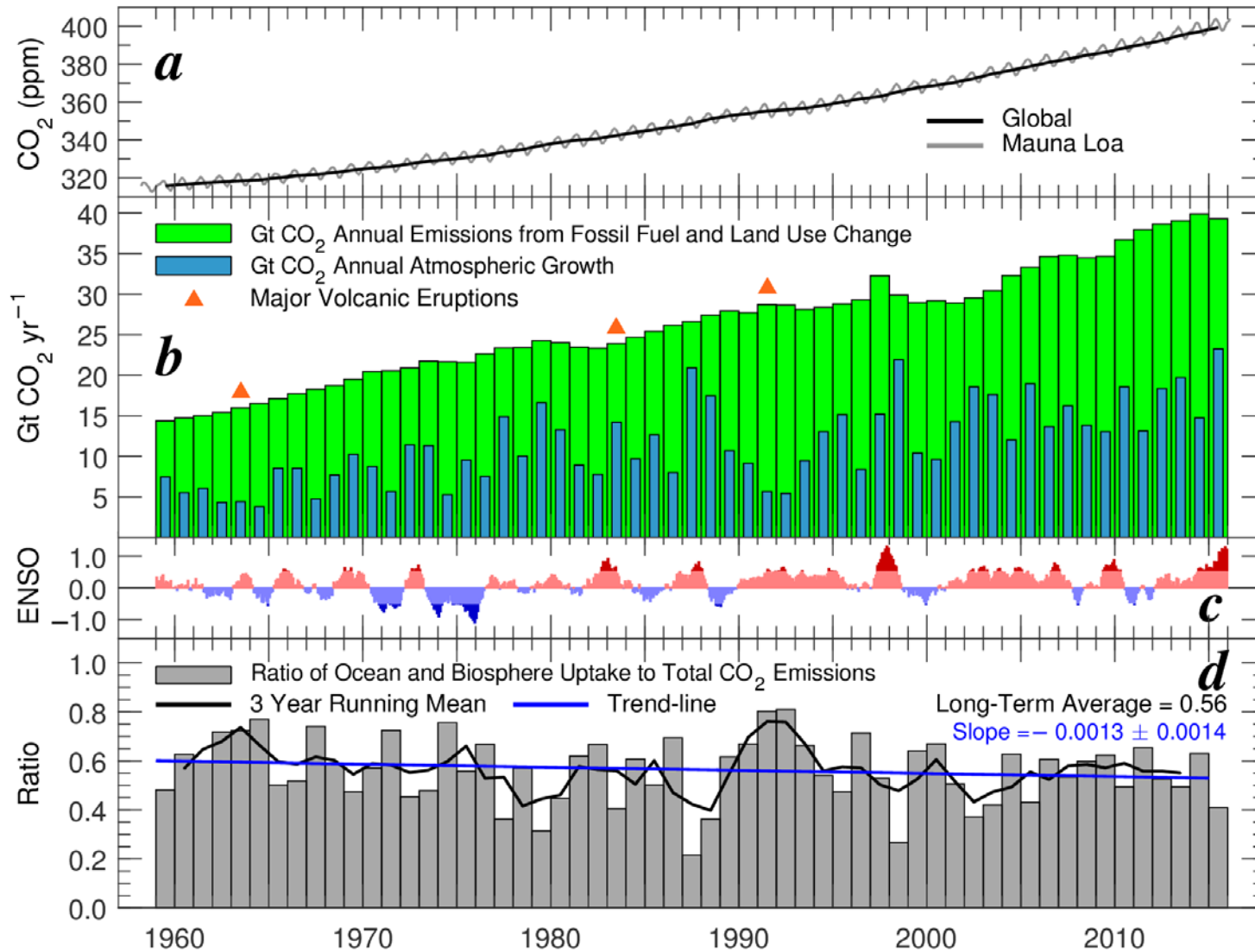
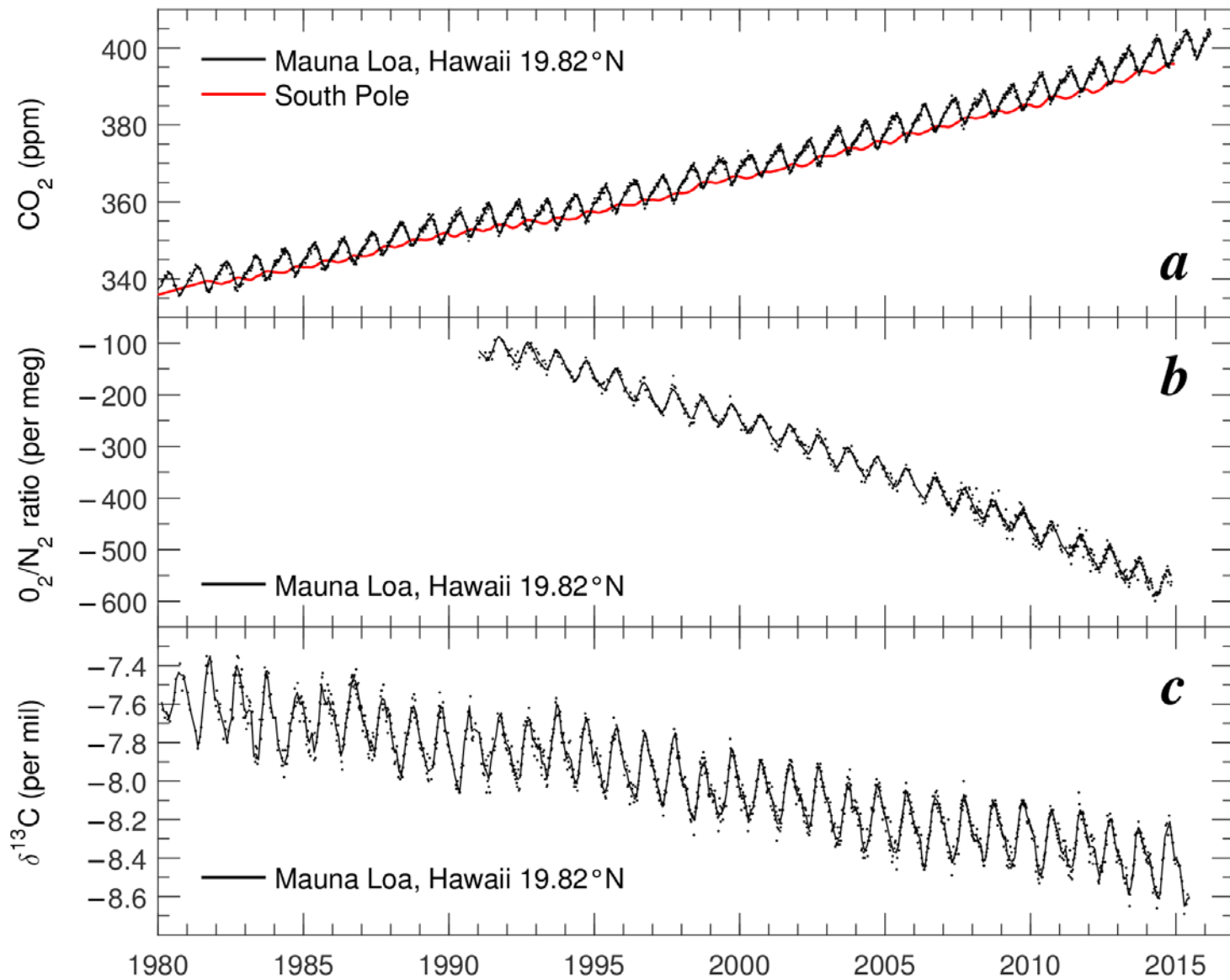


Fig 1.6, *Paris Beacon of Hope*

# Human "Fingerprint" on Atmospheric CO<sub>2</sub>



**Fig 1.7, Paris Beacon of Hope**

# Human “Fingerprint” on Atmospheric CO<sub>2</sub>

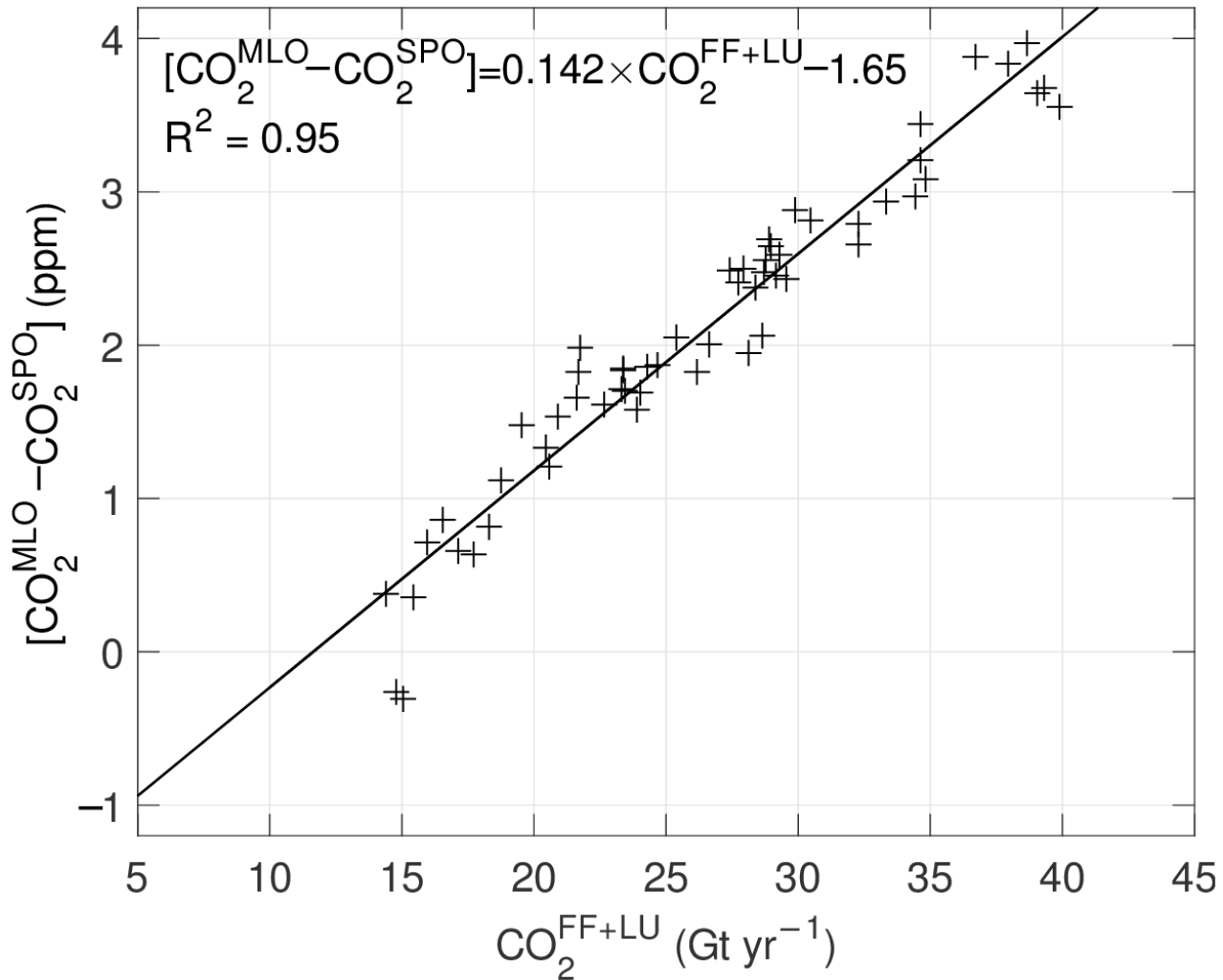
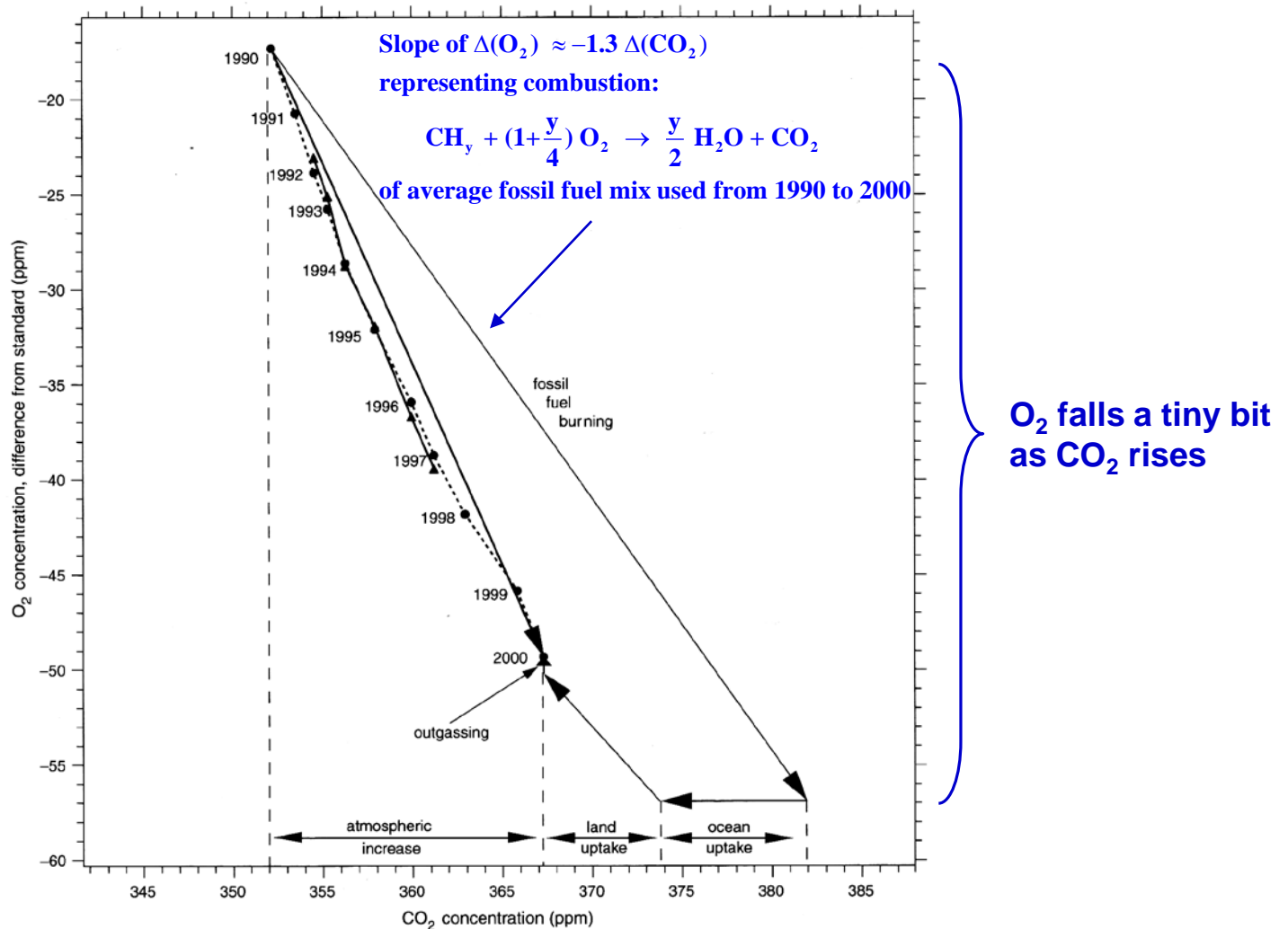


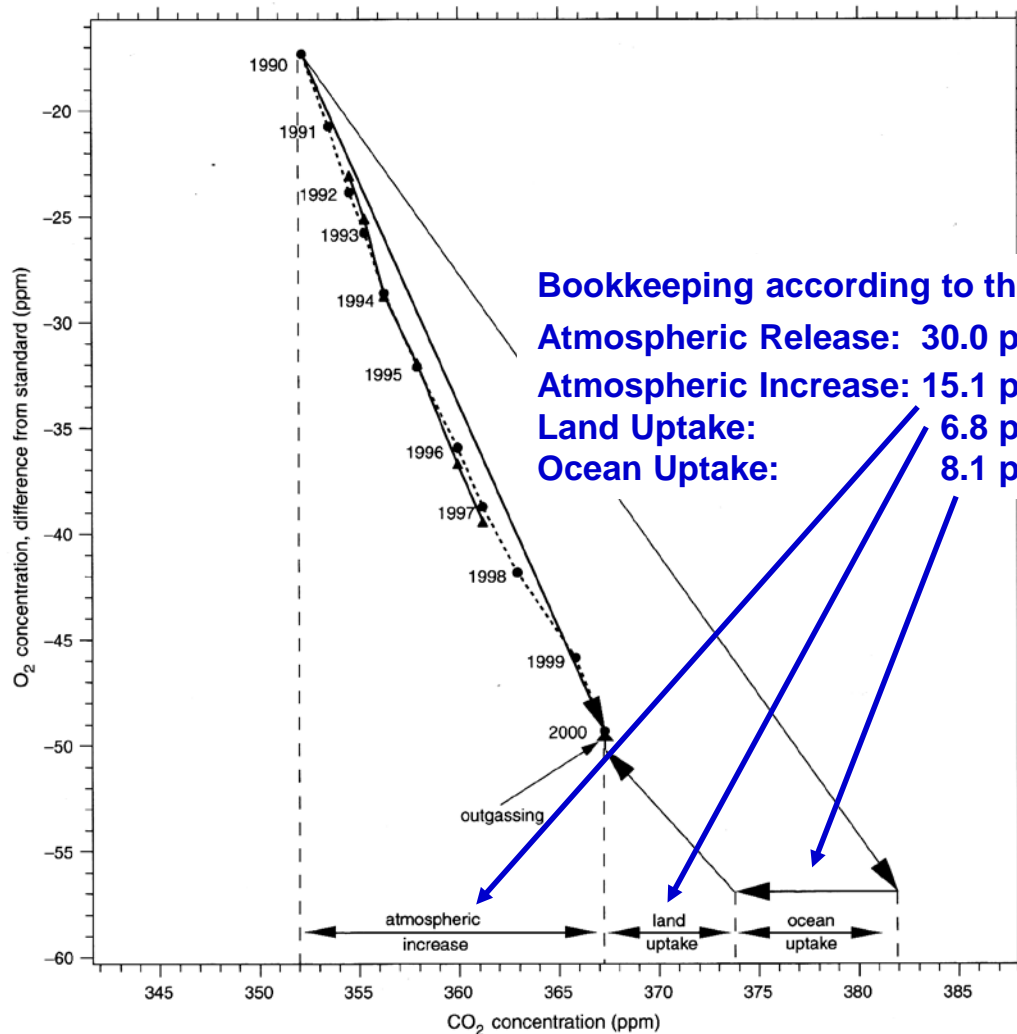
Fig 1.8, *Paris Beacon of Hope*

# Inferring CO<sub>2</sub> Uptake Based on Δ(O<sub>2</sub>)



**Figure 3.4** Partitioning of fossil fuel carbon dioxide uptake using oxygen measurements. Shown is the relationship between changes in carbon dioxide and oxygen concentrations. Observations are shown by solid circles and triangles. The arrow labelled 'fossil fuel burning' denotes the effect of the combustion of fossil fuels based on the O<sub>2</sub> : CO<sub>2</sub> stoichiometric relation of the different fuel types. Uptake by land and ocean is constrained by the stoichiometric ratio associated with these processes, defining the slopes of the respective arrows.

# Inferring CO<sub>2</sub> Uptake Based on Δ(O<sub>2</sub>)



**Bookkeeping according to this study:**

**Atmospheric Release: 30.0 ppm (66 Gt)**

**Atmospheric Increase: 15.1 ppm (~50% airborne fraction)**

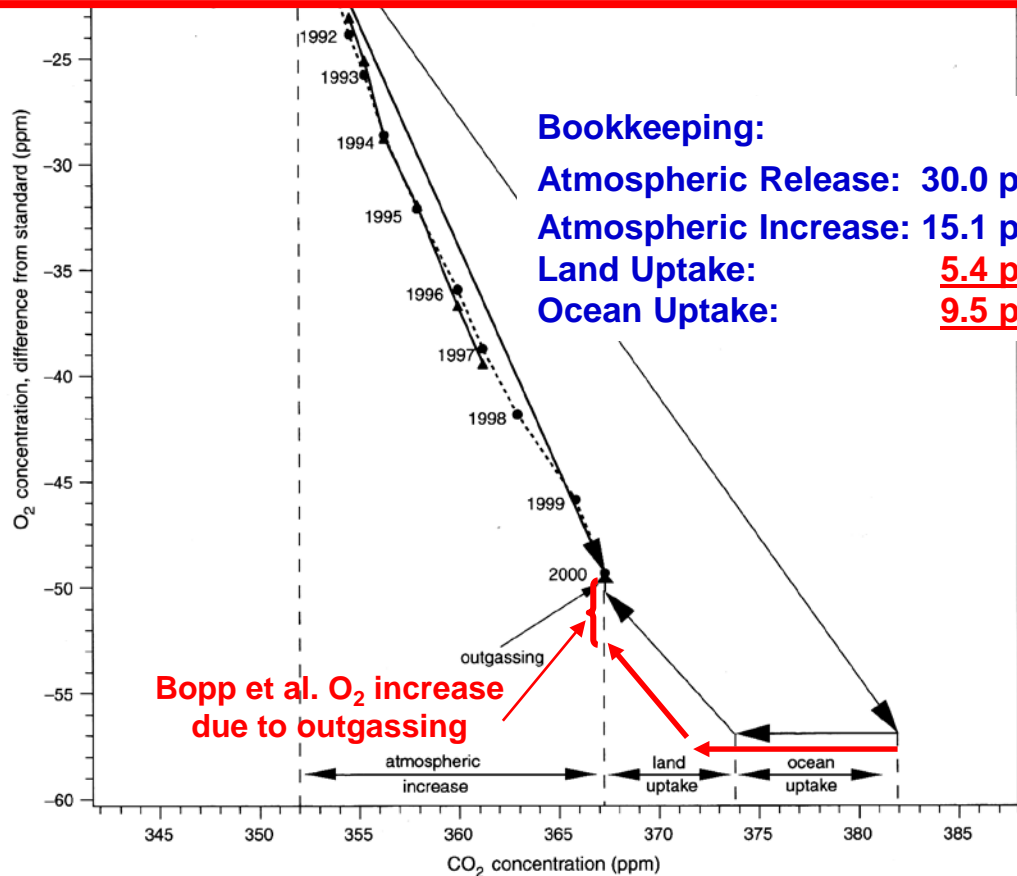
**Land Uptake: 6.8 ppm (46% of uptake)**

**Ocean Uptake: 8.1 ppm (54% of uptake)**

**Figure 3.4** Partitioning of fossil fuel carbon dioxide uptake using oxygen measurements. Shown is the relationship between changes in carbon dioxide and oxygen concentrations. Observations are shown by solid circles and triangles. The arrow labelled 'fossil fuel burning' denotes the effect of the combustion of fossil fuels based on the O<sub>2</sub> : CO<sub>2</sub> stoichiometric relation of the different fuel types. Uptake by land and ocean is constrained by the stoichiometric ratio associated with these processes, defining the slopes of the respective arrows.



**Note: As the ocean warms, O<sub>2</sub> solubility decreases. In other words, as climate changes, the oceans outgas O<sub>2</sub>. Bopp et al. (GBC, 2002) applied a correction for ocean outgassing and concluded**



**Bookkeeping:**

**Atmospheric Release: 30.0 ppm (66 Gt)**

**Atmospheric Increase: 15.1 ppm (~50% airborne fraction)**

**Land Uptake: 5.4 ppm (36% of uptake)**

**Ocean Uptake: 9.5 ppm (64% of uptake)**

**Bopp et al. O<sub>2</sub> increase due to outgassing**

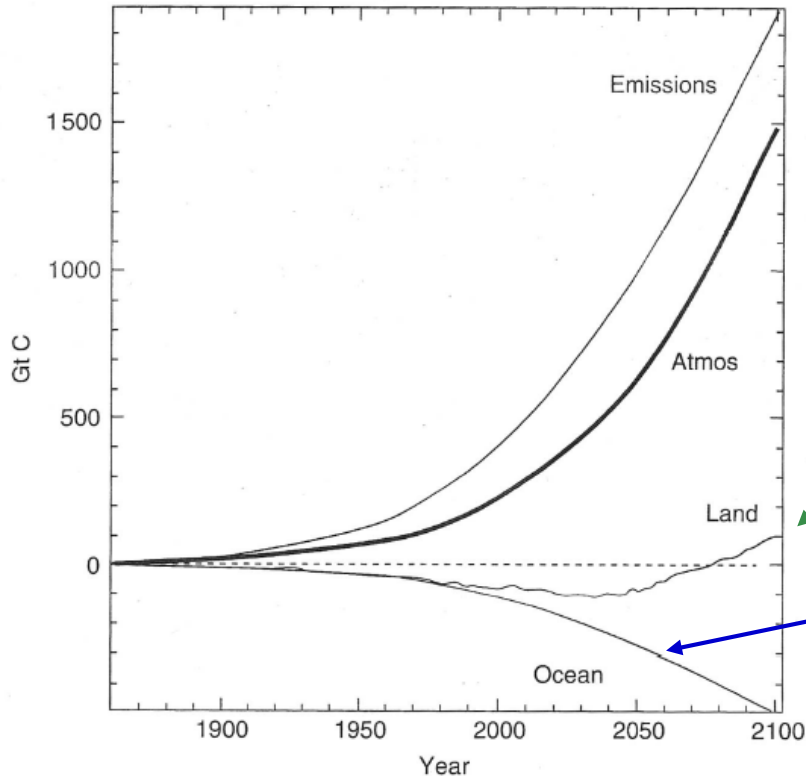
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# Uptake of Atmospheric CO<sub>2</sub> by Trees (Land Sink)

## Land sink: relatively short lived reservoir

- In this model, future water stress due to climate change eventually limits plant growth
- Feedbacks between climate change & plants could lead to almost 100 ppm additional CO<sub>2</sub> by end of century



Ocean sink: relatively long lived reservoir

In nearly all models, ocean uptake slows relative to rise in atmospheric CO<sub>2</sub>

**Figure 3.5** Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

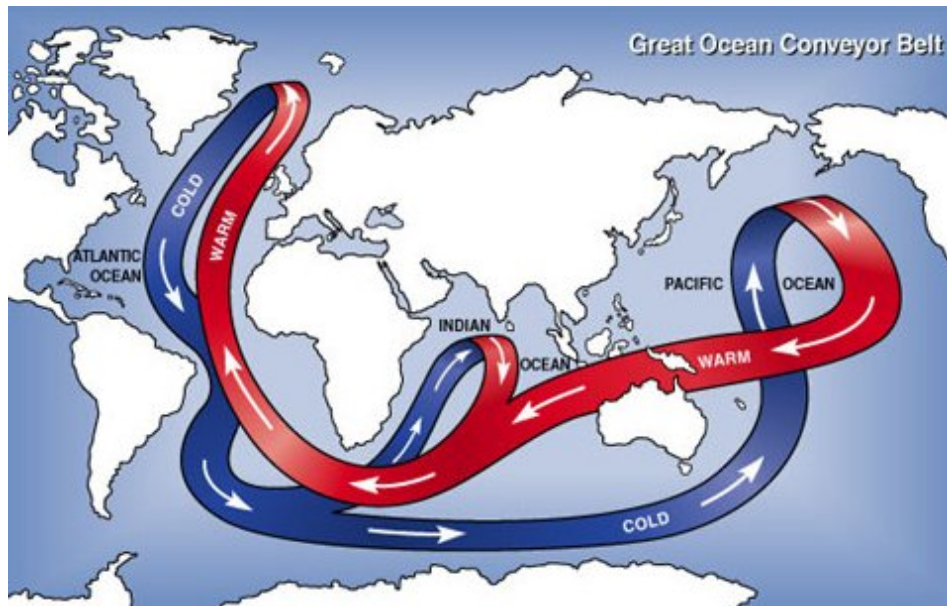
# Uptake of Atmospheric CO<sub>2</sub> by Oceans

## – Solubility Pump:

- More CO<sub>2</sub> can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO<sub>2</sub>
- Deep water forms at high latitude. As deep water sinks, ocean carbon ( $\Sigma\text{CO}_2$ ) accumulated at the surface is moved to the deep ocean interior.

## – Biological Pump:

- Ocean biology limited by availability of nutrients such as NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>-</sup>, and Fe<sup>2+</sup> & Fe<sup>3+</sup>. Ocean biology is never carbon limited.
- Detrital material “rains” from surface to deep waters, contributing to higher CO<sub>2</sub> in intermediate and deep waters



[http://science.nasa.gov/headlines/y2004/05mar\\_arctic.htm](http://science.nasa.gov/headlines/y2004/05mar_arctic.htm)

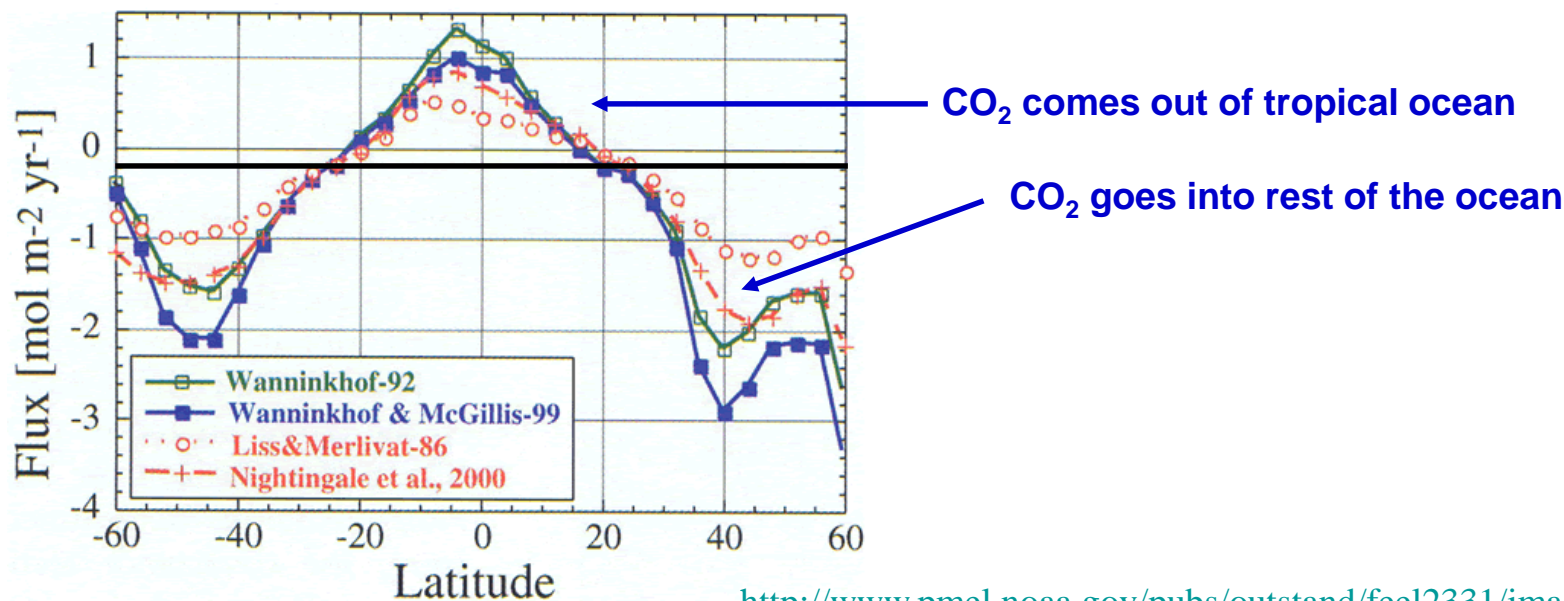
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## – Biological Pump:

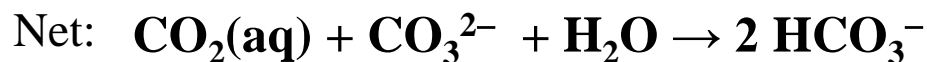
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<http://www.pmel.noaa.gov/pubs/outstand/feel2331/images/fig05.gif>

# Uptake of Atmospheric CO<sub>2</sub> by Oceans

When CO<sub>2</sub> dissolves:



Atmospheric CO <sub>2</sub>	280 ppm Pre-Industrial	400 ppm Present Day	560 ppm 2 × Pre-Indus.
Ocean Carbon	2020 × 10 <sup>-6</sup> M	2075 × 10 <sup>-6</sup> M	2122 × 10 <sup>-6</sup> M
[HCO <sub>3</sub> <sup>-</sup> ]	1772 × 10 <sup>-6</sup> M	1875 × 10 <sup>-6</sup> M	1957 × 10 <sup>-6</sup> M
[CO <sub>2</sub> (aq)]	9.1 × 10 <sup>-6</sup> M	13.0 × 10 <sup>-6</sup> M	18.2 × 10 <sup>-6</sup> M
[CO <sub>3</sub> <sup>2-</sup> ]	239 × 10 <sup>-6</sup> M	188 × 10 <sup>-6</sup> M	146 × 10 <sup>-6</sup> M
pH	8.32	8.19	8.06

$$\text{Ocean Carbon } [\Sigma \text{CO}_2] = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

Notes:

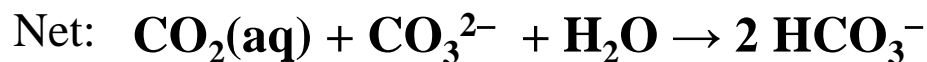
T = 293 K; Alkalinity = 2.25 × 10<sup>-3</sup> M

M ≡ mol/liter

Mathematics supporting this calculation on Extra Slide 3

# Uptake of Atmospheric CO<sub>2</sub> by Oceans

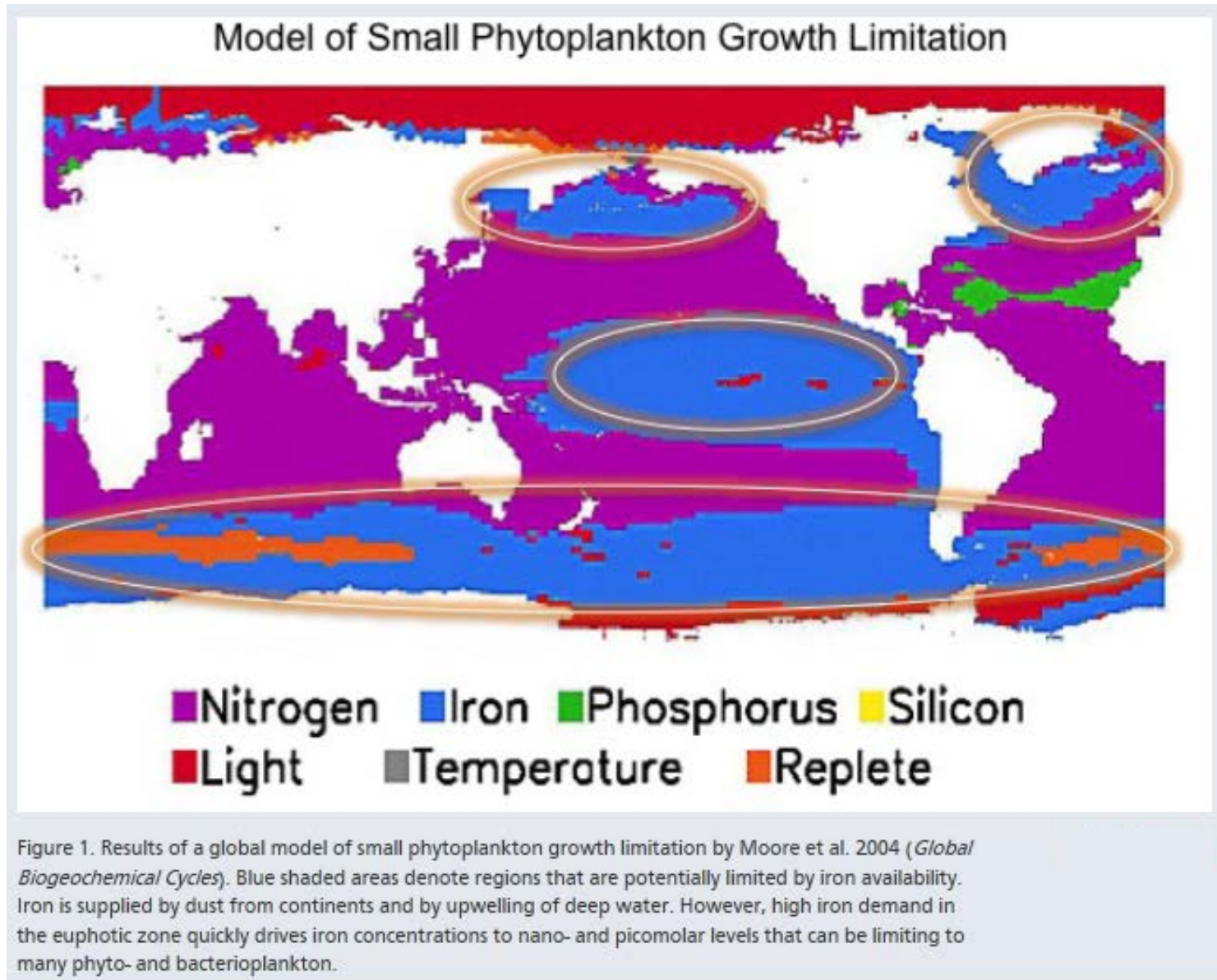
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pH	8.32	8.19	8.06

$$\begin{aligned}
 \text{Revelle Factor} &= \frac{\Delta \text{Ocean Carbon} / \langle \text{Ocean Carbon} \rangle_{\text{AVERAGE}}}{\Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}}} \\
 &= \frac{55/2047.5}{120/340} = 0.076 \text{ (from pre-industrial to present-day CO}_2\text{)} \\
 &= \frac{47/2098.5}{160/480} = 0.067 \text{ (from present-day to } 2 \times \text{ pre-industrial CO}_2\text{)}
 \end{aligned}$$

# Biology in Today's Ocean



<http://www.whoi.edu/page.do?pid=130796>



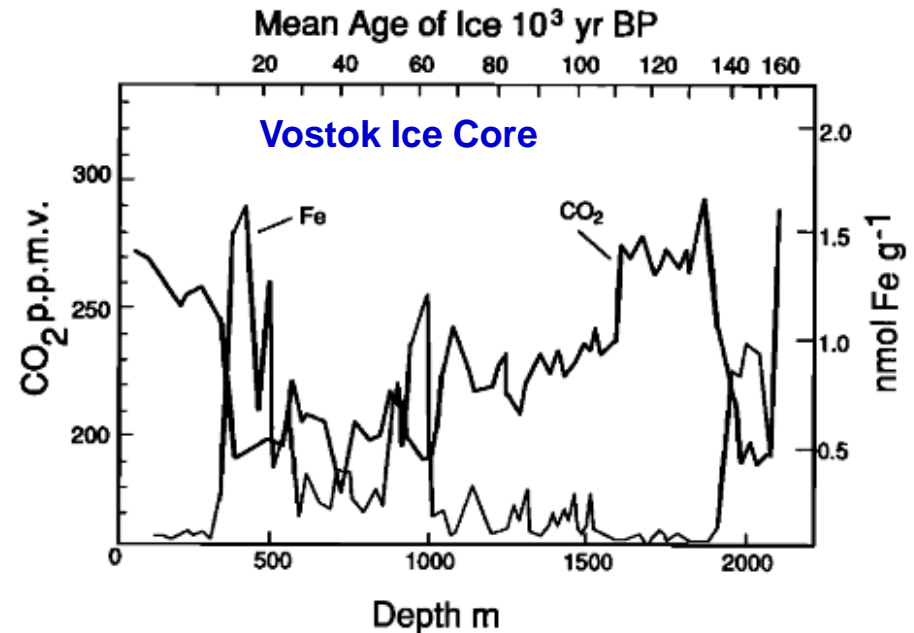
# Connection to Glacial CO<sub>2</sub>

## GLACIAL-INTERGLACIAL CO<sub>2</sub> CHANGE: THE IRON HYPOTHESIS

John H. Martin

In contrast, atmospheric dust Fe supplies were 50 times higher during the last glacial maximum (LGM). Because of this Fe enrichment, phytoplankton growth may have been greatly enhanced, larger amounts of upwelled nutrients may have been used, and the resulting stimulation of new productivity may have contributed to the LGM drawdown of atmospheric CO<sub>2</sub> to levels of less than 200 ppm. Background information and arguments in support of this hypothesis are presented.

PALEOCEANOGRAPHY, VOL. 5,  
NO. 1, PAGES 1-13 1990



See <http://onlinelibrary.wiley.com/doi/10.1029/PA005i001p00001/abstract>

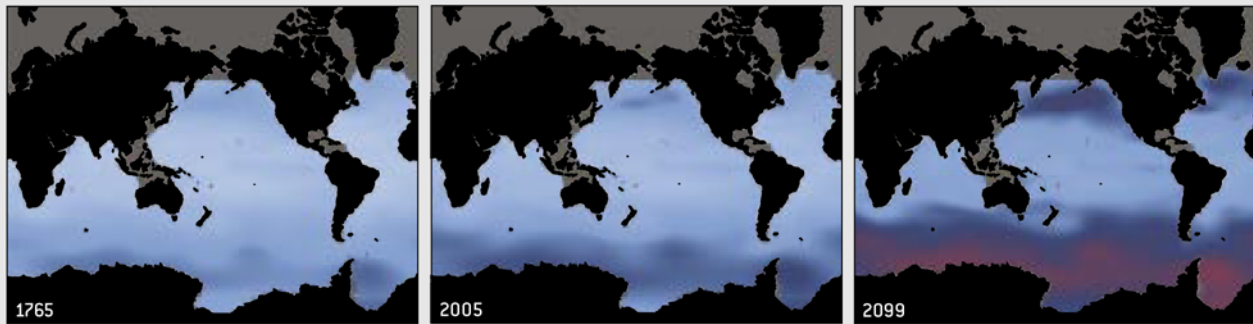
# Uptake of Atmospheric CO<sub>2</sub> by Oceans

Future ocean uptake of atmospheric CO<sub>2</sub> will lead to **ocean acidification**

**Bad news for ocean dwelling organisms that precipitate shells (basic materials)**

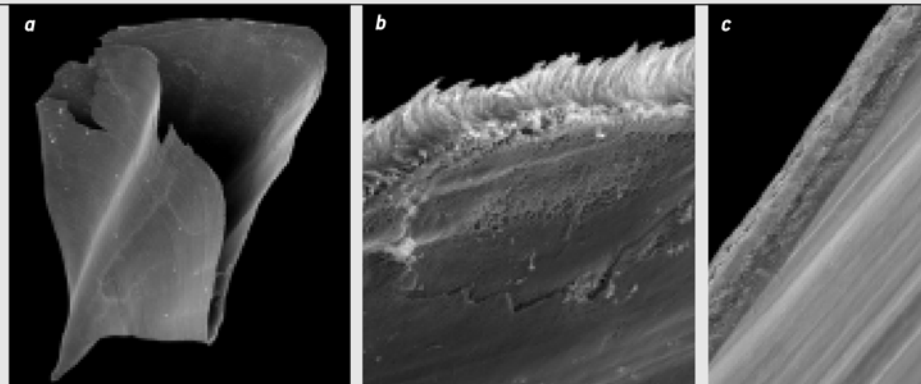
## THE (RAGGED) FUTURE OF ARAGONITE

Diminishing pH levels will weaken the ability of certain marine organisms to build their hard parts and will be felt soonest and most severely by those creatures that make those parts of aragonite, the form of calcium carbonate that is most prone to dissolution. The degree of threat will vary regionally.



Before the Industrial Revolution (*left*), most surface waters were substantially “oversaturated” with respect to aragonite (*light blue*), allowing marine organisms to form this mineral readily. But now (*center*), polar surface waters are only marginally oversaturated (*dark blue*). At the end of this century (*right*), such chilly waters, particularly those surrounding Antarctica, are expected to become undersaturated (*purple*), making it difficult for organisms to make aragonite and causing aragonite already formed to dissolve.

Pteropods form a key link in the food chain throughout the Southern Ocean. For these animals (and creatures that depend on them), the coming changes may be disastrous, as the images at the right suggest. The shell of a pteropod kept for 48 hours in water undersaturated with respect to aragonite shows corrosion on the surface [*a*], seen most clearly at high magnification [*b*]. The shell of a normal pteropod shows no dissolution [*c*].



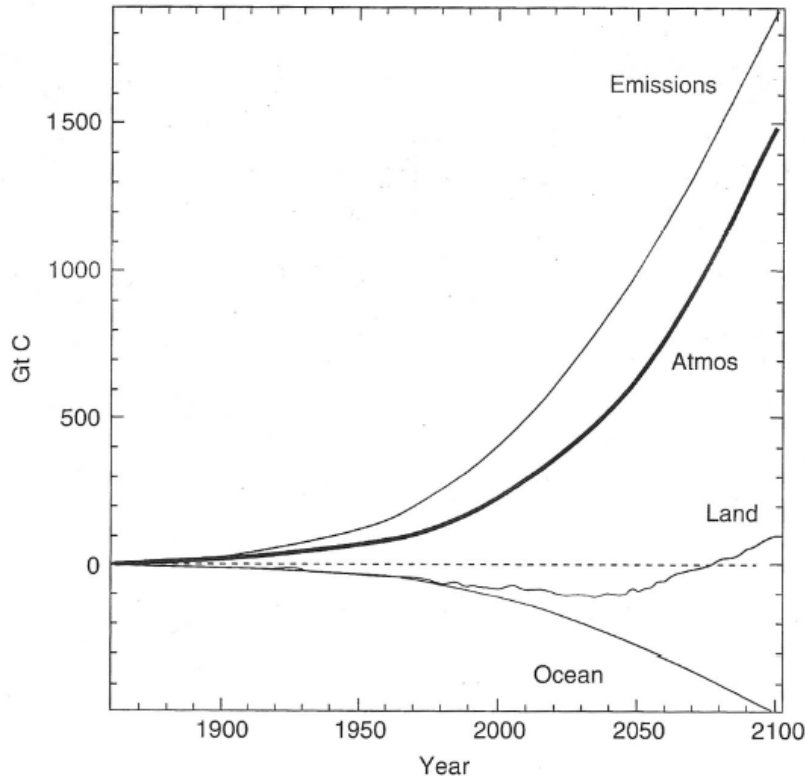
Doney, The Dangers of Ocean Acidification, *Scientific American*, March, 2006



# Uptake of Atmospheric CO<sub>2</sub> by Trees (Land Sink)

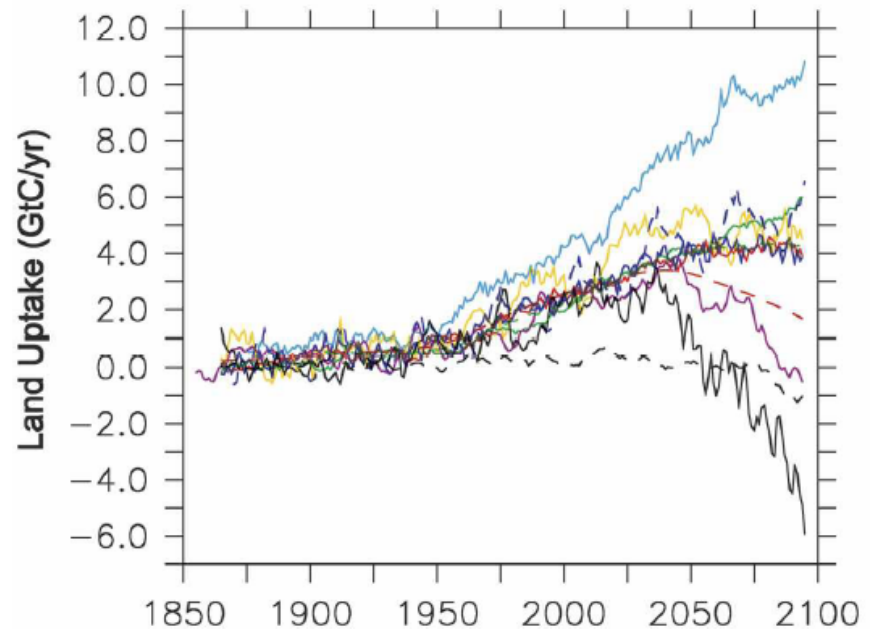
## Land sink: relatively short lived reservoir

- In this model, future water stress due to climate change eventually limits plant growth
- Feedbacks between climate change & plants lead to almost 100 ppm additional CO<sub>2</sub> by end of century



**Figure 3.5** Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

- Future fate of land sink highly uncertain according to **11** coupled climate-carbon cycle models examined by Friedlingstein et al. (2006)



# Uptake of Atmospheric CO<sub>2</sub> by Trees (Land Sink)

## Land sink

As CO<sub>2</sub> ↑, photosynthesis (all things being equal) will increase.

Known as the “**CO<sub>2</sub> fertilizer” effect**

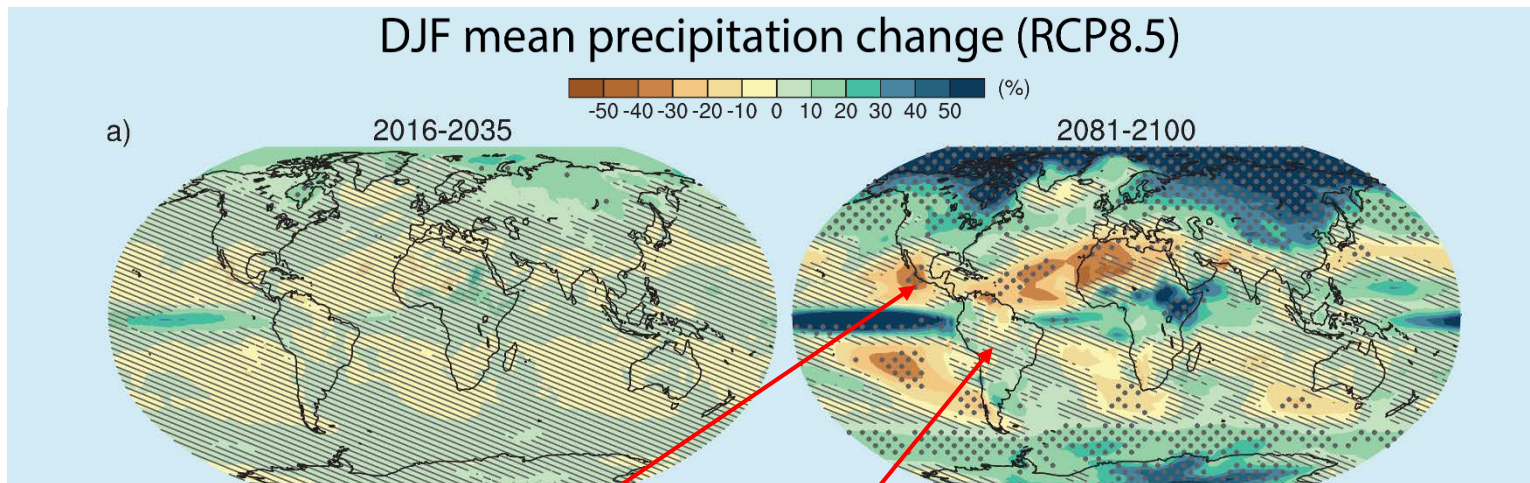
**Difficult to quantify because**

### **The carbon dioxide ‘fertilisation’ effect**

An important positive effect of increased carbon dioxide (CO<sub>2</sub>) concentrations in the atmosphere is the boost to growth in plants given by the additional CO<sub>2</sub>. Higher CO<sub>2</sub> concentrations stimulate photosynthesis, enabling the plants to fix carbon at a higher rate. This is why in glasshouses additional CO<sub>2</sub> may be introduced artificially to increase productivity. The effect is particularly applicable to what are called C3 plants (such as wheat, rice and soya bean), but less so to C4 plants (for example, maize, sorghum, sugar-cane, millet and many pasture and forage grasses). Under ideal conditions it can be a large effect; for C3 crops under doubled CO<sub>2</sub>, an average of +30%.<sup>37</sup>

# Uptake of Atmospheric CO<sub>2</sub> by Trees (Land Sink)

One more problem: Friedlingstein (2006) changes in land uptake are driven by future drought, and future precipitation is notoriously difficult to predict



**Method (a):** The default method used in Chapters 11, 12 and 14 as well as in the Annex I (hatching only) is shown in Box 12.1, Figure 1a, and is based on relating the climate change signal to internal variability in 20-year means of the models as a reference<sup>3</sup>. Regions where the multi-model mean change exceeds two standard deviations of internal variability and where at least 90% of the models agree on the sign of change are stippled and interpreted as 'large change with high model agreement'. Regions where the model mean is less than one standard deviation of internal variability are hatched and interpreted as 'small signal or low agreement of models'. This can have various reasons: (1) changes in individual models are smaller than internal variability, or (2) although changes in individual models are significant, they disagree about the sign and the multi-model mean change remains small. Using this method, the case where all models scatter widely around zero and the case where all models agree on near zero change therefore are both hatched (e.g., precipitation change over the Amazon region by the end of the 21st century, which the following methods mark as 'inconsistent model response').

Figure 1, Chapter 12, IPCC (2013)

# Exciting New Capability: Launch of Orbiting Carbon Observatory (OCO-2)

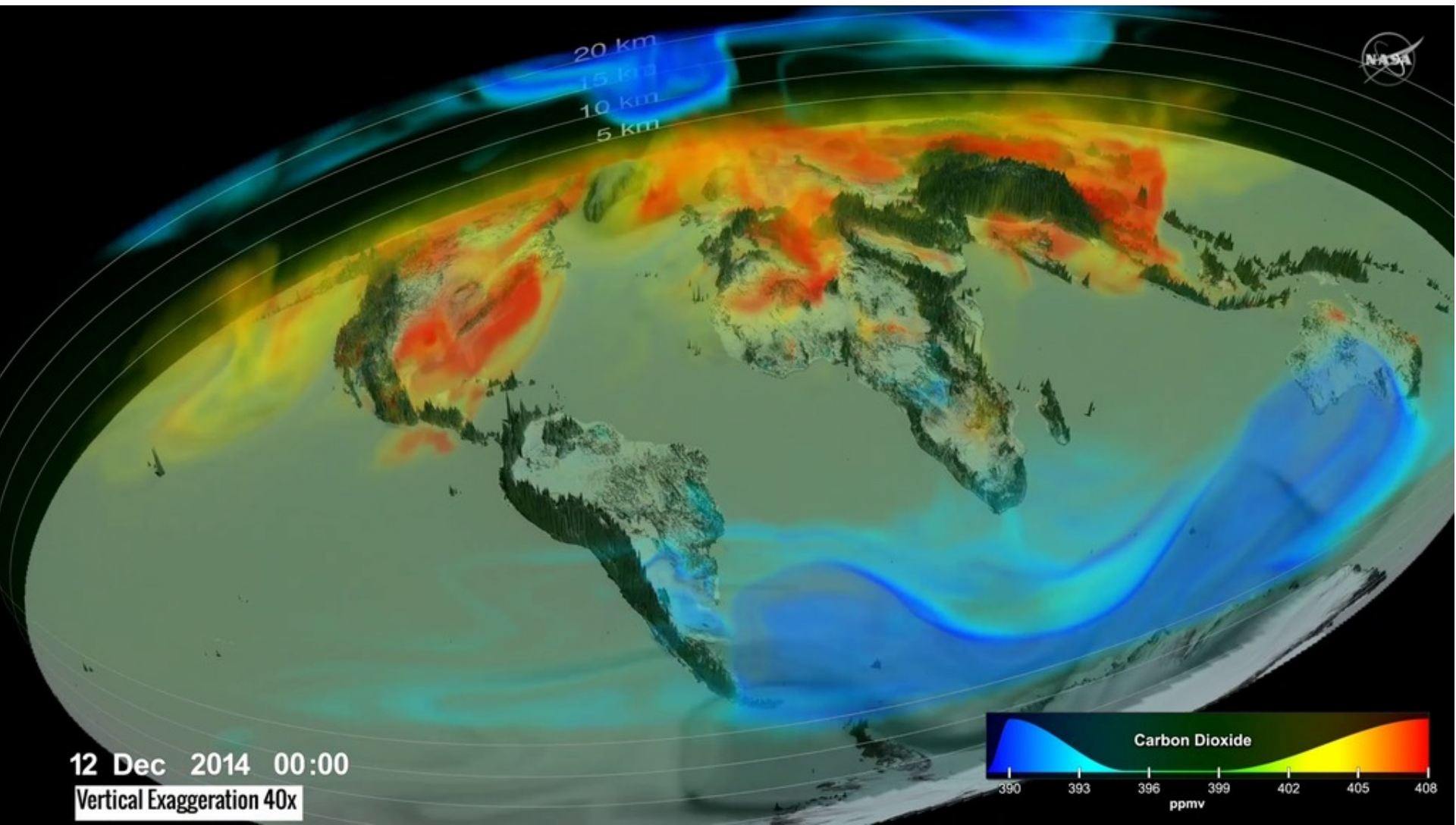


**Launch of OCO-2 on 2 July 2014, photographed by Stephen Kelly Sullivan from Malibu, California.**

<http://oco.jpl.nasa.gov> & <https://co2.jpl.nasa.gov>



# OCO-2 Data



<https://www.nasa.gov/feature/goddard/2016/eye-popping-view-of-co2-critical-step-for-carbon-cycle-science>

## Carbon Water Chemistry

Acidity of pure water is 7. This means  $[H^+] = 10^{-7}$  moles/liter or  $10^{-7}$  M.

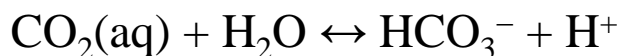
What is acidity of water in equilibrium with atmospheric  $CO_2$  ?

$$[CO_2(aq)] = H_{CO_2} p_{CO_2} = 3.4 \times 10^{-2} \text{ M / atm } p_{CO_2}$$

For  $CO_2 = 390$  ppm:

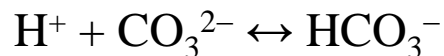
$$[CO_2(aq)] = 3.4 \times 10^{-2} \text{ M / atm } 3.9 \times 10^{-4} \text{ atm} = 1.326 \times 10^{-5} \text{ M}$$

First equilibrium between  $CO_2$ ,  $HCO_3^-$  (bicarbonate), and  $H^+$



$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2(aq)]} = 4.3 \times 10^{-7} \text{ M (at 298 K)}$$

Second equilibrium between  $CO_3^{2-}$  (carbonate),  $HCO_3^-$ , and  $H^+$



$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.7 \times 10^{-11} \text{ M (at 298 K)}$$

**Can solve if we assume charge balance:  $[H^+] = [HCO_3^-] + 2 [CO_3^{2-}]$   
- or – by taking a short-cut (see next slide)**

## Carbon Water Chemistry

Acidity of pure water is 7. What is acidity of water in equilibrium with atmospheric CO<sub>2</sub> ?

Shortcut:

$$[\text{CO}_2(\text{aq})] = H_{\text{CO}_2} p_{\text{CO}_2} = 3.4 \times 10^{-2} \text{ M} / \text{atm} p_{\text{CO}_2} = 1.326 \times 10^{-5} \text{ M} \text{ for present atmosphere}$$

$$[\text{H}^+] [\text{HCO}_3^-] = K_1 [\text{CO}_2(\text{aq})] = 4.3 \times 10^{-7} \text{ M} \times 1.326 \times 10^{-5} \text{ M} = 5.70 \times 10^{-12} \text{ M}^2$$

*Assume* charge balance is primarily between [H<sup>+</sup>] and [HCO<sub>3</sub><sup>-</sup>]:

i.e., that [H<sup>+</sup>] ≈ [HCO<sub>3</sub><sup>-</sup>] and that both are >> [CO<sub>3</sub><sup>2-</sup>]

$$[\text{H}^+] [\text{H}^+] = 5.70 \times 10^{-12} \text{ M}^2 \Rightarrow [\text{H}^+] = 2.388 \times 10^{-6} \text{ M}$$

$$pH = -\log_{10} [\text{H}^+] = \mathbf{5.6} \text{ (390 ppm, 298 K)}$$

Is the *assumption* justified? :

$$[\text{CO}_3^{2-}] = K_2 [\text{HCO}_3^-] / [\text{H}^+] \approx 4.7 \times 10^{-11} \text{ M}$$

[H<sup>+</sup>] & [HCO<sub>3</sub><sup>-</sup>] are both ~ 2.4 × 10<sup>-6</sup> M which is >> 4.7 × 10<sup>-11</sup> M

As noted in class, the actual ocean is basic. The net charge from a series of **cations** (positively charged ions) and minor **anions** (negatively charged ions) is balanced by the total negative charge of the bicarbonate and carbonate ions. We write:

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

where Alk stands for Alkalinity

Henry's Law and the equations for the first and second dissociation constants yield:

$$p\text{CO}_2(\text{vmr}) = \frac{[\text{CO}_2(\text{aq})]}{\alpha} \quad K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(\text{aq})]} \quad K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

The three equations above can be re-arranged to yield:  $p\text{CO}_2(\text{vmr}) = \left( \frac{K_2}{\alpha K_1} \right) \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]}$

If we substitute  $[\text{HCO}_3^-] = \text{Alk} - 2 [\text{CO}_3^{2-}]$  into the eqn above, we arrive at a quadratic eqn for  $[\text{CO}_3^{2-}]$  as a function of  $p\text{CO}_2$  and Alk. Note that  $\alpha$ ,  $K_1$ , and  $K_2$  vary as a function of temperature (T) and ocean salinity (S) (<http://en.wikipedia.org/wiki/Salinity>)

If T, Alk, & S are specified, it is straightforward to solve for  $[\text{CO}_3^{2-}]$  from the quadratic eqn.

Values for  $[\text{CO}_2(\text{aq})]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{H}^+]$  are then found from Henry's law & the dissoc eqns.

Finally, Ocean Carbon is found from  $[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ .

Numerical values on the slides entitled "Uptake of Atmospheric  $\text{CO}_2$  by Oceans" were found in this manner, using Fortran program [http://www.atmos.umd.edu/~rjs/class/code/ocean\\_carbon.f](http://www.atmos.umd.edu/~rjs/class/code/ocean_carbon.f)