

# Global Carbon Cycle AOSC 433/633 & CHEM 433/633

Ross Salawitch & Tim Canty

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2013>

## Goals for today:

- Overview of the Global Carbon Cycle, “scratching below the surface” of the reading material
- Land and ocean uptake of CO<sub>2</sub>
- Connect to prior lectures:  $\Delta F$  &  $\Delta T$ , the “CO<sub>2</sub> response function”, as well as glacial CO<sub>2</sub>

## Lecture 5 7 February 2013

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1

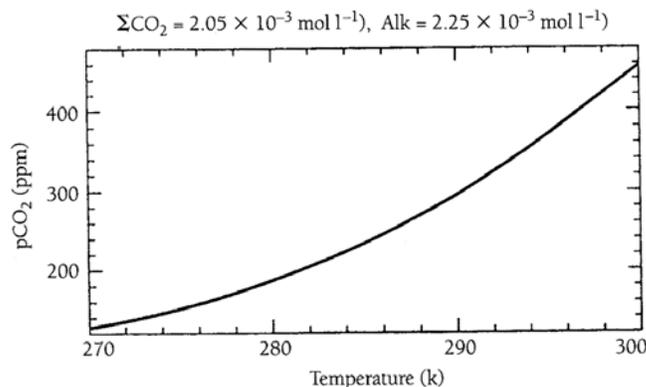
## Admission Ticket, Lecture 4

### Positive Feedback:

climate responds to an initial perturbation in a manner that amplifies the perturbation

### Earth's orbit and CO<sub>2</sub> / CH<sub>4</sub>:

change in Earth's orbit leads to more sunlight during NH summer  
this warms the high-latitude ocean, causing CO<sub>2</sub> to be released  
higher CO<sub>2</sub> leads to additional warming because CO<sub>2</sub> is a GHG  
higher T melts permafrost, releasing trapped CH<sub>4</sub>  
higher CH<sub>4</sub> contributes to even more additional warming

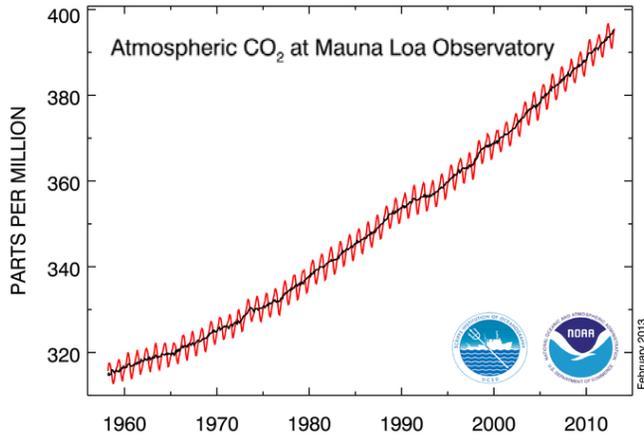


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2

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



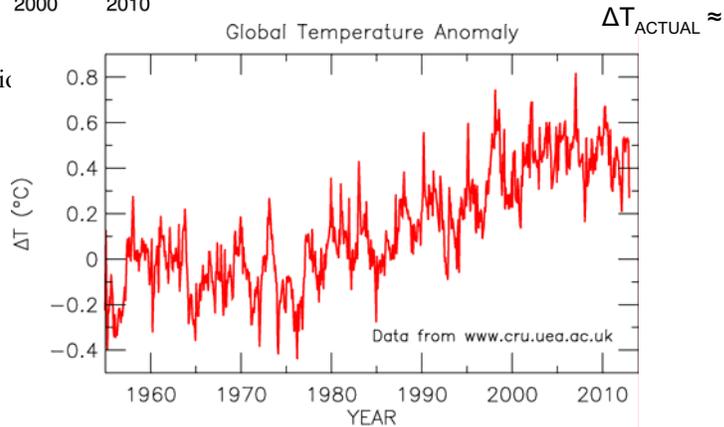
$\Delta(\text{CO}_2)$  years 1959 to 2012 =

$\Delta F =$

$\Delta T_{\text{EXPECTED}} =$

Legacy of Charles Keeling, Scripps Institutio

<http://www.esrl.noaa.gov/gmd/ccgg/trends>



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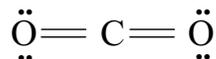
## CO<sub>2</sub> Essentially Inert in the Atmosphere

**Decreasing oxidation number (reduction reactions)**

-4	0	+2	+4
<b>CH<sub>4</sub></b> Methane	<b>CH<sub>2</sub>O</b> Formaldehyde	<b>CO</b> Carbon Monoxide	<b>CO<sub>2</sub></b> Carbon dioxide

**Increasing oxidation number (oxidation reactions)**

Oxidation state represents number of electrons:  
added to an element (negative #) or removed from an element (positive #)



C in CO<sub>2</sub>: has donated two electrons to each oxygen atom,  
completing the L shell of electrons & resulting  
in an electron configuration analogous to helium

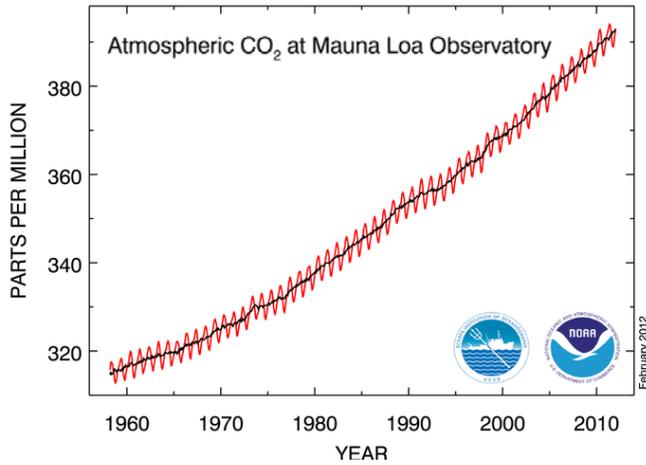
**CO<sub>2</sub>, the most oxidized form of carbon, is essentially inert in the atmosphere.  
Yet, many atmospheric scientists focus their research on the “global carbon cycle”.**

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4

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



$\Delta$  (CO<sub>2</sub>) years 1959 to **2011** = 75.6 ppm

$\Delta$  mass of C = 75.6 ppm ( $10^{-6}$  / ppm)  $\times$   $5.2 \times 10^{21}$  gm  $\times$   
 (12 gm C /mole / 29 gm/mole)  
 =  $1.63 \times 10^{17}$  gm C  
 =  $1.63 \times 10^{17}$  gm C  $\times$   $10^{-6}$  ton/gm  
 =  $1.63 \times 10^{11}$  tons C  
 =  $163 \times 10^9$  tons C = Gtons of C

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

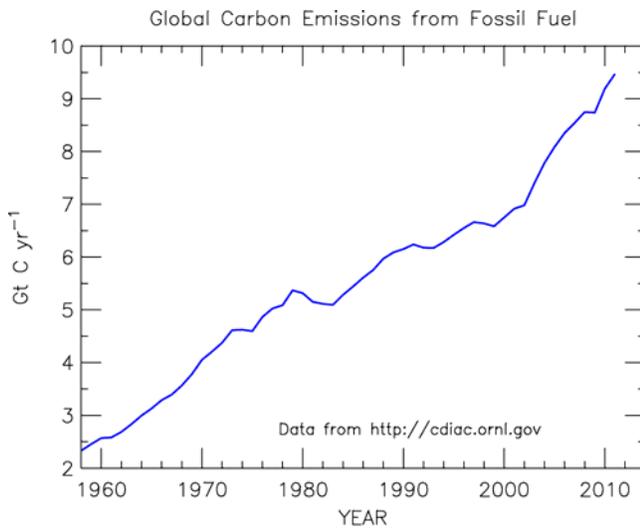
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5

# Global Carbon Cycle



Fossil fuel emissions, 1959 to 2011 = 296 Gt C

$\Delta$  (CO<sub>2</sub>), 1959 to 2011 = 162 Gt C

~55 % of carbon emitted remains in the atmosphere  
 Houghton reading states ~45 %  
 "about half" will suffice ☺

Rest goes to either ?

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6

# Human Release of Carbon

Human activity is presently releasing about 9 Gt (giga tons) or 9,000,000,000 ( $9 \times 10^9$ ) tons of Carbon per year.

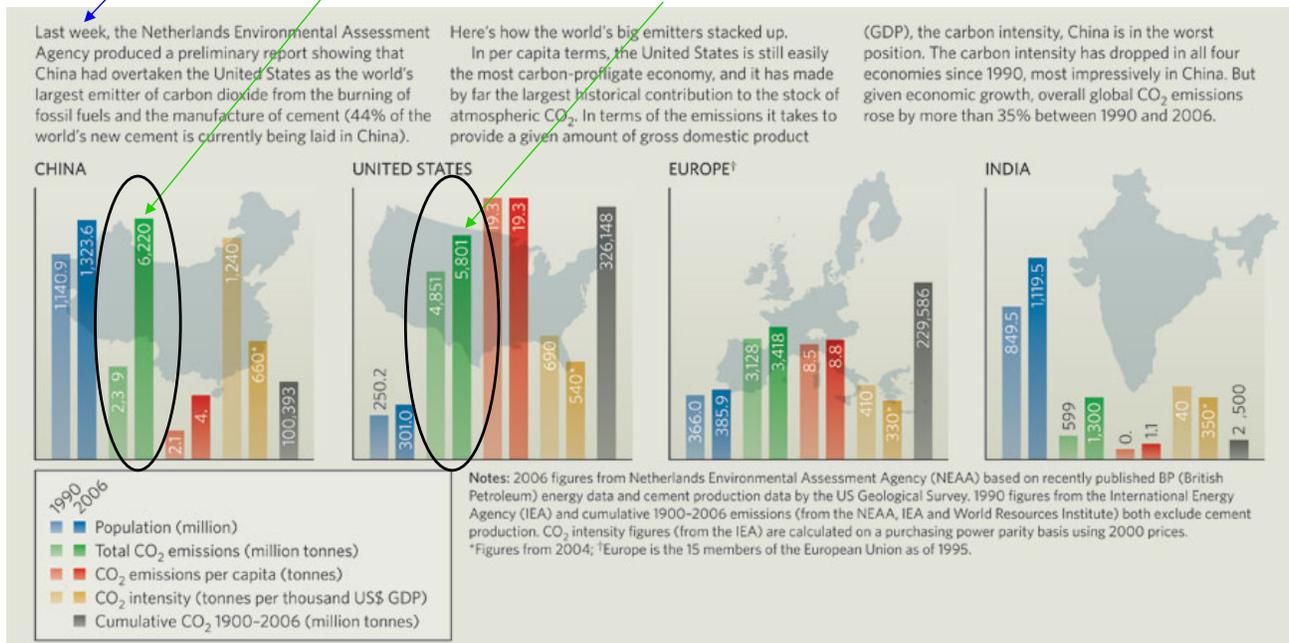
How much is 9 Gt of carbon ?!?

20 June 2007

## World Carbon Emissions

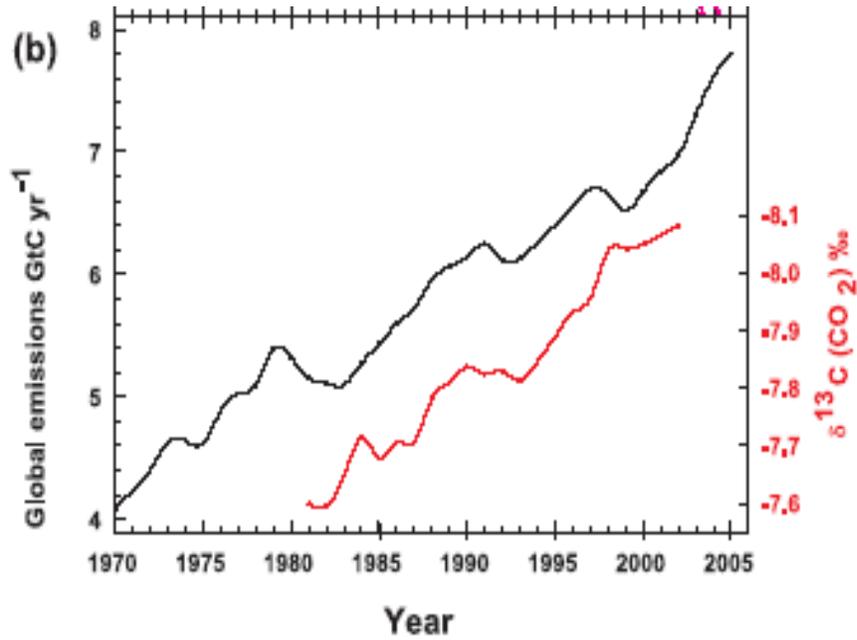
China: 1.70 Gt C per year

US: 1.58 Gt C per year



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)

# $^{13}\text{CO}_2$ Time Evolution: "Fingerprint" of Fossil Fuel Burning



Chapter 2, IPCC 2007

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9

## Atmospheric $\text{CO}_2$ since ~1860

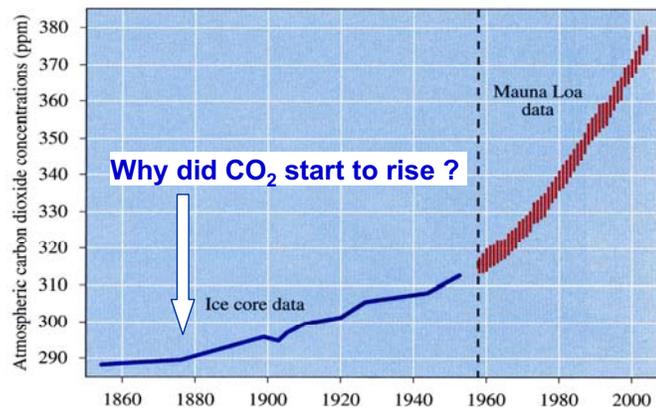


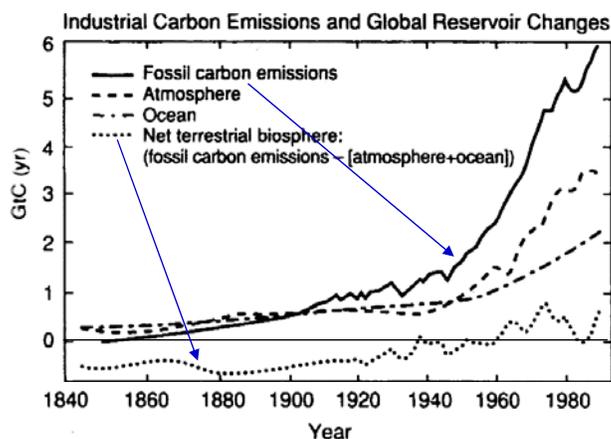
Figure 3.5, *Chemistry in Context*

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10

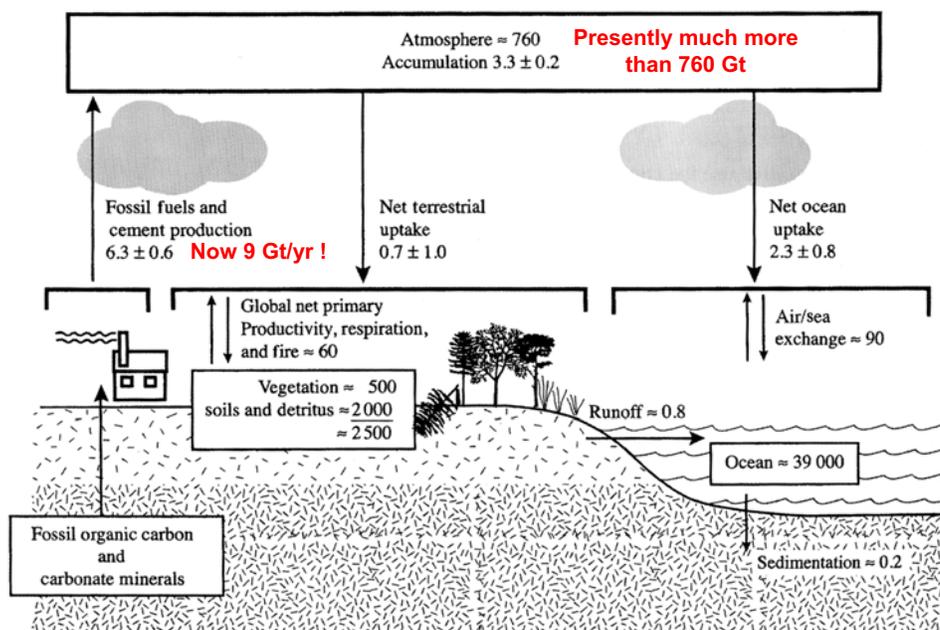
# Atmospheric CO<sub>2</sub> since ~1860



(a)

**Figure 3.3** (a) Fossil carbon emissions (based on statistics of fossil fuel and cement production) and estimates of global reservoir changes: atmosphere (deduced from direct observations and ice core measurements), ocean (calculated with the Geophysical Fluid Dynamics Laboratory (GFDL), University of Princeton, ocean carbon model) and net terrestrial biosphere (calculated as remaining imbalance) from 1840 to 1990. The calculation implies that the terrestrial biosphere was a net source to the atmosphere prior to 1940 (negative values) and has been a net sink since about 1960.

# Global Carbon Cycle



**Figure 3.1** The global carbon cycle, showing the carbon stocks (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).

# Global Carbon Cycle

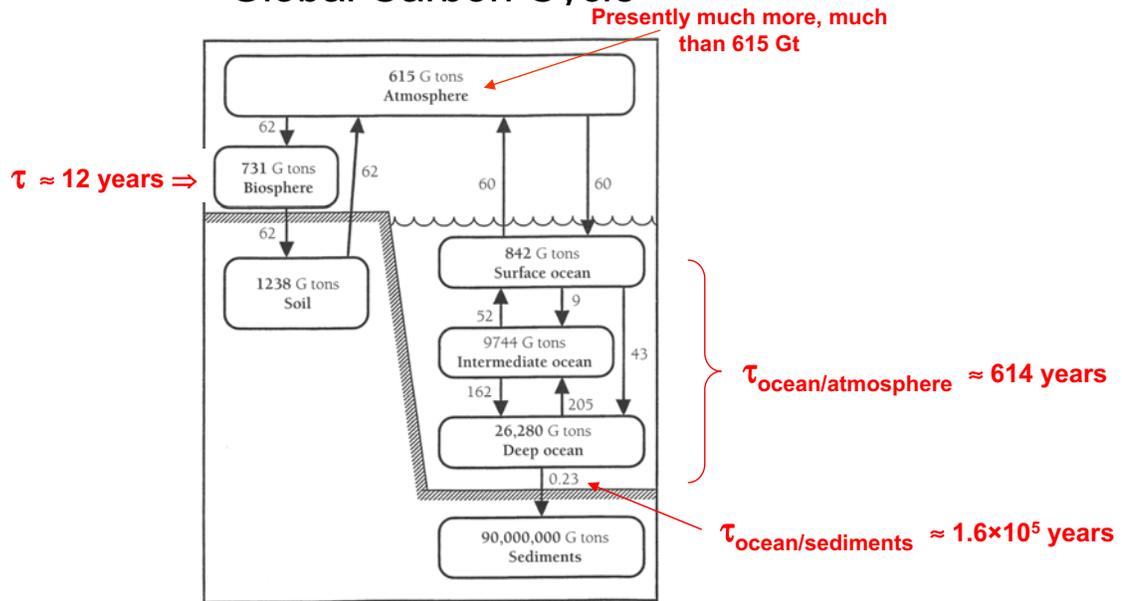


Figure 11.8 Composite model for the global carbon cycle, combining data in Figures 11.5 and 11.6. Reservoir contents are in units of  $10^9$  tons C; transfer rates are in  $10^9$  tons C  $\text{yr}^{-1}$ . Carbon is deposited in sediment both as  $\text{CaCO}_3$  and as organic matter. There is a small release of  $\text{CO}_2$  in steady state from the ocean; this source is employed in weathering of crustal rocks.

McElroy, The Atmospheric Environment, 2002

## 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 ( $\text{W m}^{-2} \text{ppb}^{-1}$ )	Global Warming Potential for Given Time Horizon			
				SAR† (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO <sub>2</sub>	See below <sup>a</sup>	$1.4 \times 10^{-5}$	1	1	1	1
Methane <sup>c</sup>	CH <sub>4</sub>	12 <sup>c</sup>	$3.7 \times 10^{-4}$	21	72	25	7.6
Nitrous oxide	N <sub>2</sub> O	114	$3.03 \times 10^{-3}$	310	289	298	153

Notes:

† 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

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!

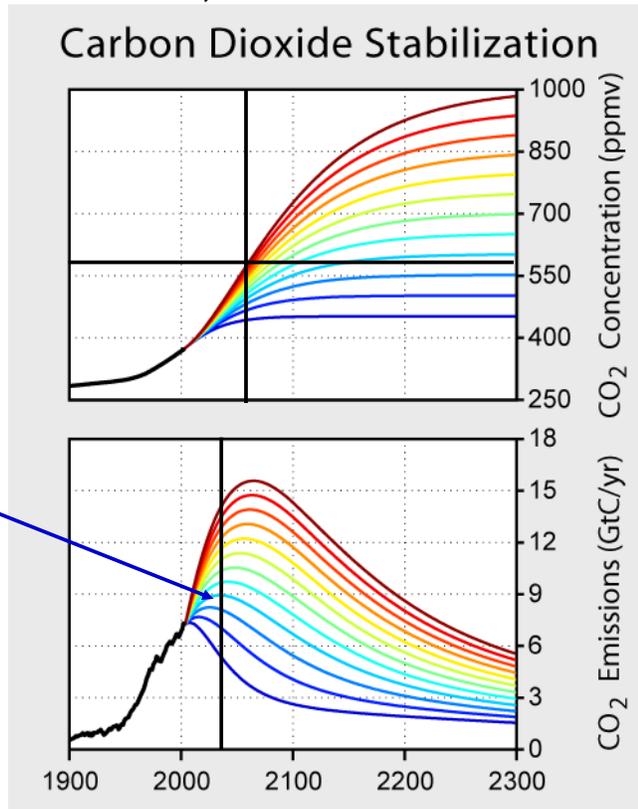


Image: "Global Warming Art" : [http://www.globalwarmingart.com/wiki/Image:Carbon\\_Stabilization\\_Scenarios\\_png](http://www.globalwarmingart.com/wiki/Image:Carbon_Stabilization_Scenarios_png)

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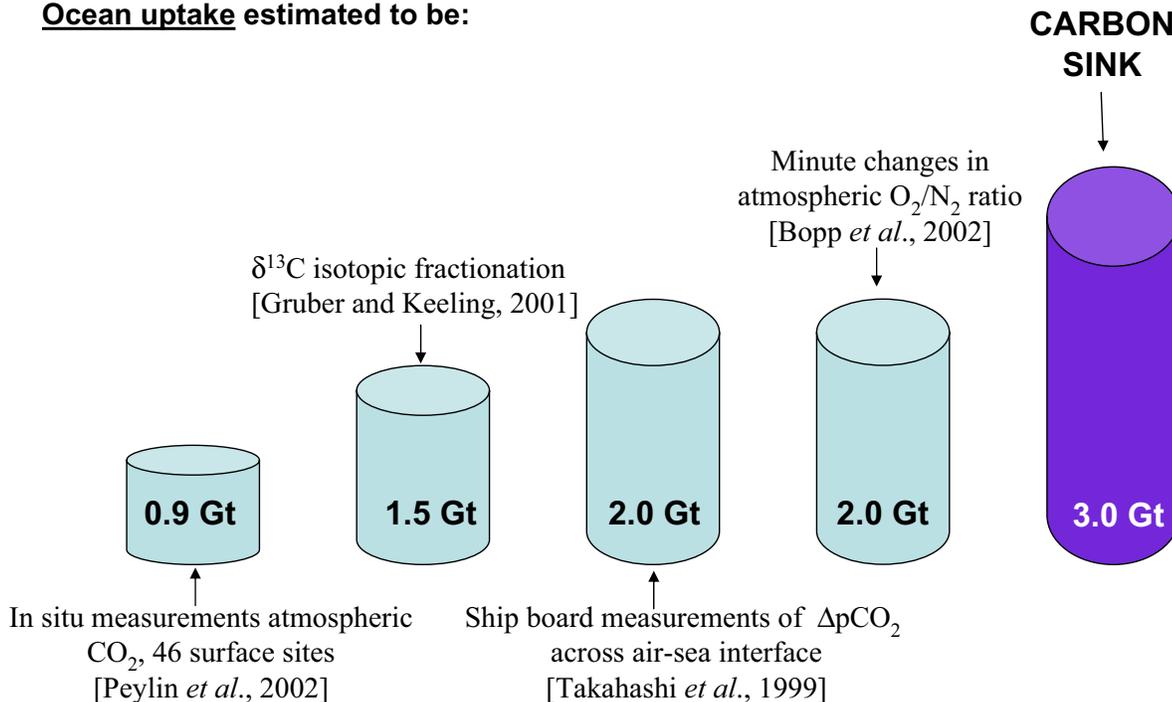
## Global Carbon Cycle

Where is the CO<sub>2</sub> being sequestered?

During the 1990s, humans released ~6 Gt C/yr.

If ~50% stayed in atmosphere, then  $0.5 \times 6 \text{ Gt C/yr} \approx 3.0 \text{ Gt C/yr}$  went to land and oceans

**Ocean uptake estimated to be:**



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# Global Carbon Cycle

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**Land uptake estimated to be:**

0.7 ± 0.7 GtC/yr for North America

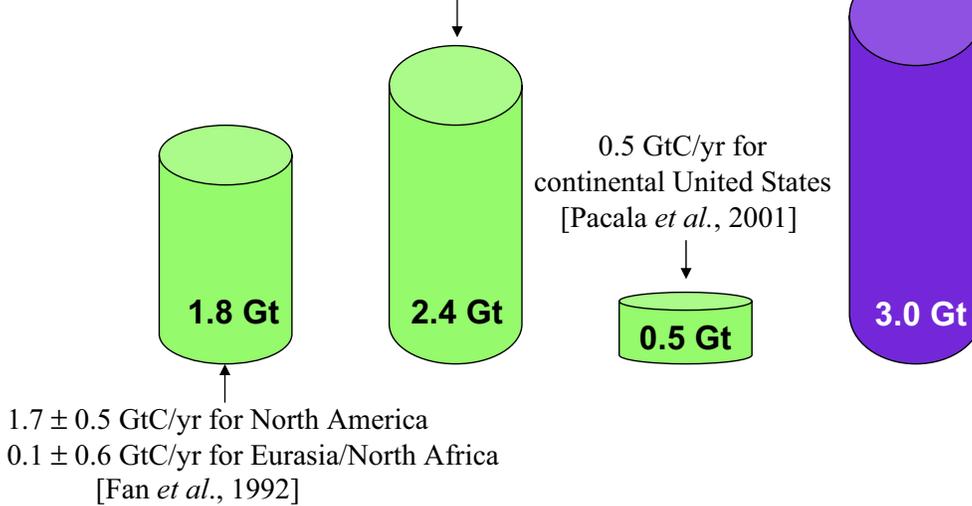
0.5 ± 0.8 GtC/yr for Europe

1.2 ± 0.8 GtC/yr for North Asia

[Bousquet *et al.*, 2000]

**CARBON**

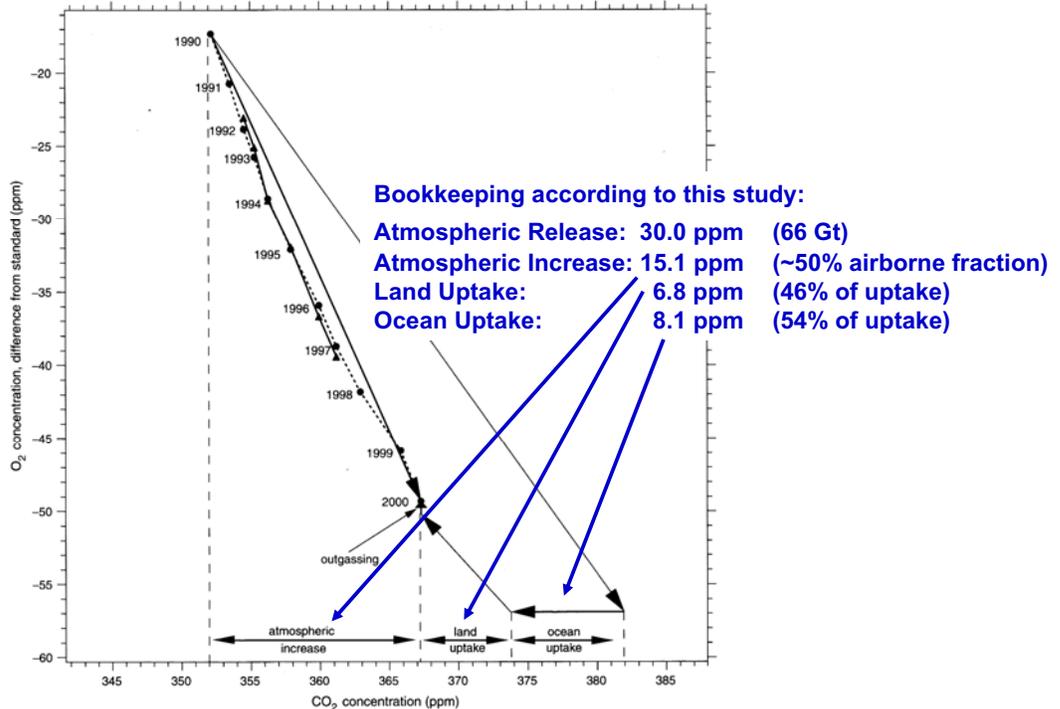
**SINK**



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## 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 labeled '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.

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# 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>

Page 166, Houghton

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19

# 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 and plants lead to several 100 ppm additional CO<sub>2</sub> by end of century

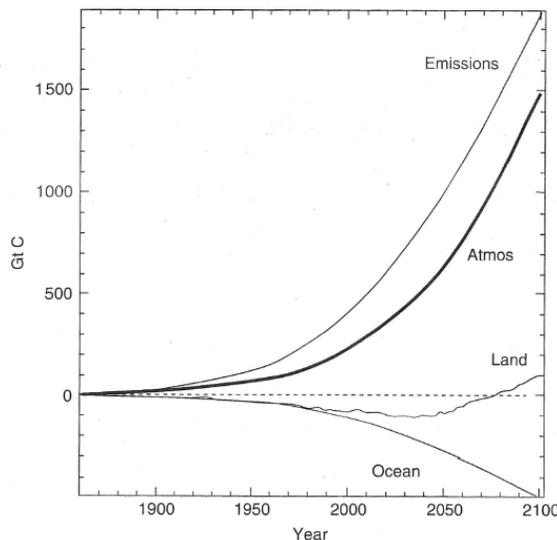
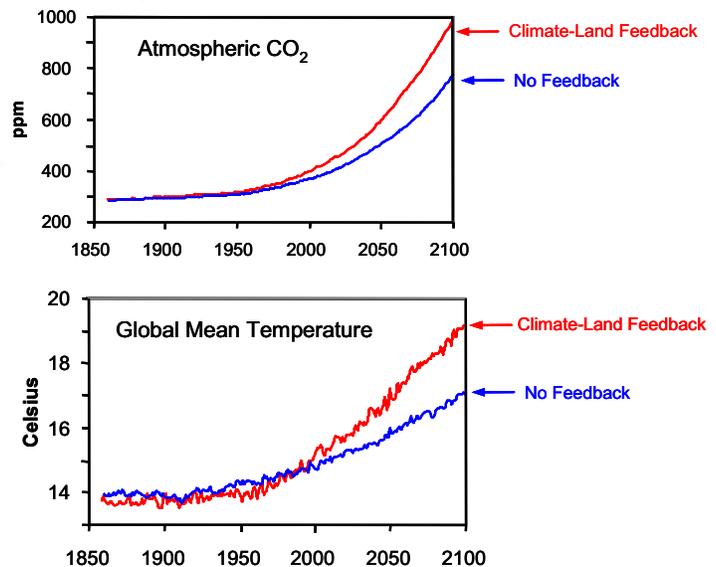


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Page 41, Houghton

### Projected future CO<sub>2</sub> and T for a single fossil fuel carbon emission scenario



Cox et al., *Nature*, 2000

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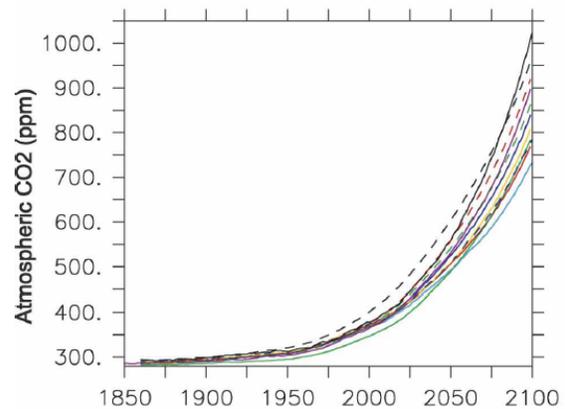
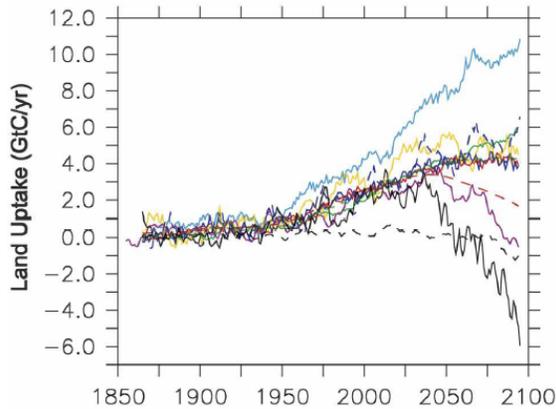
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20

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

Land sink: relatively short lived reservoir

- IPCC 2007 did not consider carbon cycle feedbacks in latest assessment, as there is no scientific consensus on the direction (much less magnitude) of this effect !



**Intercomparison of 250 years of simulated carbon uptake by land and the resulting increase in atmospheric CO<sub>2</sub> by 11 coupled carbon cycle – climate models, using an identical prescribed fossil fuel emission scenario (Friedlingstein *et al.*, 2006)**

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21

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

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<sub>2</sub> ?

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22

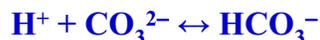
## Uptake of Atmospheric CO<sub>2</sub> by Oceans

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

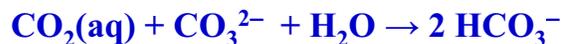
Henry's law governs ratio of CO<sub>2</sub>(aq) to pCO<sub>2</sub>,

where pCO<sub>2</sub> is the atmospheric CO<sub>2</sub> mixing ratio:  $\text{CO}_2(\text{aq}) = \alpha \text{pCO}_2$

The following aqueous phase equilibrium reactions occur:



If water is exposed to higher levels of pCO<sub>2</sub>, leading to larger CO<sub>2</sub>(aq), the following net reaction is considered to occur:



As CO<sub>2</sub> dissolves, CO<sub>3</sub><sup>2-</sup> is converted to HCO<sub>3</sub><sup>-</sup>

Also, the following aqueous equilibrium is maintained:

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11} \text{ M (at 298 K)}$$

So ... as CO<sub>2</sub>(aq) rises due to rising atmospheric CO<sub>2</sub>  
CO<sub>3</sub><sup>2-</sup> will fall and [HCO<sub>3</sub><sup>-</sup>] will rise and therefore ...  
[H<sup>+</sup>] must **RISE** (for above equilibrium to be maintained)

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

Acidity of actual ocean is much more complex than pure rainwater: *ocean is slightly basic*

Dominant **cations** are Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>

Most common **anions** are Cl<sup>-</sup>, Br<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>

Positive charge of cations *slightly larger* than negative charge of anions:

difference is called "**Ocean Alkalinity**" and is balanced by HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>

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

Atmospheric CO<sub>2</sub>, CO<sub>2</sub>(aq), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> follow same relation as given on prior slide.

We define Ocean Carbon (traditionally DIC for dissolved inorganic carbon) as :

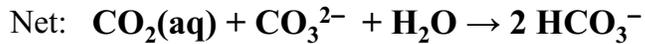
$$\text{Ocean Carbon } [\Sigma \text{CO}_2] = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

and note that the relation between Ocean Carbon and its components depends on temperature, alkalinity, salinity (saltiness), and atmospheric CO<sub>2</sub>

**The mathematics relating ocean acidity to pCO<sub>2</sub>, T & Alkalinity  
is given on Extra Slide #3**

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

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



Atmospheric CO <sub>2</sub>	280 ppm Pre-Industrial	385 ppm Present Day	560 ppm 2 × Pre-Indus.
Ocean Carbon	2020 × 10 <sup>-6</sup> M	2070 × 10 <sup>-6</sup> M	2122 × 10 <sup>-6</sup> M
[HCO <sub>3</sub> <sup>-</sup> ]	1772 × 10 <sup>-6</sup> M	1865 × 10 <sup>-6</sup> M	1957 × 10 <sup>-6</sup> M
[CO <sub>2</sub> (aq)]	9.1 × 10 <sup>-6</sup> M	12.6 × 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	193 × 10 <sup>-6</sup> M	146 × 10 <sup>-6</sup> M
pH	8.32	8.20	8.06

$$\begin{aligned} \text{Revelle Factor} &= \frac{\Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}}}{\Delta \text{Ocean Carbon} / \langle \text{Ocean Carbon} \rangle_{\text{AVERAGE}}} \\ &= \frac{105/332.5}{50/2045} = 12.9 \text{ (from pre-industrial to present-day CO}_2\text{)} \\ &= \frac{175/472.5}{52/2096} = 14.9 \text{ (from present-day to 2} \times \text{ pre-industrial CO}_2\text{)} \end{aligned}$$

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25

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

$$\begin{aligned} \Delta \text{Ocean Carbon} / \langle \text{Ocean Carbon} \rangle_{\text{AVERAGE}} \text{ used to be } & \frac{\Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}}}{12.9} \\ \text{or } & 0.078 \times \Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}} \end{aligned}$$

$$\begin{aligned} \Delta \text{Ocean Carbon} / \langle \text{Ocean Carbon} \rangle_{\text{AVERAGE}} \text{ now } & \frac{\Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}}}{14.9} \\ \text{or } & 0.067 \times \Delta \text{Atmos}_{\text{CO}_2} / \langle \text{Atmos}_{\text{CO}_2} \rangle_{\text{AVERAGE}} \end{aligned}$$

**Capacity of ocean to absorb carbon decreases over time!**

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26

# Revelle Factor

In 1957, Revelle co-authored a paper with Hans Suess that suggested Earth's oceans would absorb excess carbon dioxide generated by humanity in the future at a rate less than predicted...

**Revelle and Suess described the "buffer factor", now known as the "Revelle factor", which is the resistance to atmospheric carbon dioxide being absorbed by the ocean surface layer posed by bicarbonate chemistry.** Essentially, to enter the ocean, carbon dioxide gas has to partition into one of the components of carbonic acid: carbonate ion ( $\text{CO}_3^{2-}$ ), bicarbonate ion ( $\text{HCO}_3^-$ ), or carbonic acid ( $\text{H}_2\text{CO}_3$ ). This chemistry limits how fast atmospheric carbon dioxide can enter the surface ocean, with the rate limiting reactant, **carbonate ion**, decreasing as atmospheric  $\text{CO}_2$  rises.

Al Gore mentions Roger Revelle as a "personal inspiration" in a segment of *An Inconvenient Truth*

From [http://en.wikipedia.org/wiki/Roger\\_Revelle](http://en.wikipedia.org/wiki/Roger_Revelle)  
with some editing ☺

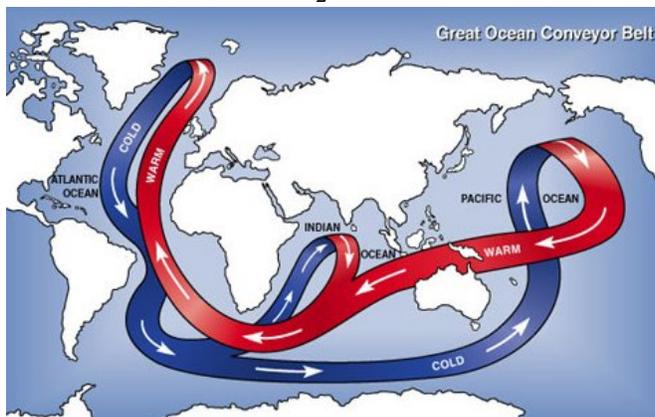
## Uptake of Atmospheric $\text{CO}_2$ by Oceans

### – Solubility Pump:

- More  $\text{CO}_2$  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  $\text{CO}_2$
- 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  $\text{NO}_3^-$ ,  $\text{PO}_4^-$ , and  $\text{Fe}^{2+}$  &  $\text{Fe}^{3+}$ . Ocean biology is never carbon limited.
- Detrital material "rains" from surface to deep waters, contributing to higher  $\text{CO}_2$  in intermediate and deep waters



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

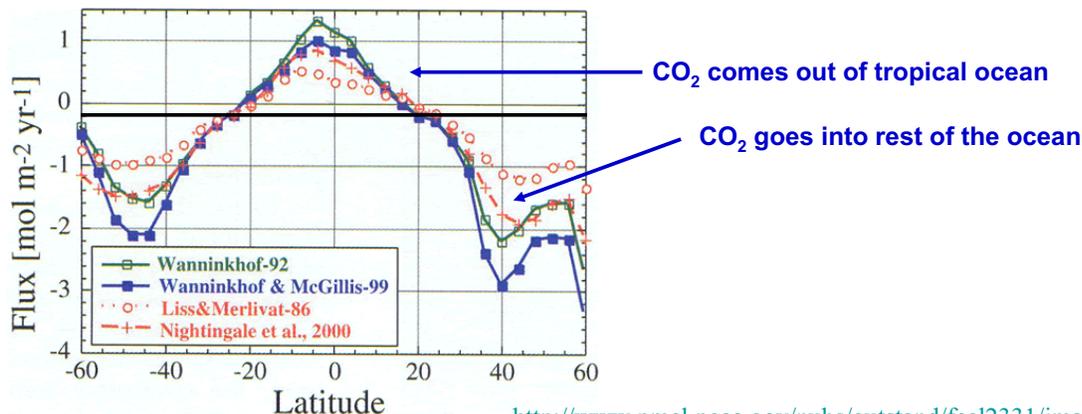
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<http://www.pmel.noaa.gov/pubs/outstand/feel2331/images/fig05.gif>

29

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

### Glacial-to-interglacial variations in the carbon isotopic composition of atmospheric CO<sub>2</sub>

NATURE · VOL 357

11 JUNE 1992

Bruno D. Marino, Michael B. McElroy, Ross J. Salawitch & W. Geoffrey Spaulding\*

Lower concentrations of CO<sub>2</sub> during glacial times are attributed to an increased supply of nutrients to the surface of the low-latitude ocean, and to biological and physical influences resulting in an increase in the abundance of CO<sub>3</sub><sup>2-</sup> in WSW.

WSW: Warm Surface Waters

See <http://www.nature.com/nature/journal/v357/n6378/abs/357461a0.html>

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

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

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.

See <http://www.agu.org/journals/pa/v005/i001/PA005i001p00001>

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30

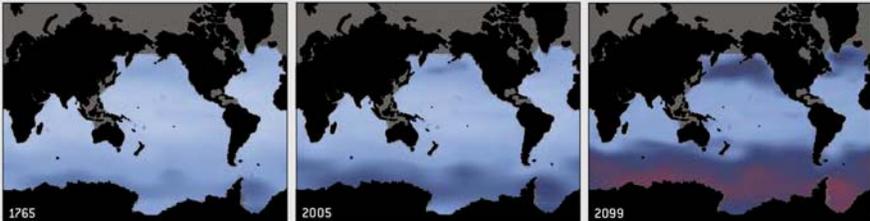
# Uptake of Atmospheric CO<sub>2</sub> by Oceans

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)**

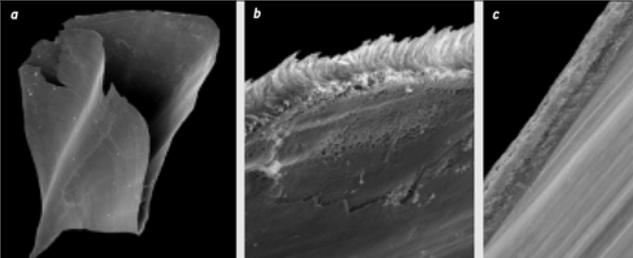
**THE (RAGGED) FUTURE OF ARAGONITE**

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

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31

## Extra Slide 1

### Carbon Water Chemistry

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

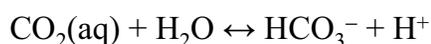
What is acidity of water in equilibrium with atmospheric CO<sub>2</sub> ?

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

For CO<sub>2</sub> = 390 ppm:

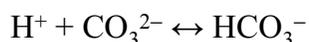
$$[CO_2(aq)] = 3.4 \times 10^{-2} \text{ M} / \text{atm } 3.9 \times 10^{-4} \text{ atm} = 1.326 \times 10^{-5} \text{ M}$$

First equilibrium between CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> (bicarbonate), and H<sup>+</sup>



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

Second equilibrium between CO<sub>3</sub><sup>2-</sup> (carbonate), HCO<sub>3</sub><sup>-</sup>, and H<sup>+</sup>



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

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

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32

## Extra Slide 2

# Carbon Water Chemistry

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

Shortcut:

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

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

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

$$\text{i.e., that } [\text{H}^+] \approx [\text{HCO}_3^-] \text{ and that both are } \gg [\text{CO}_3^{2-}]$$

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

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

Is the **assumption** justified? :

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

$$[\text{H}^+] \text{ \& } [\text{HCO}_3^-] \text{ are both } \sim 2.4 \times 10^{-6} \text{ M which is } \gg 4.7 \times 10^{-11} \text{ M}$$

## Extra Slide 3

# Ocean Acidity

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:

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

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

If we substitute [HCO<sub>3</sub><sup>-</sup>] = Alk - 2 [CO<sub>3</sub><sup>2-</sup>] into the eqn above, we arrive at a quadratic eqn for [CO<sub>3</sub><sup>2-</sup>] as a function of pCO<sub>2</sub> and Alk. Note that α, K<sub>1</sub>, and K<sub>2</sub> vary as a function of temperature (T) and ocean salinity (S) (<http://en.wikipedia.org/wiki/Salinity>)

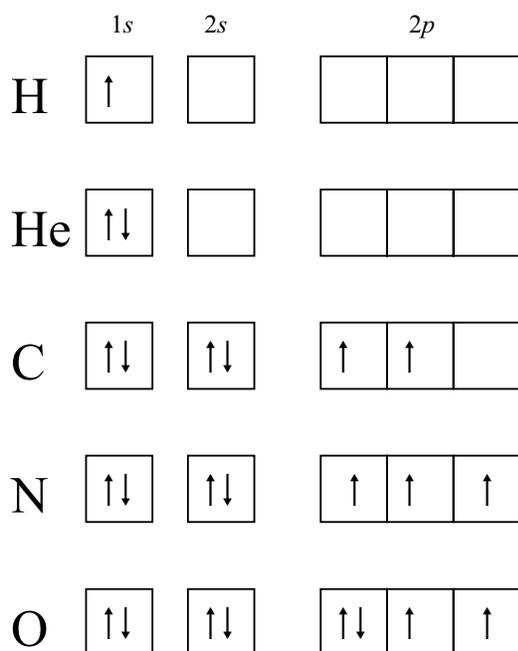
If T, Alk, & S are specified, it is straightforward to solve for [CO<sub>3</sub><sup>2-</sup>] from the quadratic eqn.

Values for [CO<sub>2</sub>(aq)], [HCO<sub>3</sub><sup>-</sup>], and [H<sup>+</sup>] are then found from Henry's law & the dissoc eqns.

Finally, Ocean Carbon is found from [CO<sub>2</sub>(aq)] + [HCO<sub>3</sub><sup>-</sup>] + [CO<sub>3</sub><sup>2-</sup>].

Numerical values on the slides entitled "Uptake of Atmospheric CO<sub>2</sub> by Oceans" were found in this manner, using Fortran program [http://www.atmos.umd.edu/~rjs/class/spr2012/code/ocean\\_carbon.f](http://www.atmos.umd.edu/~rjs/class/spr2012/code/ocean_carbon.f)

## Orbital Configurations



If a molecule is *oxidized*:

it has lost an electron

O : greedy for electrons

If a molecule is *reduced*:

it has *gained* an electron

H : eager to give away its lone electron