Global Carbon Cycle

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2024
https://umd.instructure.com/courses/1367293

Goals for today:

- **Overview of the Global Carbon Cycle "scratching below the surface"**
- **Ocean and land uptake of CO_2 : past and future**
- **Policy to reduce emissions of CO_2**

Lecture 5

12 September 2024

Geological Evolution of Earth's Atmosphere:
Early Atmosphere: Photosynthesis

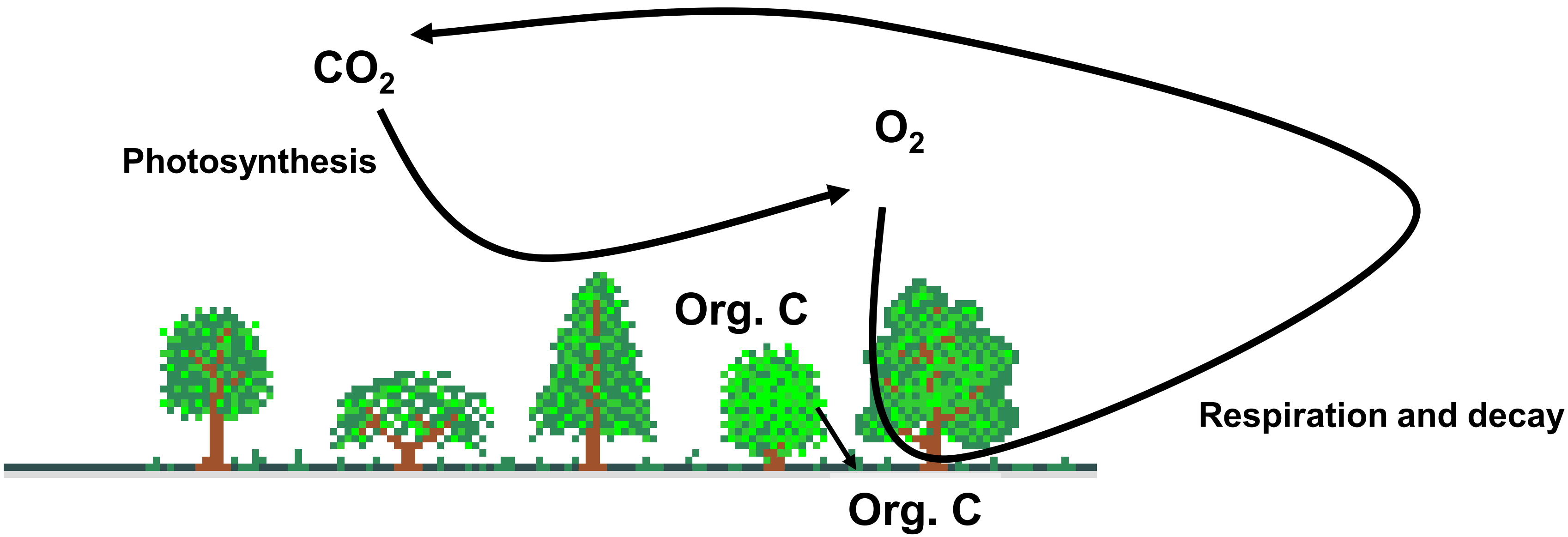
Lecture 01

- **Photosynthesis: Source of O_2**

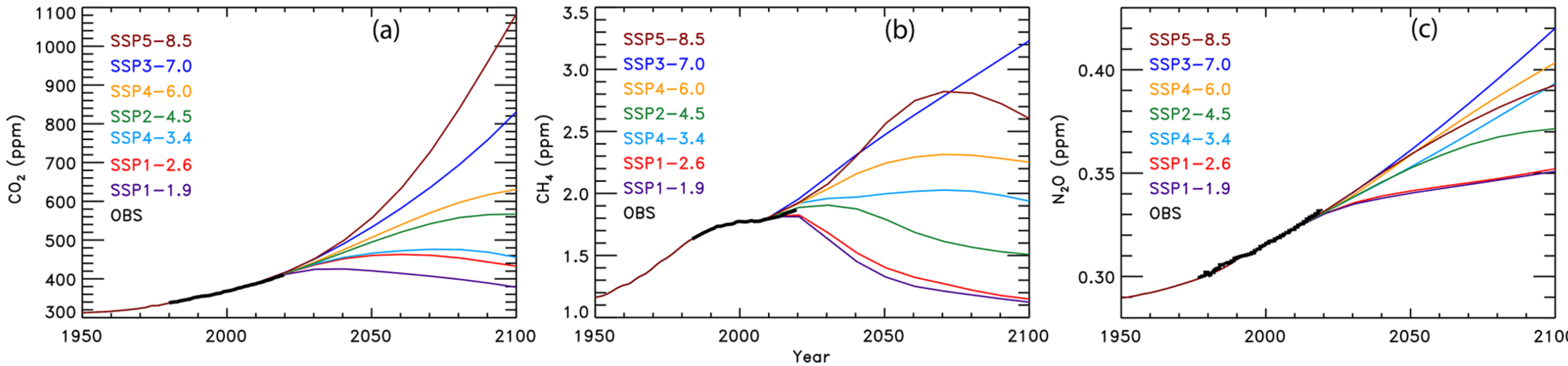
$$6CO_2 + 6H_2O + energy \rightarrow C_6H_{12}O_6 + 6\ O_2$$

- **Respiration and Decay: Sink of O_2**

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6CO_2 + 6H_2O + energy$$



Background



- SSP: Share Socioeconomic Pathways (SSPs)
  Number represents ΔRF of climate (W m^{-2}) at the end of this century
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups
- What is the utility of "command central" providing GHG scenarios to the climate model groups?

Figure from McBride et al., 2021: https://esd.copernicus.org/articles/12/545/2021

Motivation 1

CO_2 is long lived: society must reduce emissions soon or we will be committed to dramatic, future increases in [CO_2]

Curves for which [CO_2] levels off at ~550 ppm or less have emissions peaking NOW !

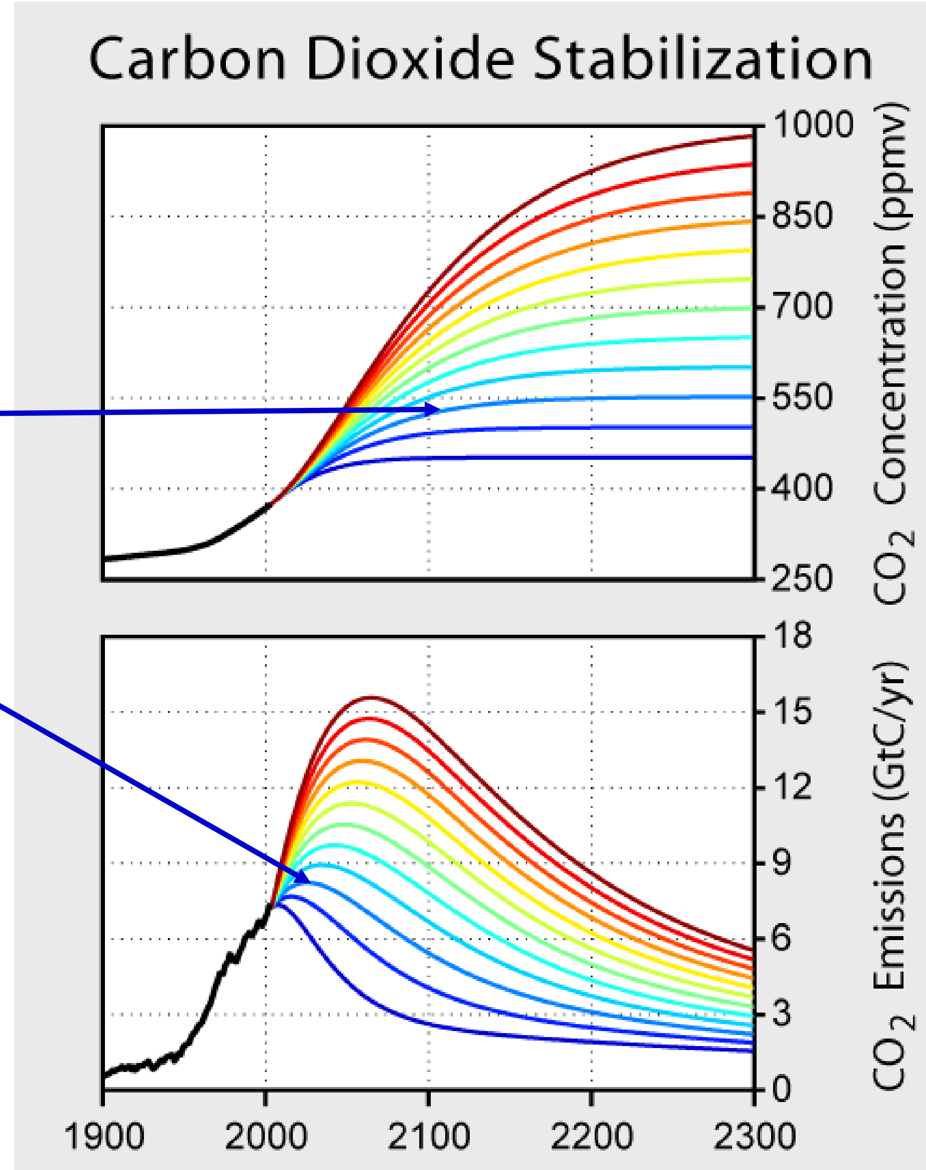
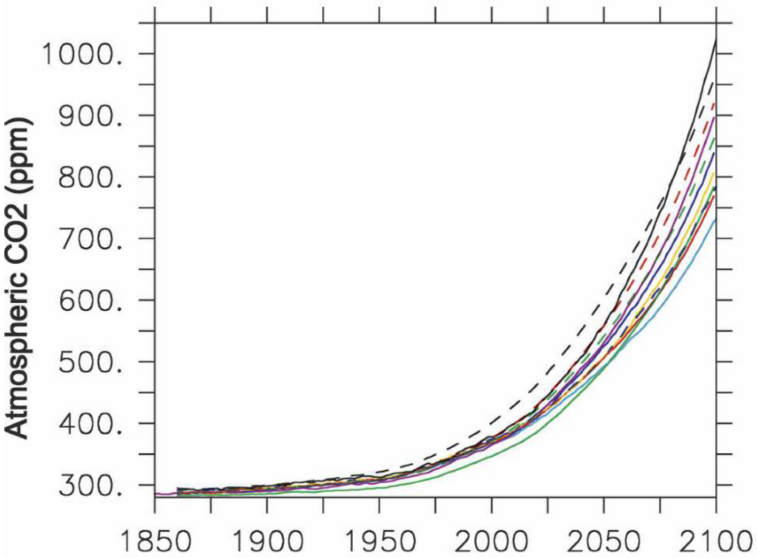
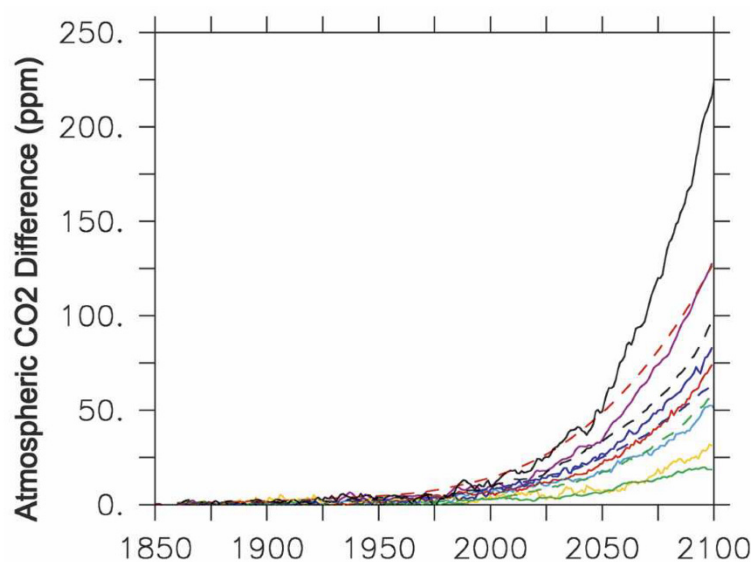


Image: "Global Warming Art" : http://archive.is/JT5rO

Motivation 2



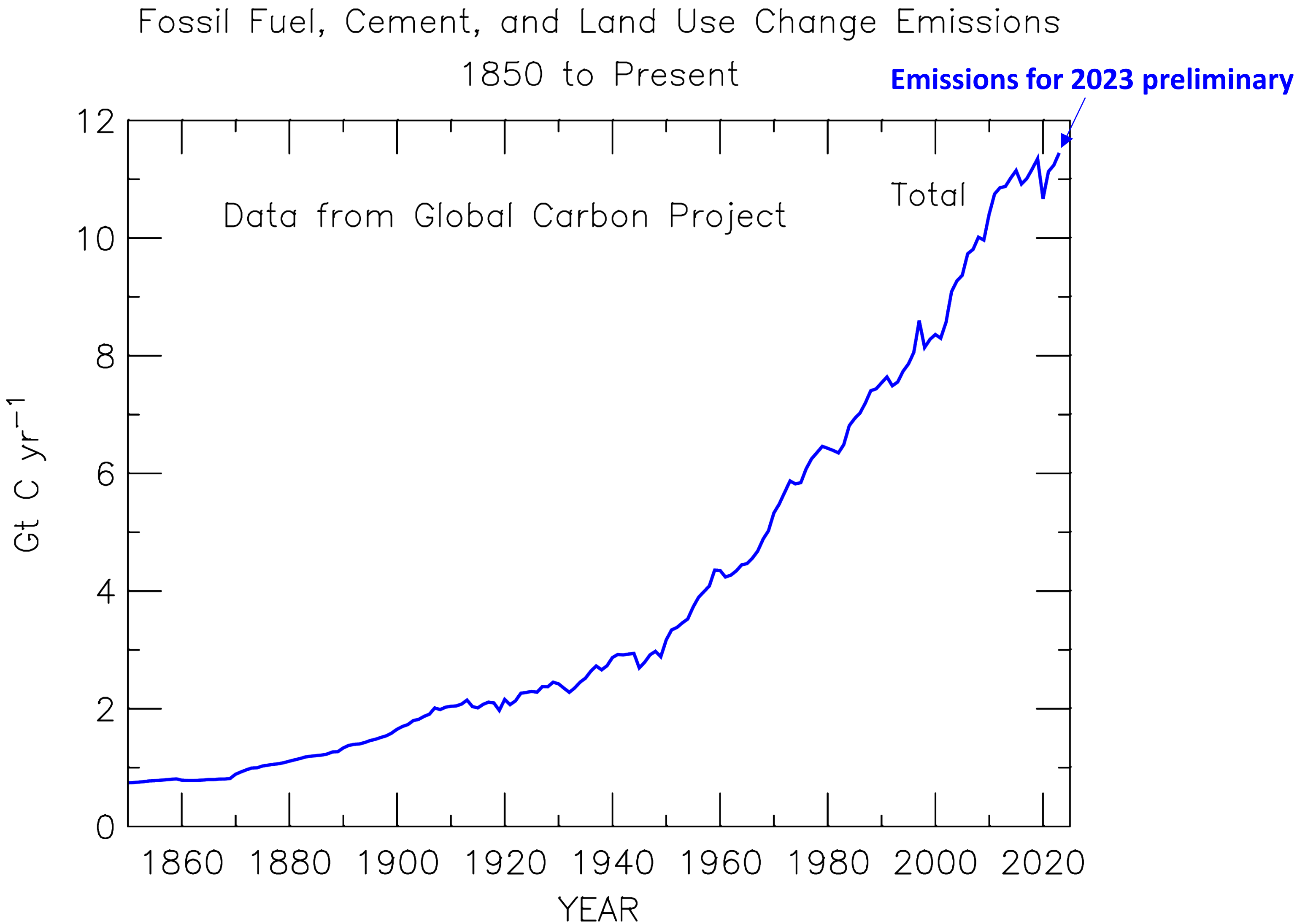


- Prior slides examined atmospheric CO_2 from a single model of the global carbon cycle

- Friedlingstein et al. (2006) compared CO_2 from **11** different coupled climate-carbon cycle models, each constrained by the *same* specified time series of anthropogenic 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 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!)



Note: Gt is an abbreviation for giga tons, or 10^9 tons. Here we are using *metric tons*:
1 metric ton = 10^3 kg ; therefore, 1 Giga ton = 10^{15} g, where g is grams.

Modern CO_2 Record

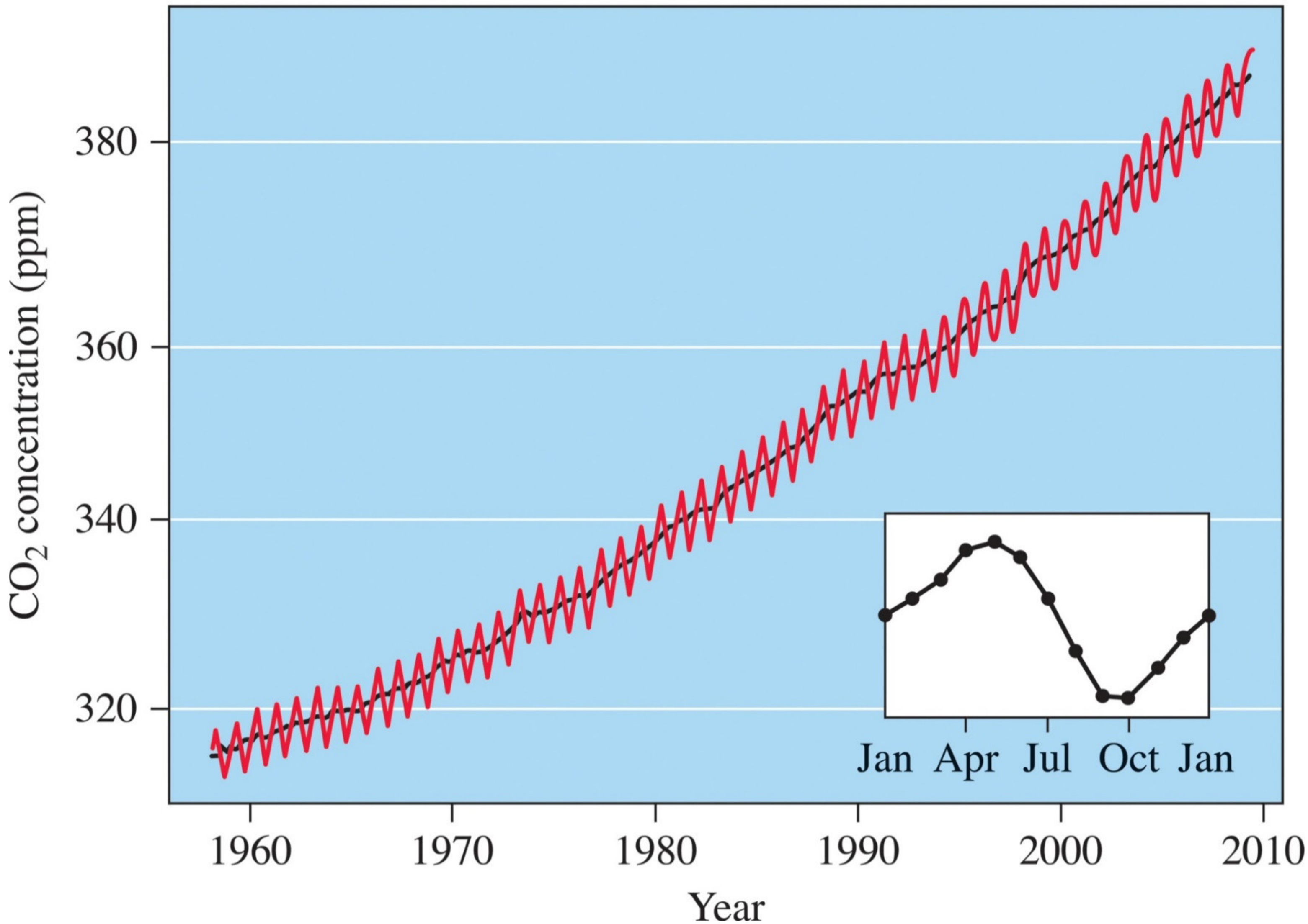


Figure 3.3, Chemistry in Context

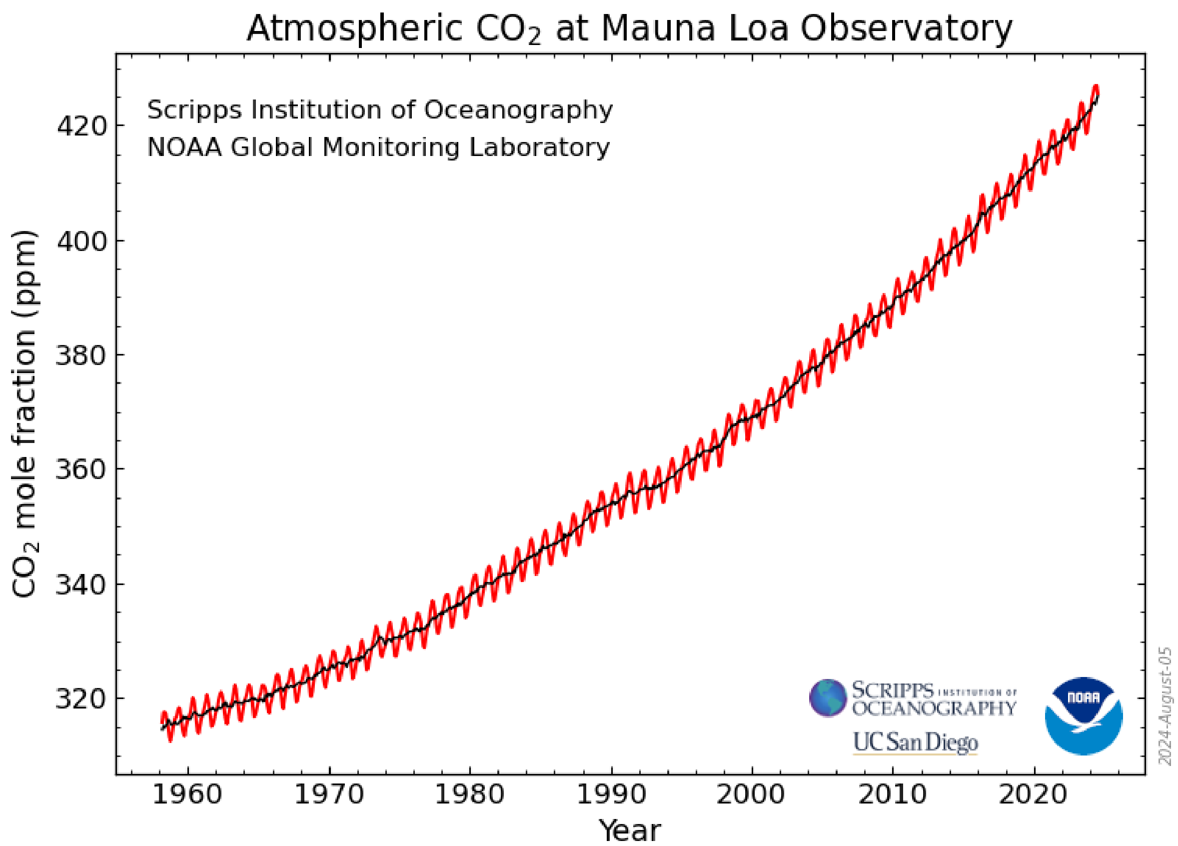
Modern CO_2 Record

Combustion:

Gasoline (octane) $2\ C_8H_{18} + 25\ O_2$ + Small Source of Energy → $16\ CO_2 + 18\ H_2O$ + Lots of Energy

Natural gas (methane) $CH_4 + 2\ O_2$ + Small Source of Energy → $CO_2 + 2\ H_2O$ + Lots of Energy

Coal $C_{135}H_{96}O_9NS + 309\ O_2$ + Small Source of Energy → $135\ CO_2 + 48\ H_2O$ + Lots of Energy + Other Pollutants



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

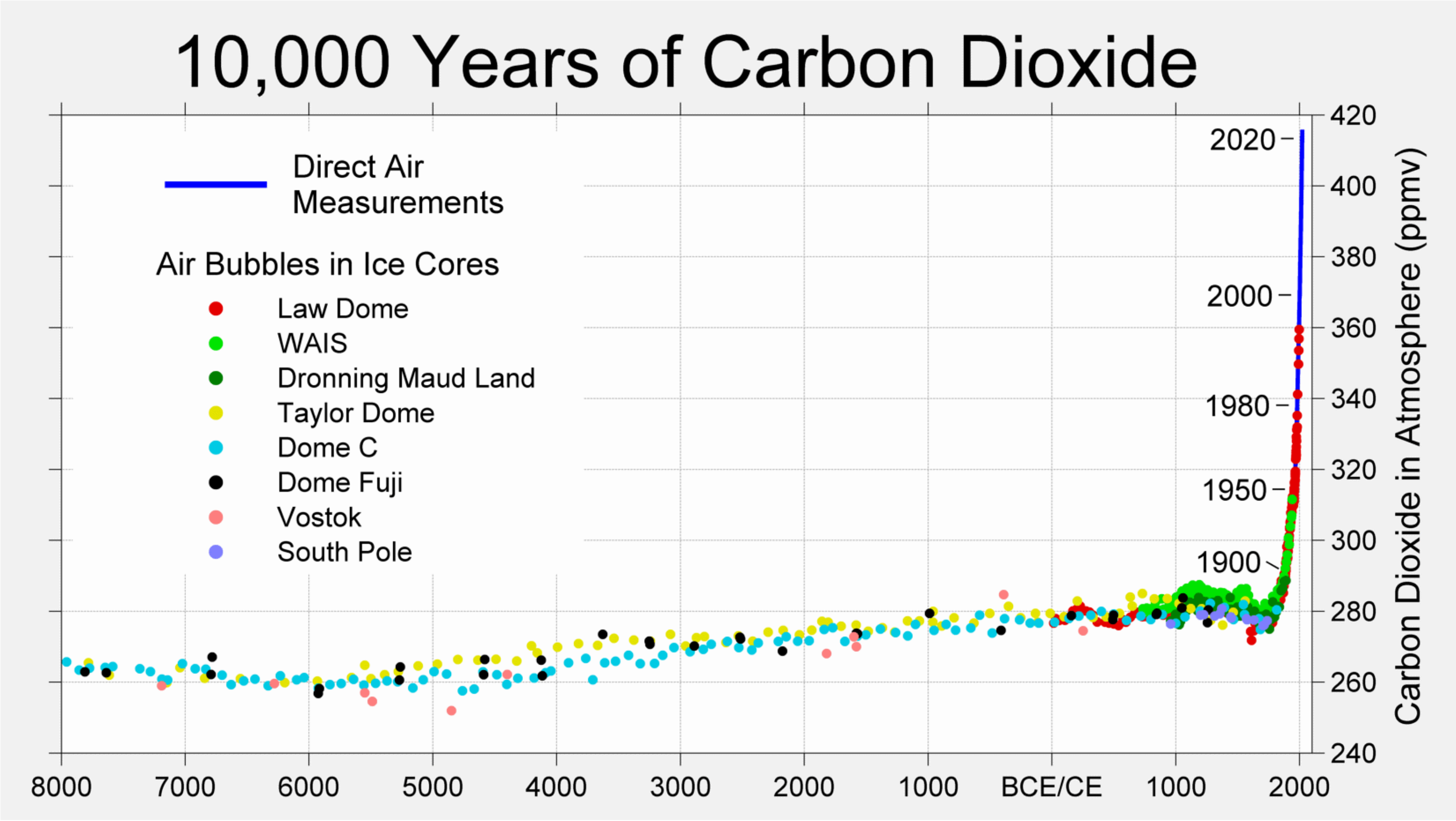
https://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png

See also https://www.co2.earth/daily-co2 and https://gml.noaa.gov/ccgg/trends/global.html

Carbon Dioxide (CO_2): The Past Eight Millennium

Combustion:

Gasoline (octane)	$2\ C_8H_{18} + 25\ O_2$ + Small Source of Energy	→	$16\ CO_2 + 18\ H_2O$ + Lots of Energy
Natural gas (methane)	$CH_4 + 2\ O_2$ + Small Source of Energy	→	$CO_2 + 2\ H_2O$ + Lots of Energy
Coal	$C_{135}H_{96}O_9NS + 309\ O_2$ + Small Source of Energy	→	$135\ CO_2 + 48\ H_2O$ + Lots of Energy + Other Pollutants



https://twitter.com/RARohde/status/1443890623371677698

Robert Rohde: https://twitter.com/RARohde

Modern CO_2 Record

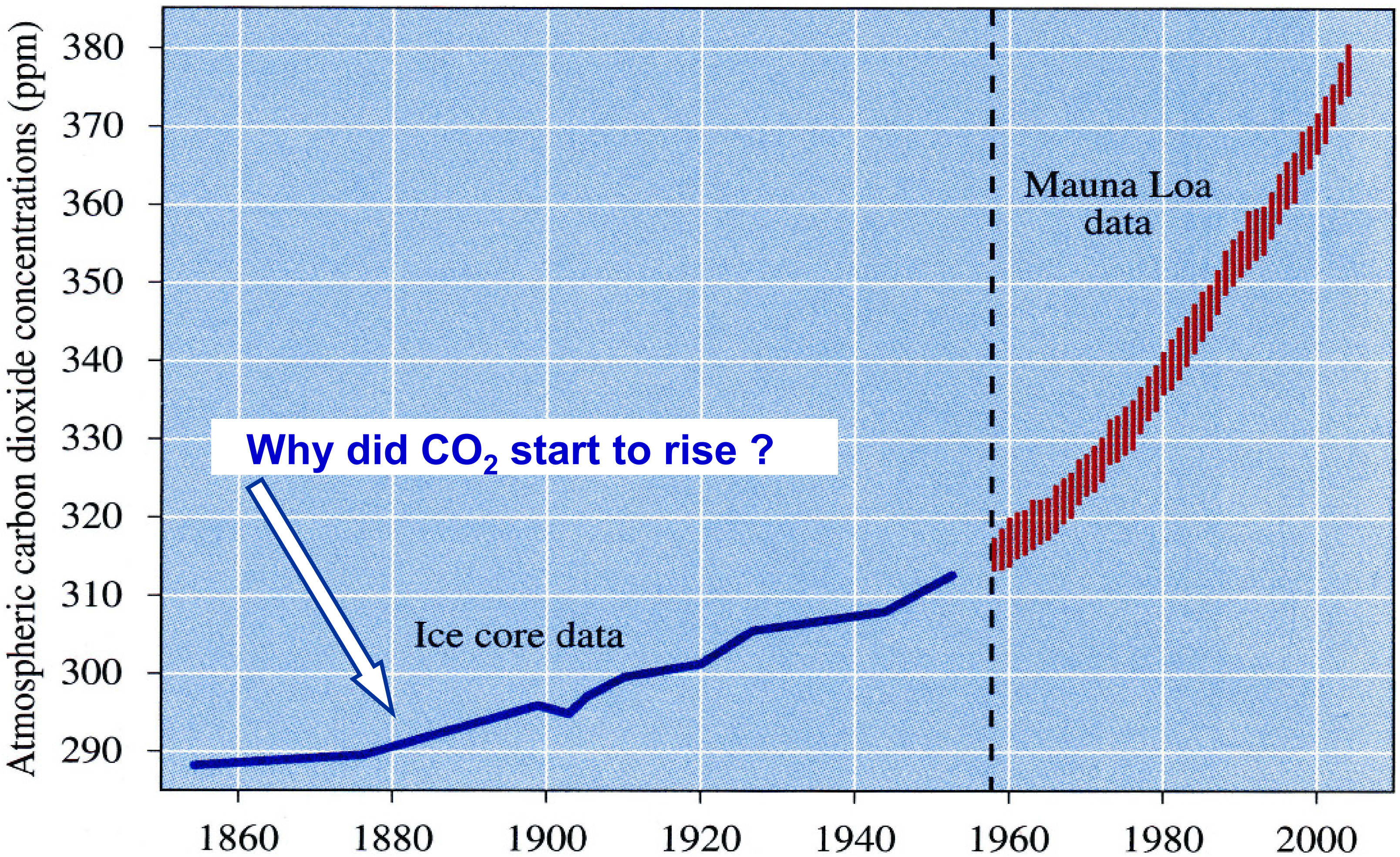
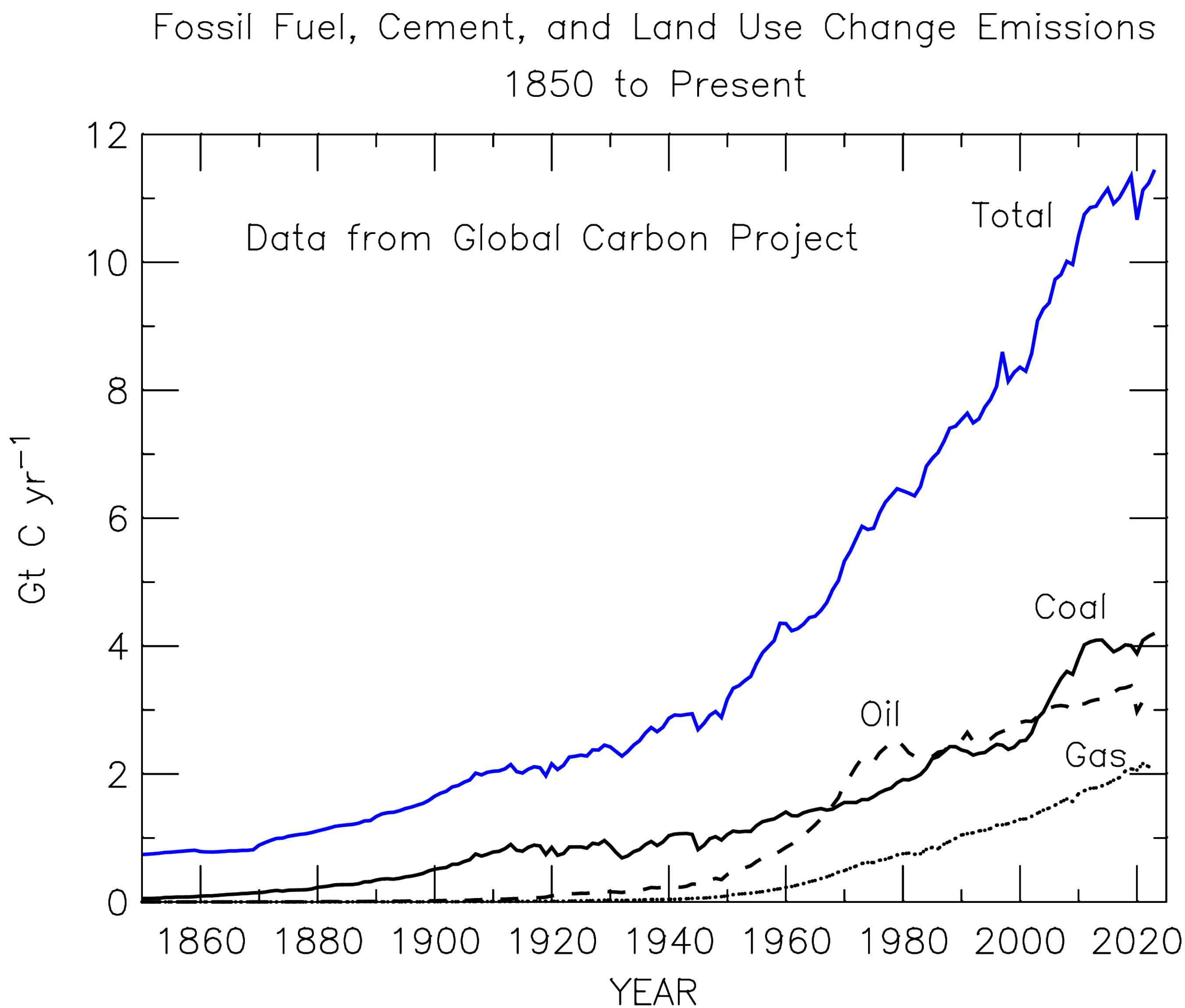


Figure 3.5, *Chemistry in Context, 7th Edition*


Fossil Fuel, Cement, and Land Use Change Emissions
1850 to Present
Data from Global Carbon Project
Total
Coal
Oil
Gas
Gt C yr^{-1}
0
2
4
6
8
10
12
1860
1880
1900
1920
1940
1960
1980
2000
2020
YEAR

Human "Fingerprints" on Atmospheric CO_2

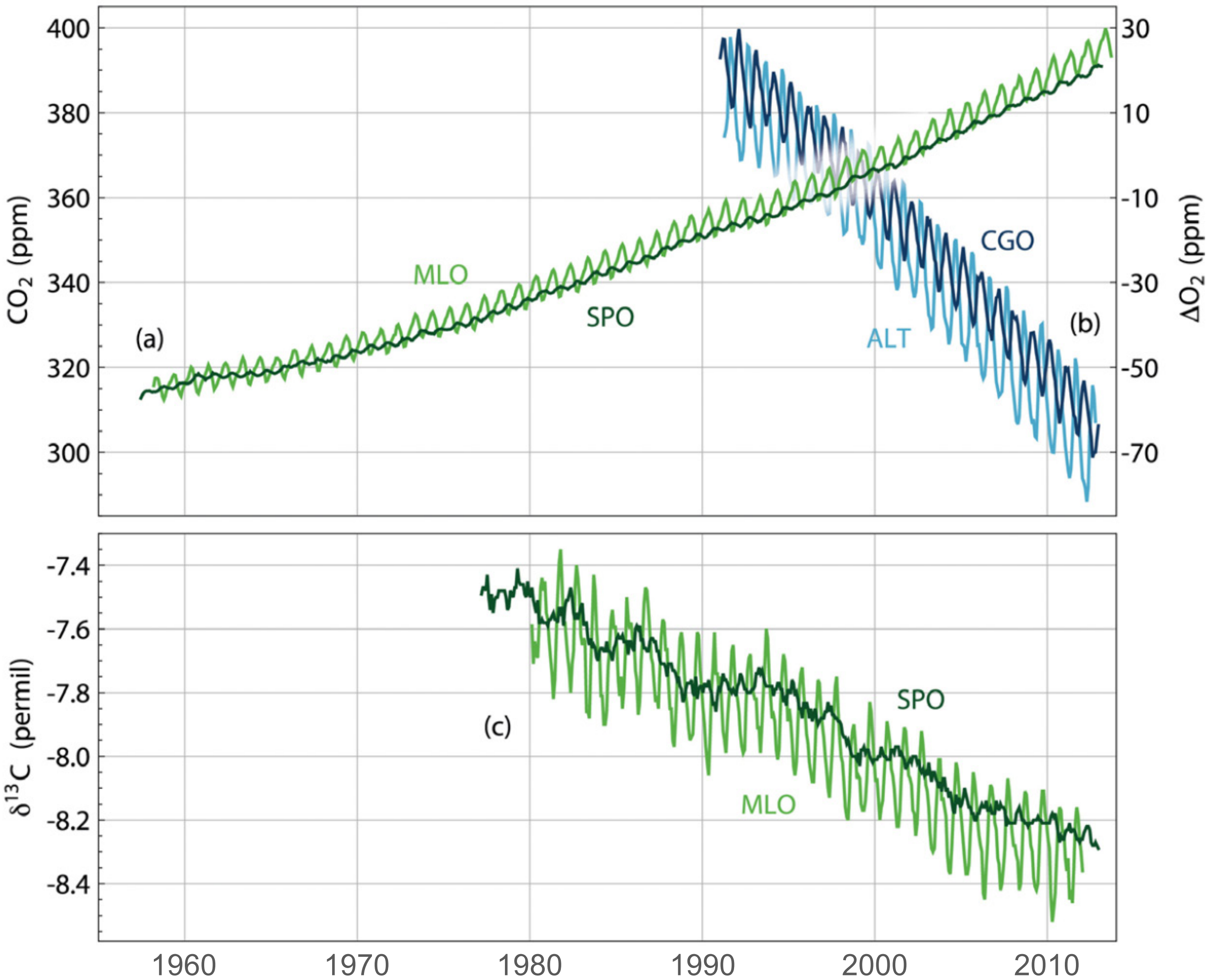
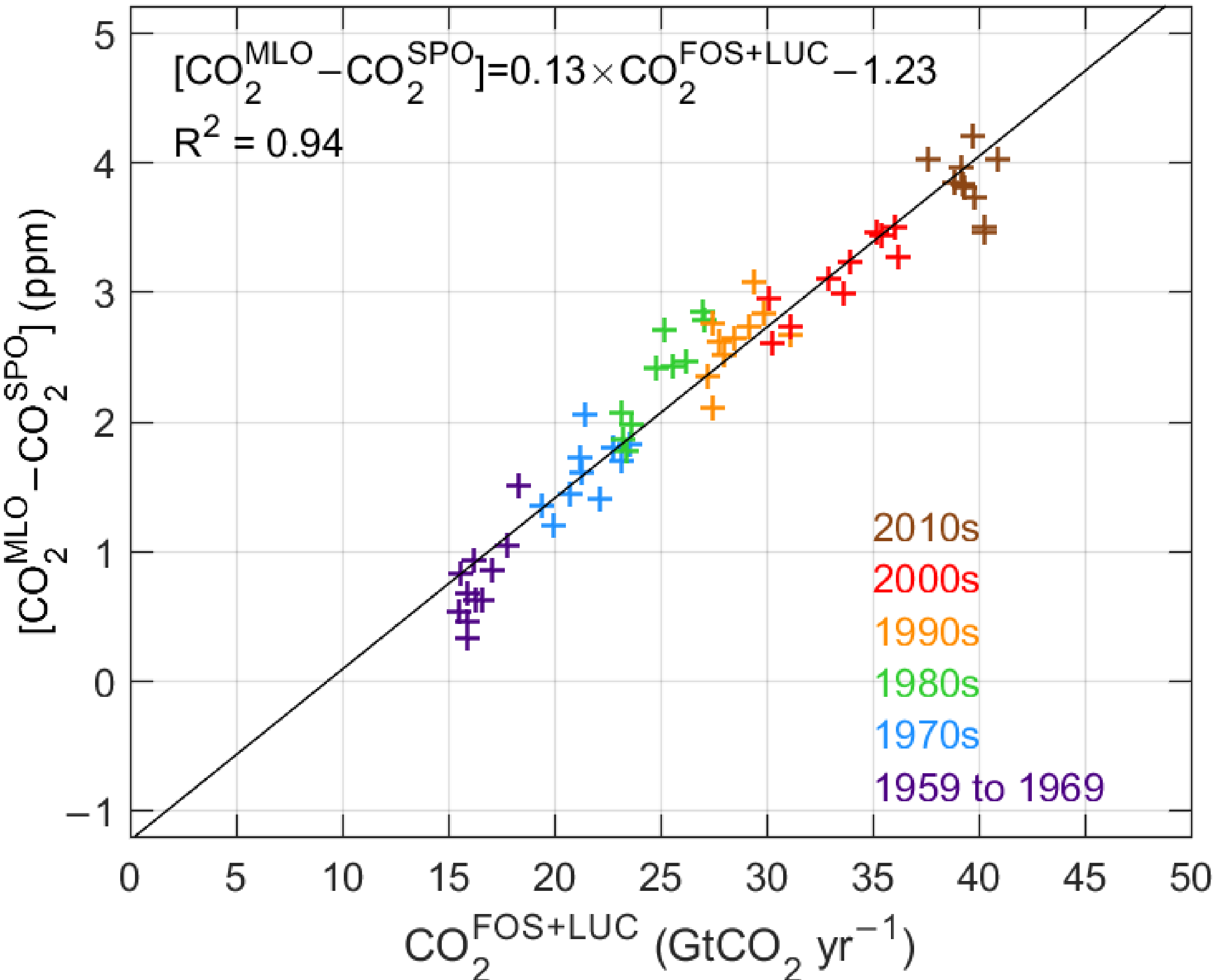


Figure 3.4 Atmospheric concentrations observed at representative stations of (a) carbon dioxide from Mauna Loa (MLO) Northern Hemisphere and South Pole (SPO) Southern Hemisphere; (b) Oxygen from Alert (ALT) Canada, 82°N, and Cape Grim (CGO), Australia, 41°S; (c) $^{13}C/^{12}C$ from Mauna Loa (MLO) and South Pole (SPO) stations.

Fig 3.4, Houghton

Human “Fingerprints” on Atmospheric CO_2



MLO: Mauna Loa Observatory
SPO: South Pole Observatory
FOS: Fossil Fuel Combustion
LUC: Land Use Change (Deforestation)

Fig 1.8 updated, *Paris Beacon of Hope*

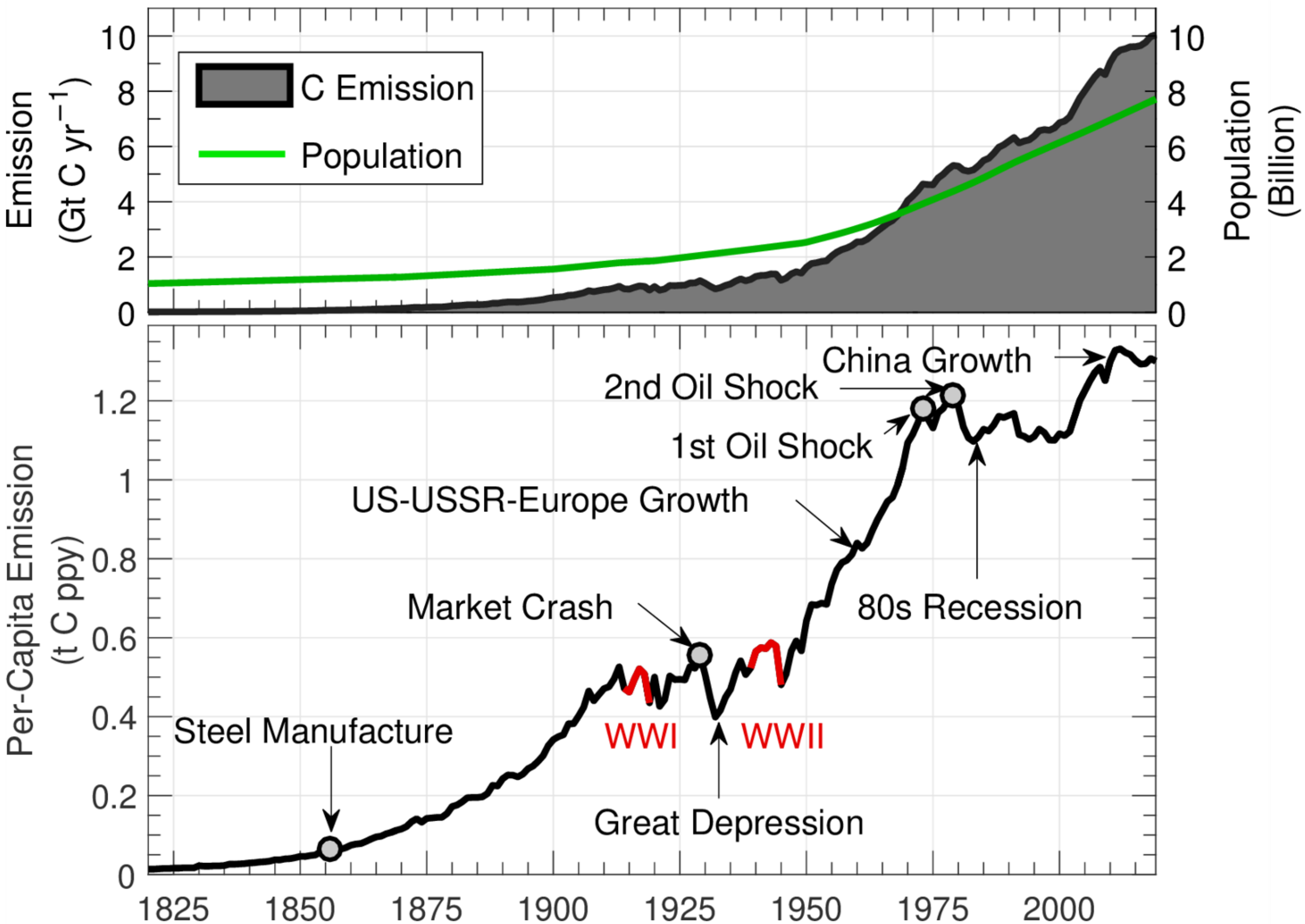
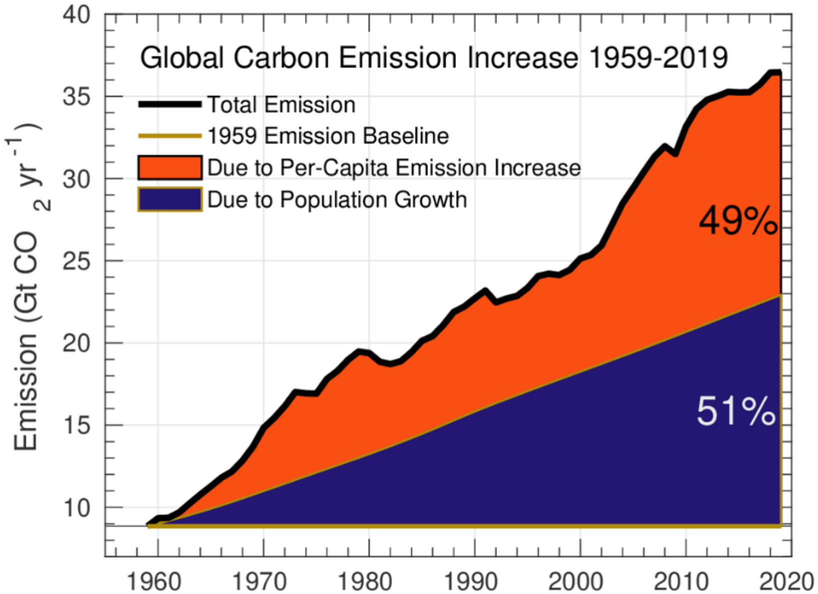


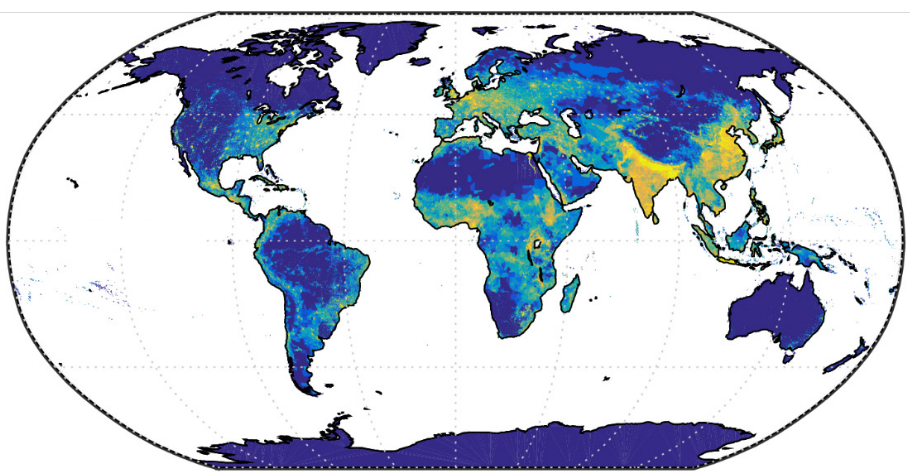
Figure courtesy Walt Tribett

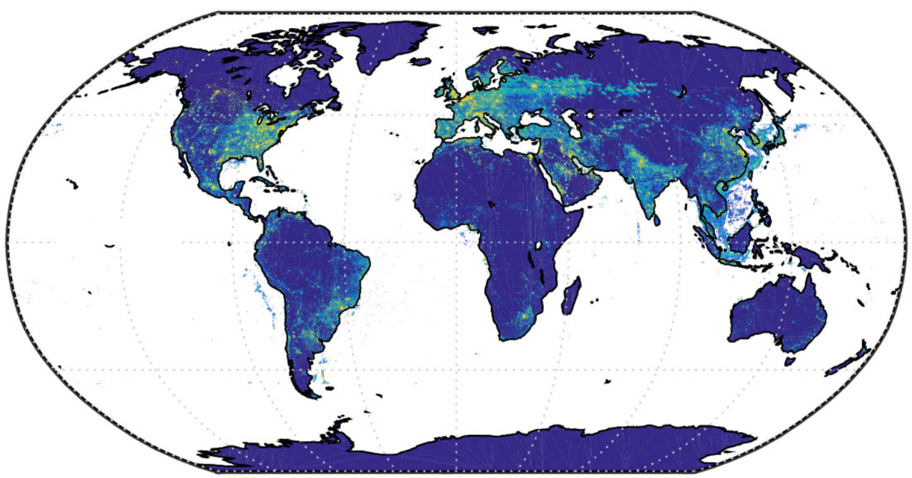
After Fig 3.1 *Paris Beacon of Hope*

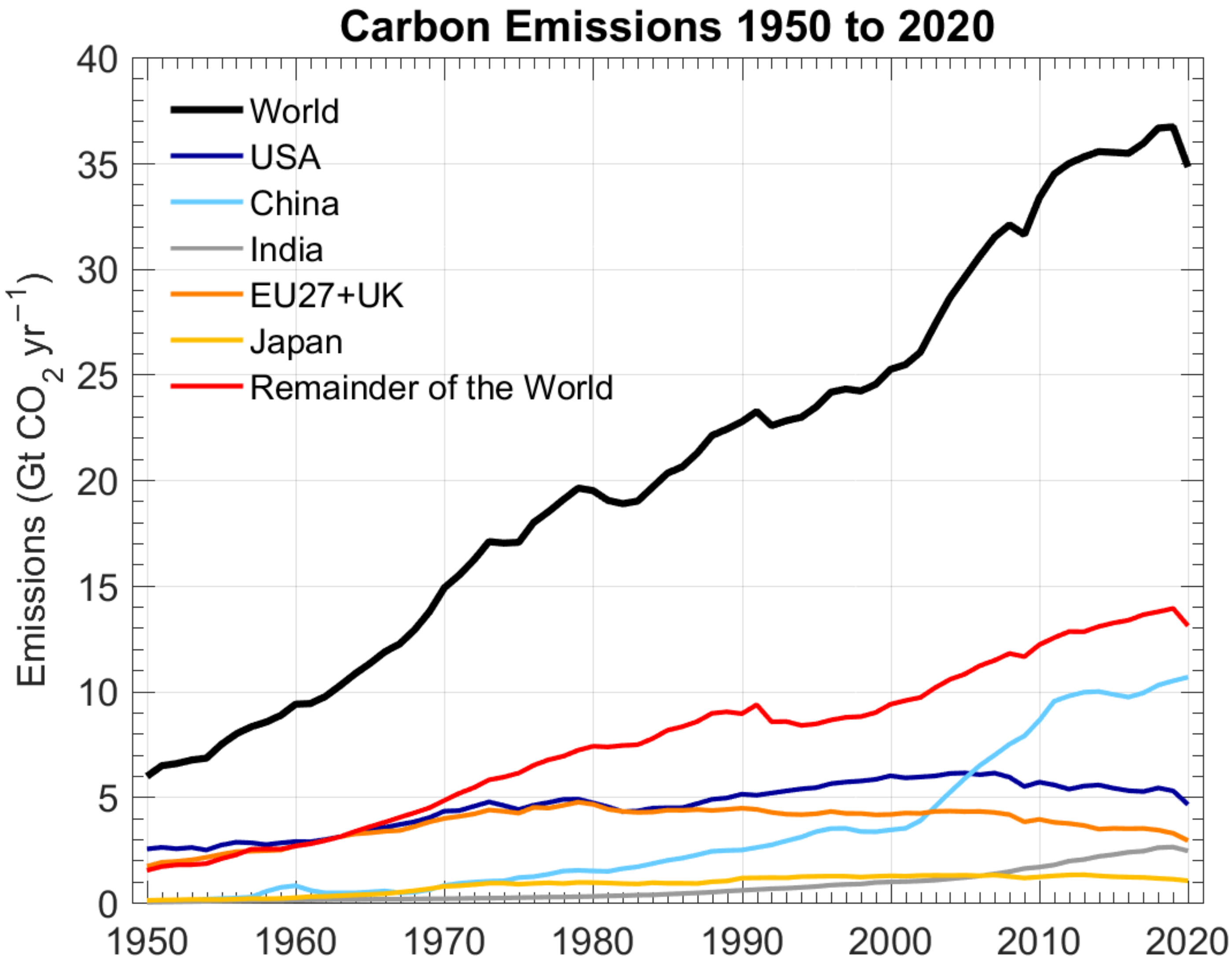
Fossil Fuel Emissions

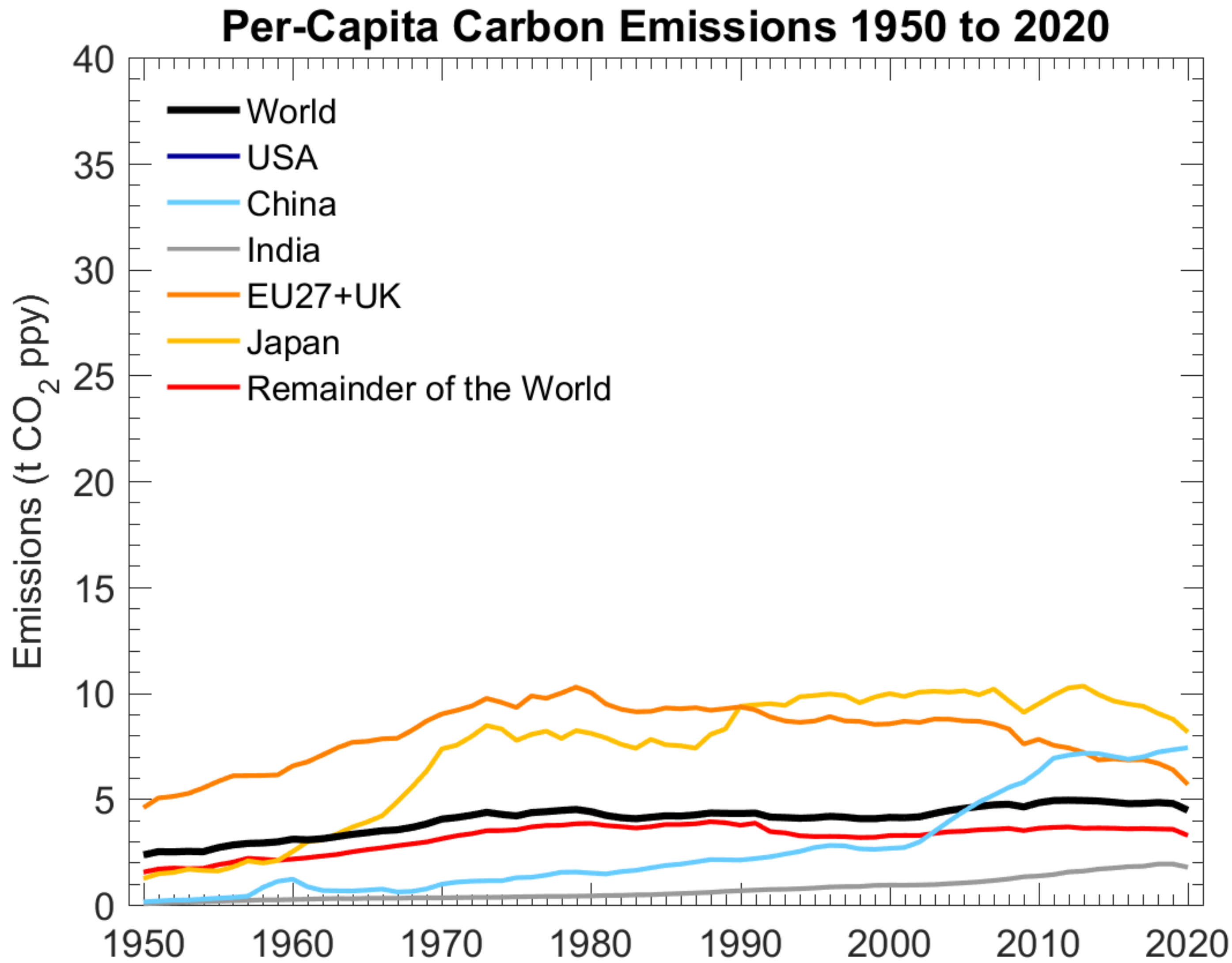


Population increase & **per-capita rise** both contribute, nearly equally to the global rise in C emissions



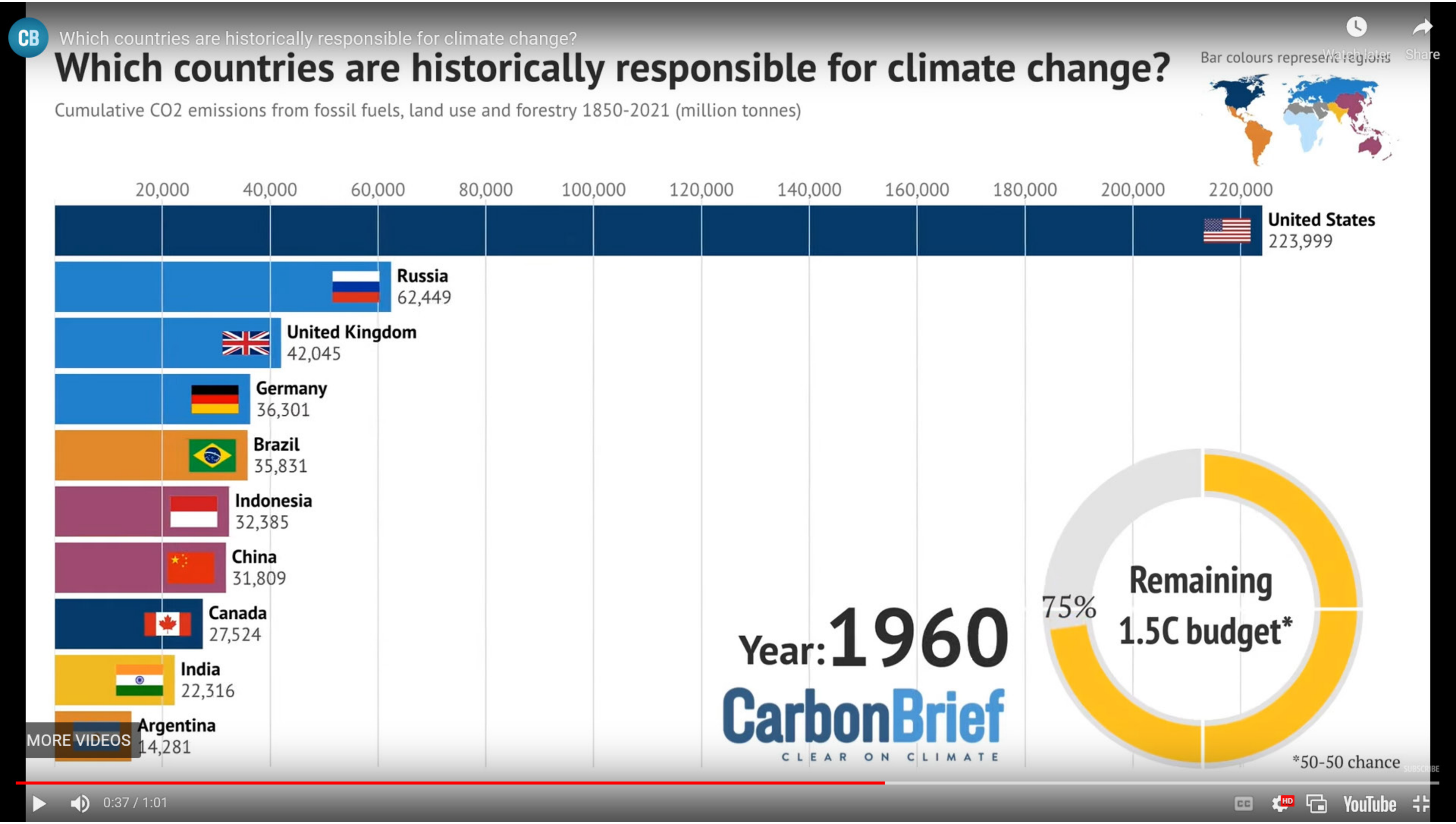



Carbon Emissions 1950 to 2020
Emissions (Gt CO_2 yr^{-1})
0
5
10
15
20
25
30
35
40
1950
1960
1970
1980
1990
2000
2010
2020
World
USA
China
India
EU27+UK
Japan
Remainder of the World



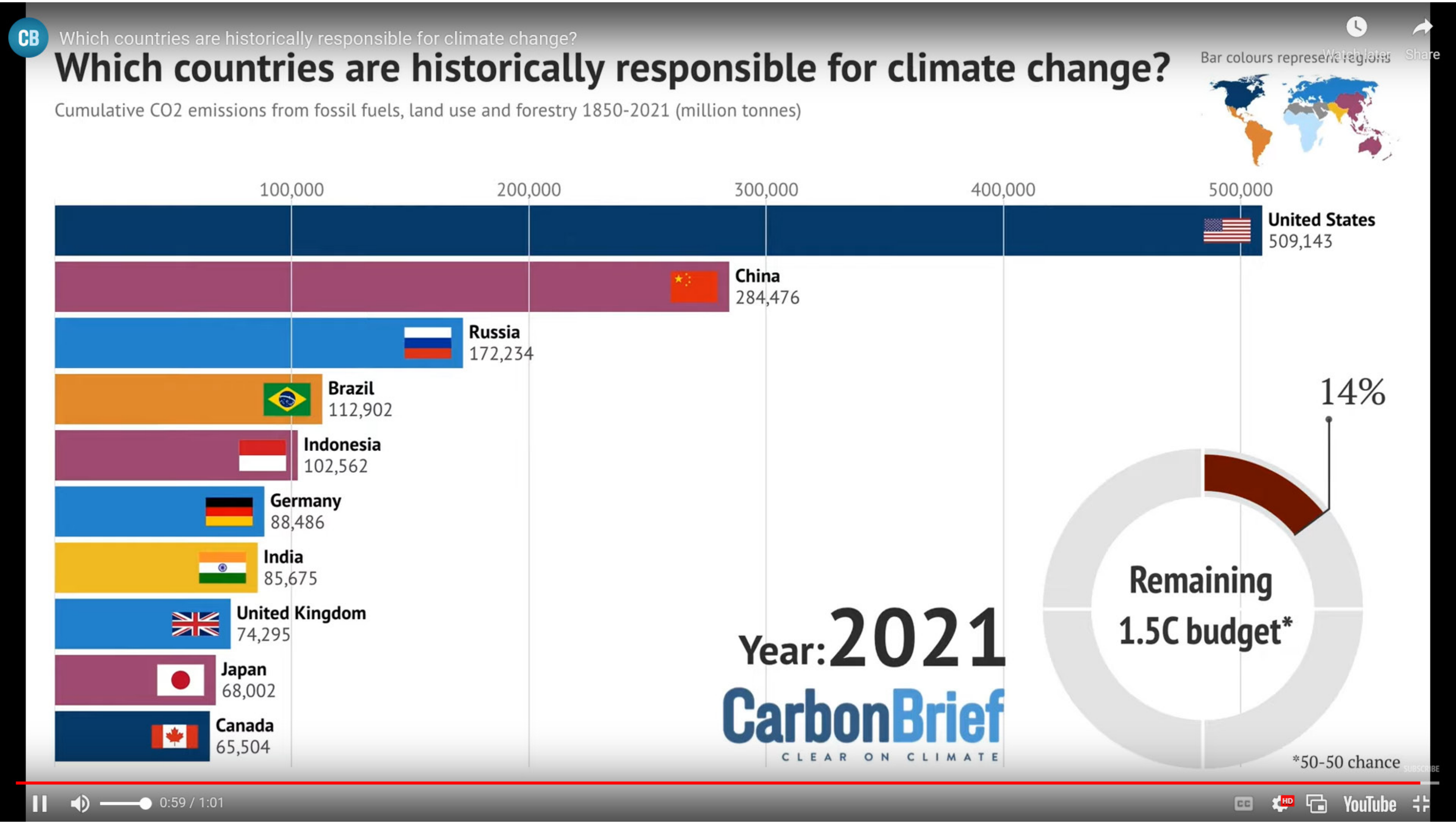
Per-Capita Carbon Emissions 1950 to 2020
Emissions (t CO_2 ppy)
0
5
10
15
20
25
30
35
40
1950
1960
1970
1980
1990
2000
2010
2020
World
USA
China
India
EU27+UK
Japan
Remainder of the World

Fossil Fuel Emission Animation



https://www.carbonbrief.org/analysis-which-countries-are-historically-responsible-for-climate-change

Fossil Fuel Emission Animation

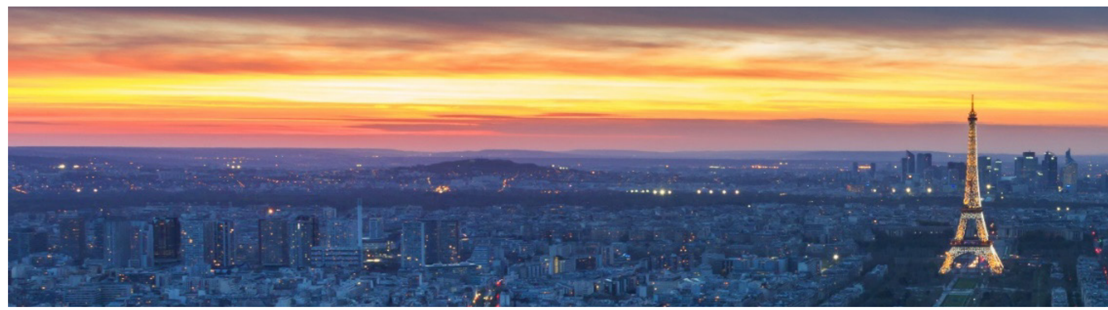


https://www.carbonbrief.org/analysis-which-countries-are-historically-responsible-for-climate-change

Obama & Xi

US / China Announcement ⇒ Paris Climate Agreement

Nov 2014: Presidents Obama & Xi announced
- **U.S. would reduce GHG emissions to 27% below 2005 by 2025**
- **China would peak GHG emissions 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"

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

- Submitted prior to Dec 2015 meeting in Paris
- Consist of either **unconditional** (promise) or **conditional** (contingent) pledges
- Generally extend from early 2016 to year 2030

Global Carbon Cycle

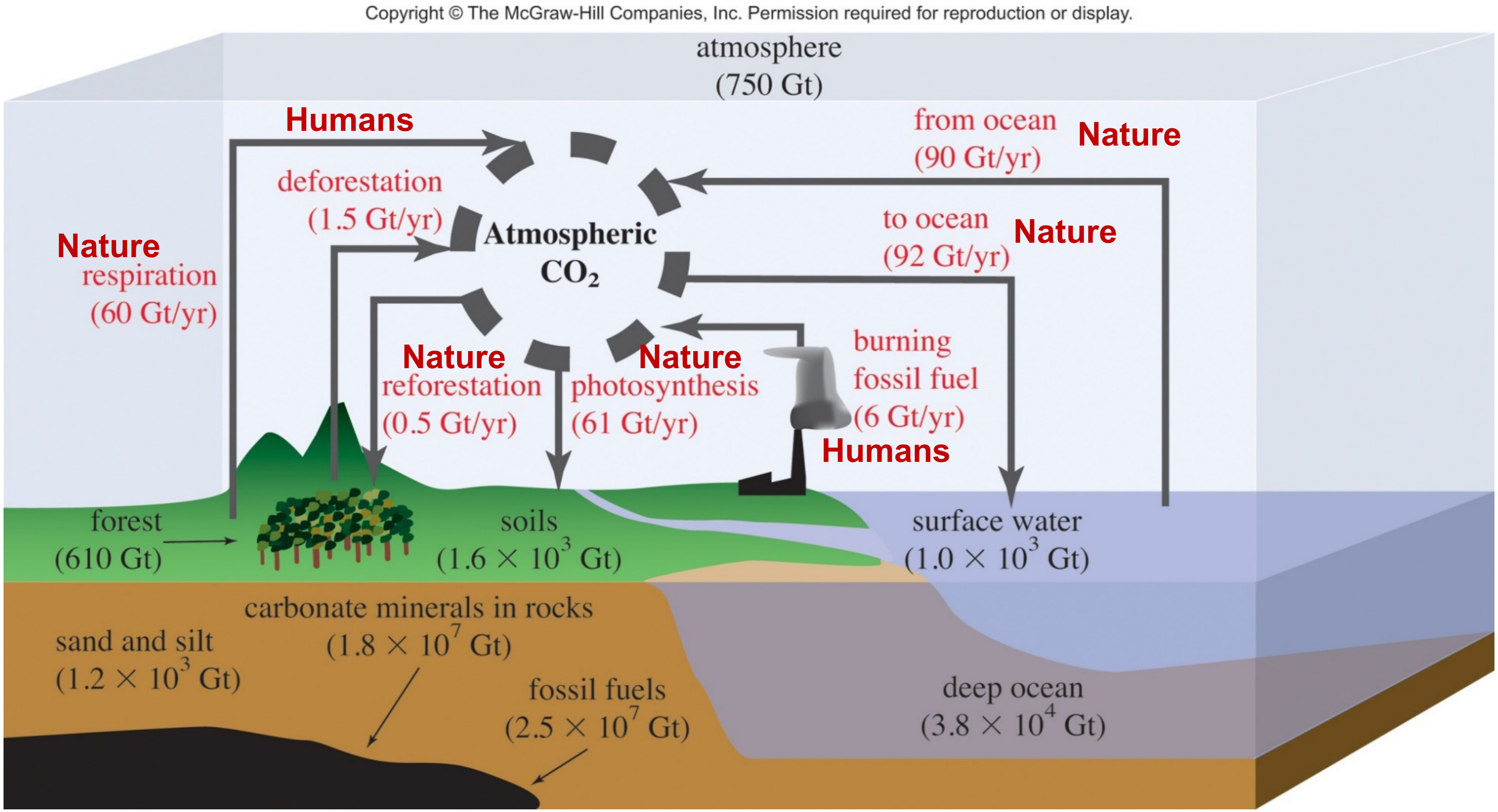


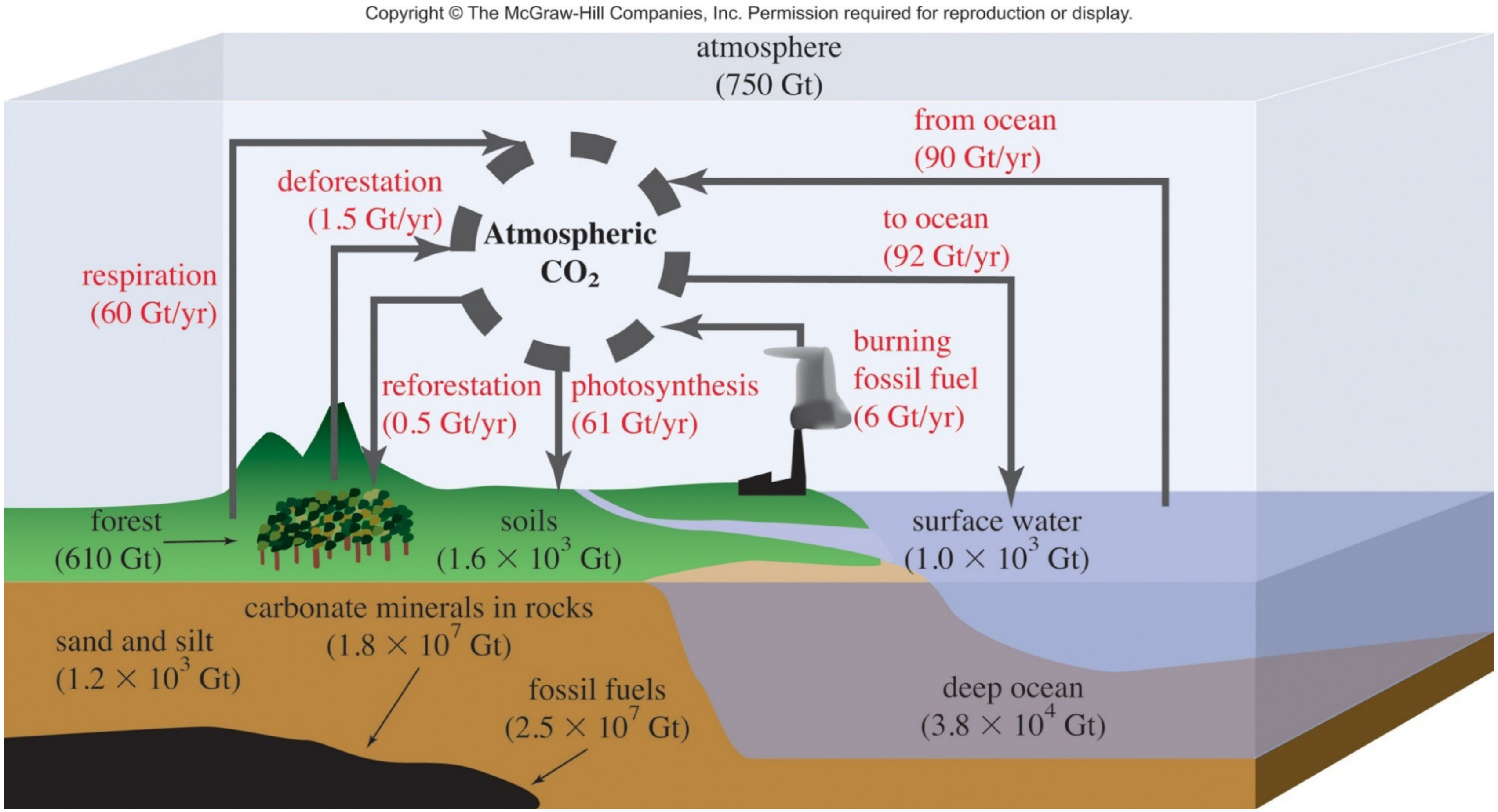
Fig 3.20, Chemistry in Context

CC:

Land Sink = (61 + 0.5) – (60) Gt C / yr = 1.5 Gt C / yr
Ocean Sink = 92 – 90 Gt C / yr = 2 Gt C / yr

In other words, ~3.5 Gt C / yr out of 7.5 Gt C / yr from burning fossil fuel & deforestation was being absorbed by world's oceans & terrestrial biosphere.

Global Carbon Cycle



Ocean Carbon: 1.0×10^3 Gt + 3.8×10^4 Gt = 3.9×10^4 Gt

Fig 3.20, Chemistry in Context

Ocean contains ~50 times more Carbon than the atmosphere, which is why oceanic processes are "the dog that wags the tail" of atmospheric CO_2 on glacial to interglacial time scales

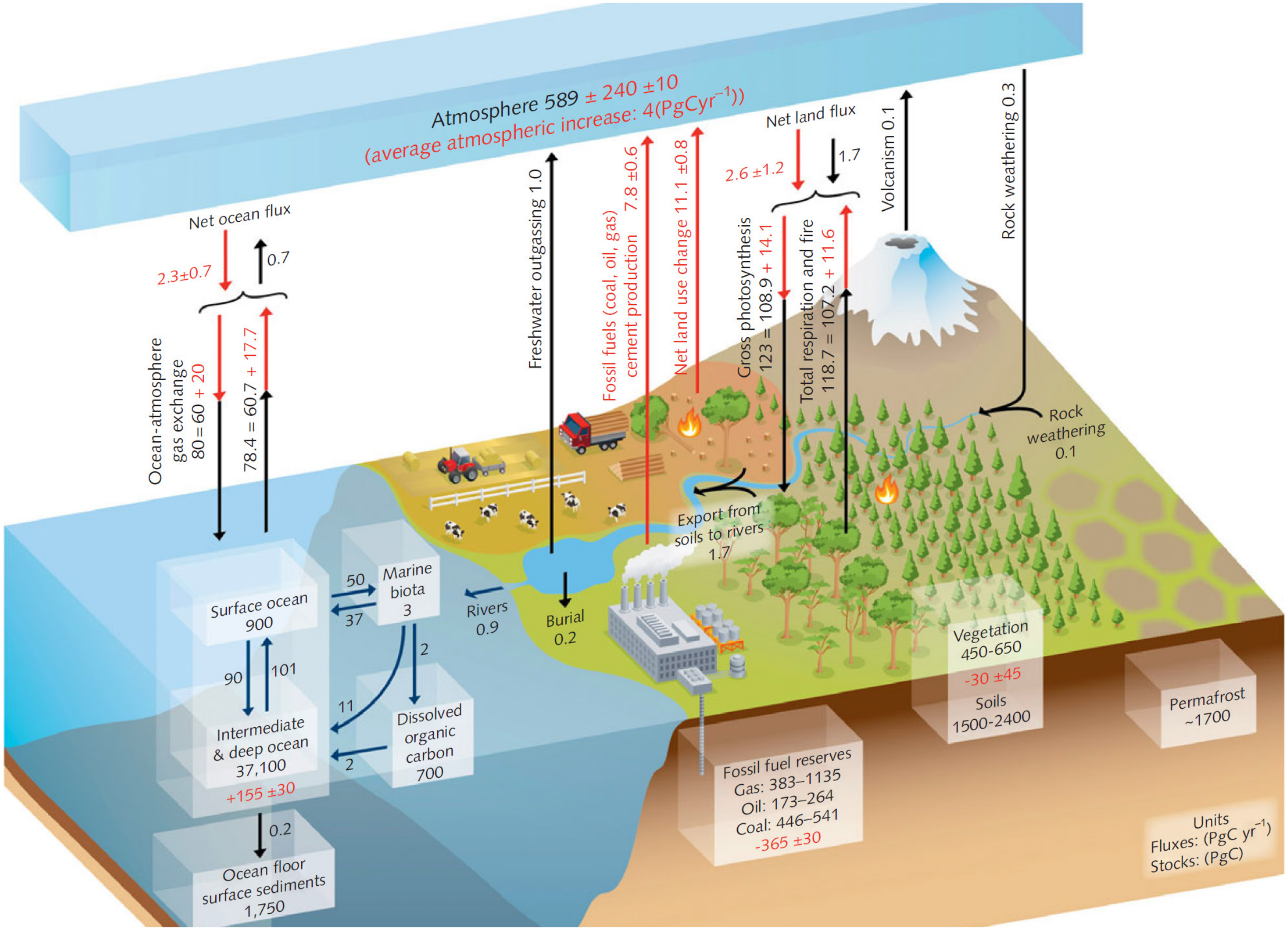


Fig 3.1, Houghton

Houghton:

Land Sink	**= 2.6 ± 1.2 Gt C / yr**
Ocean Sink	**= 2.3 ± 0.7 Gt C / yr**

In other words, ~4.9 Gt C / yr out of 7.8 + 1.1 = 8.9 Gt C / yr from burning fossil fuel & deforestation was being absorbed by world's oceans & terrestrial biosphere for the time period of this figure, which is 2000 to 2009

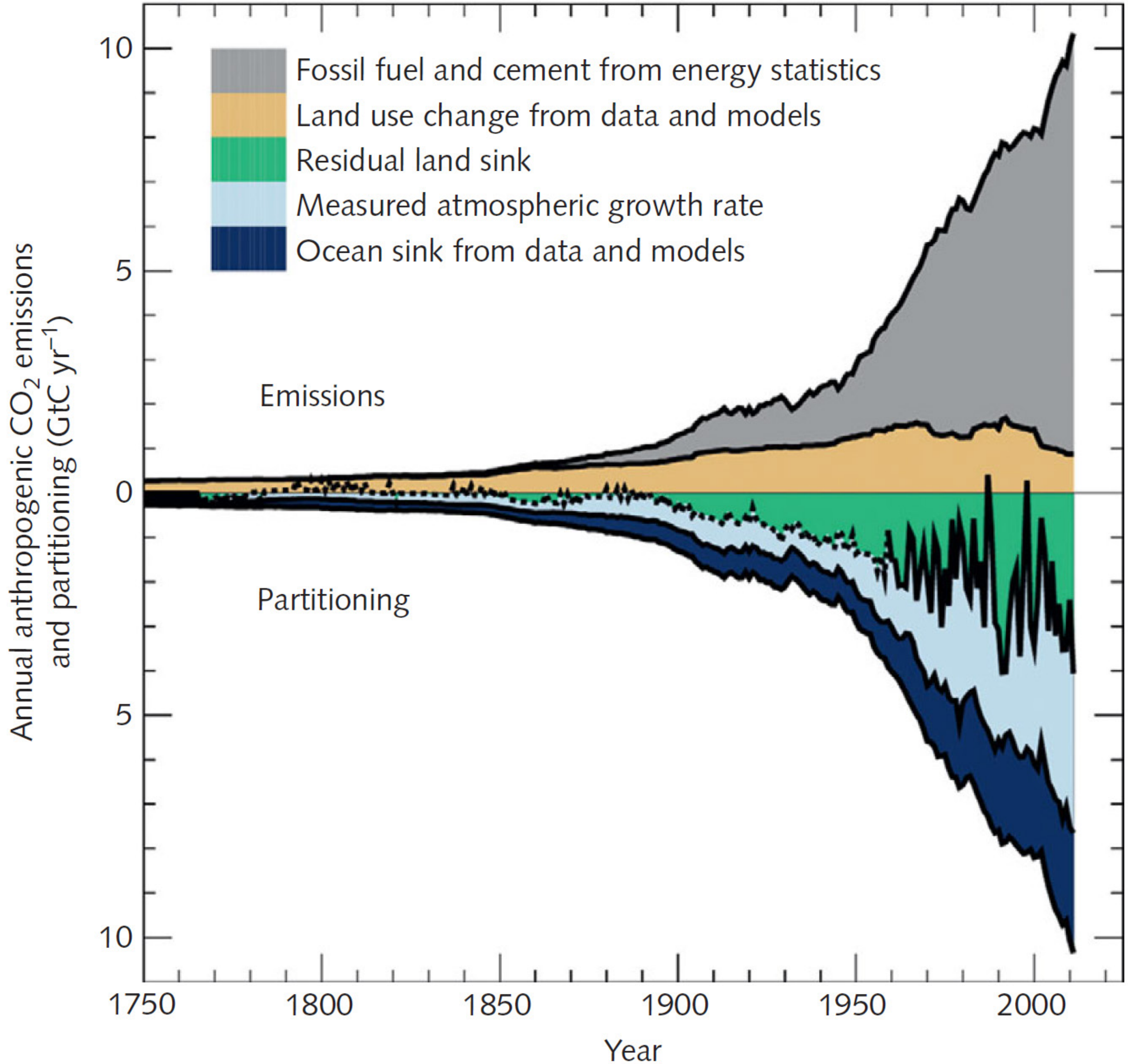
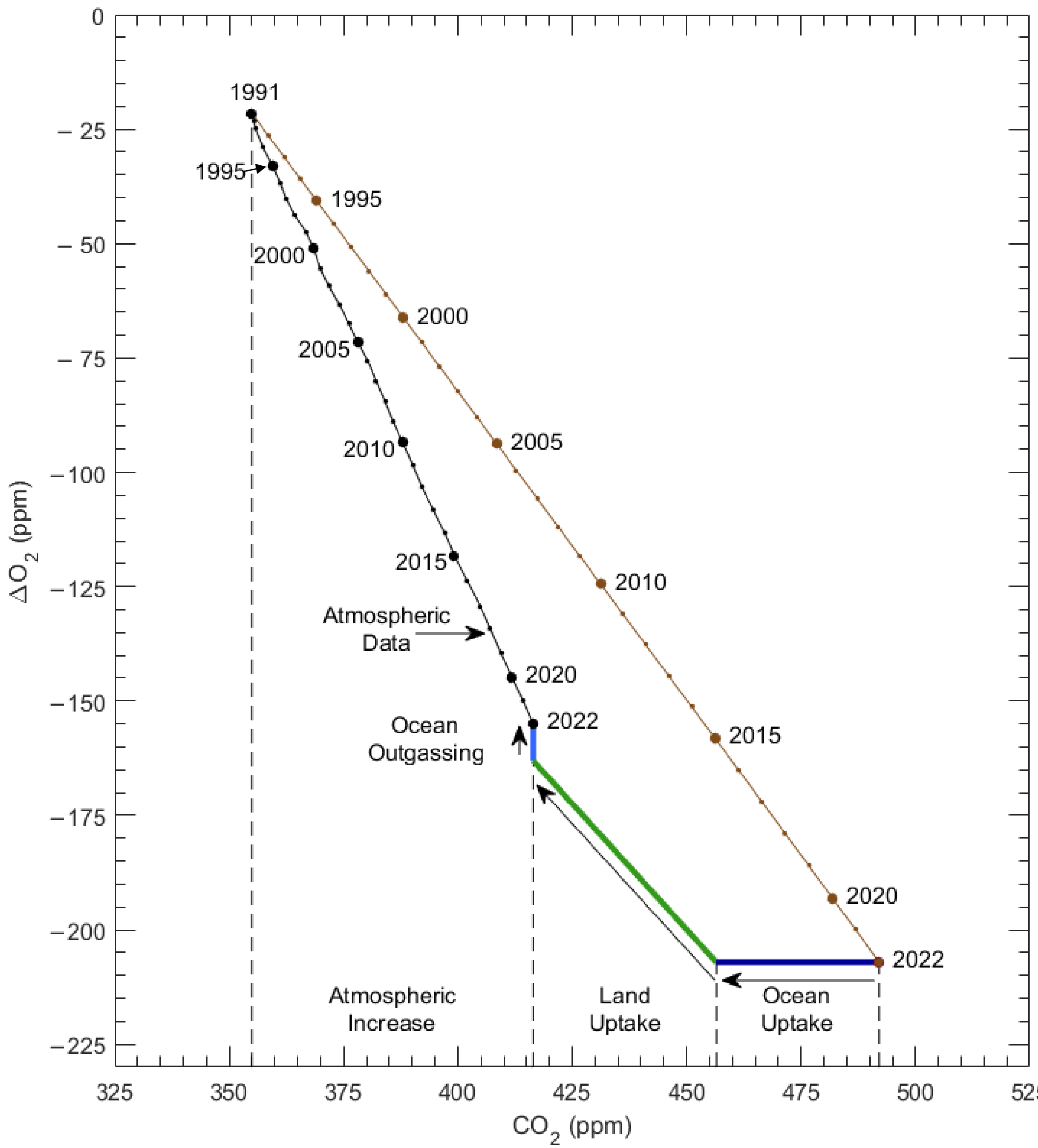


Fig 3.3, Houghton

Inferring CO_2 Uptake Based on ΔO_2

Figure courtesy
Brian Bennett



Uptake of Atmospheric CO_2 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_2 by end of century

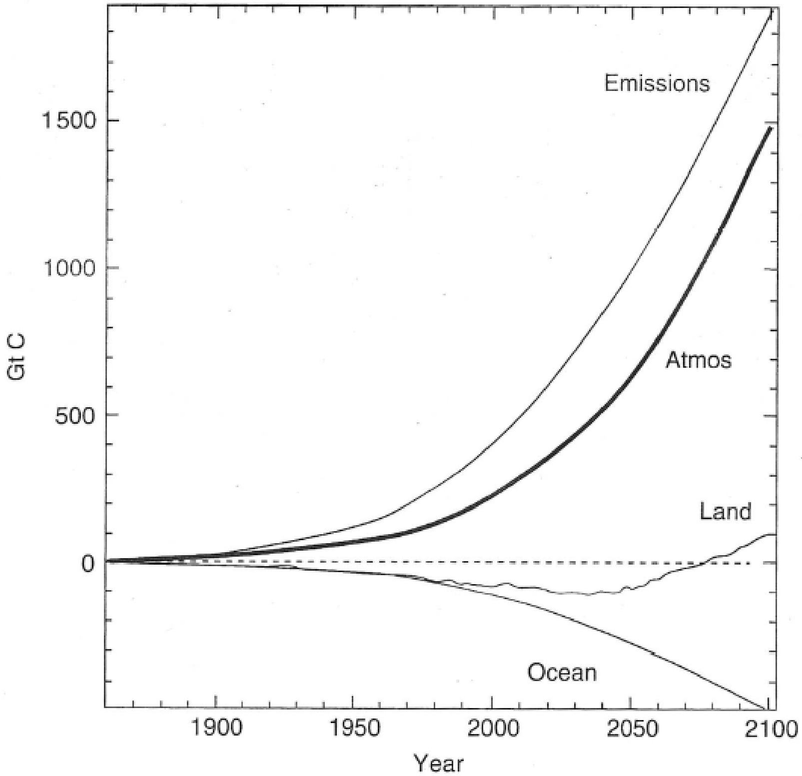
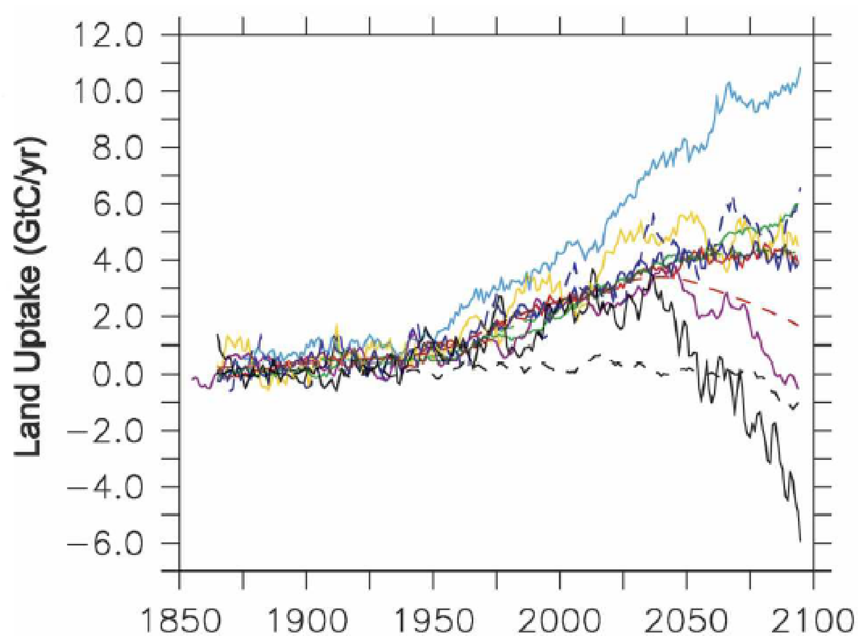


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Figure 3.5, Houghton 3[d] Edition

- 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_2 by Trees (Land Sink)

Land sink

As CO_2 ↑, photosynthesis (all things being equal) will increase.

Known as the **"CO_2 fertilizer" effect**

The carbon dioxide fertilisation effect is an example of a biological feedback process. It is a negative feedback because, as carbon dioxide increases, it tends to increase the uptake of carbon dioxide by plants and therefore reduce the amount in the atmosphere, decreasing the rate of global warming.

Page 43, Houghton

Uptake of Atmospheric CO_2 by Trees (Land Sink)

Land sink

As CO_2 ↑, photosynthesis (all things being equal) will increase.

Known as the **"CO_2 fertilizer" effect**

Difficult to quantify empirically in a greenhouse setting because ?

The results of this study suggest that competition for light was the major factor influencing community composition, and that CO_2 influenced competitive outcome largely through its effects on canopy architecture. Early in the experiment competition for nutrients was intense.

Fakhri A. Bazzaz, 1990: https://www.jstor.org/stable/pdf/2097022.pdf

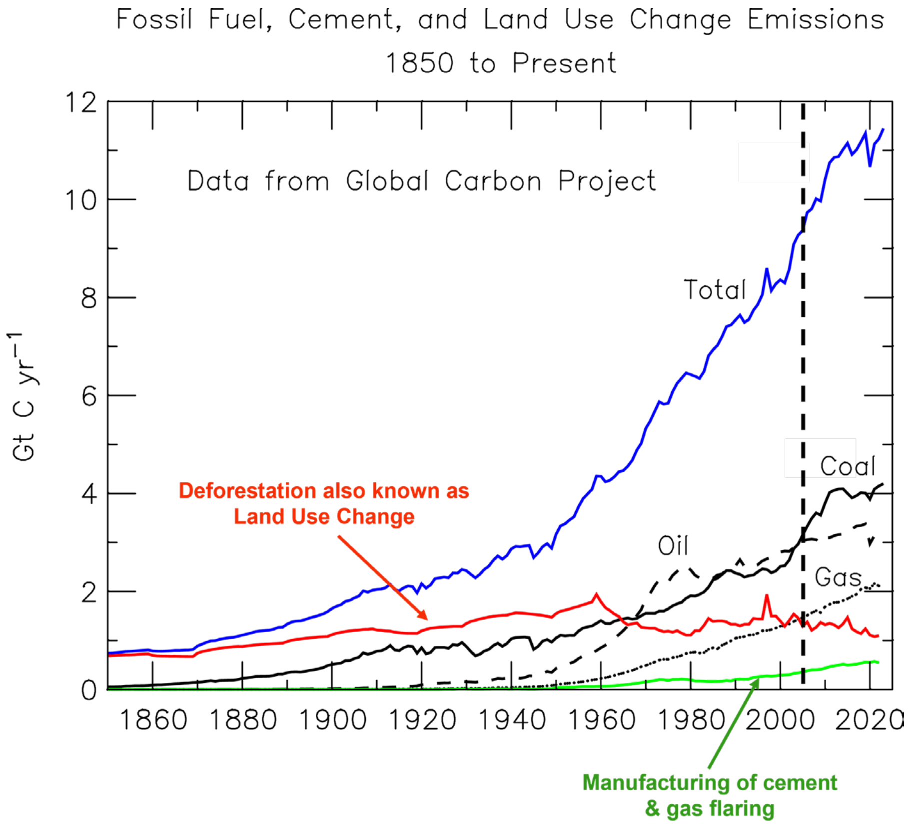
Many Free-Air Carbon dioxide Enrichment (FACE) experiments have been developed, throughout the world including a new experiment in Brazil, to attempt to understand how the terrestrial biosphere will respond to rising levels of atmospheric CO_2

http://aspenface.mtu.edu

https://www.nature.com/news/polopoly_fs/1.12855!/menu/main/topColumns/topLeftColumn/pdf/496405a.pdf?origin=ppub

https://www.nature.com/scitable/knowledge/library/effects-of-rising-atmospheric-concentrations-of-carbon-13254108

Future Fossil Fuel Emissions and Reserves



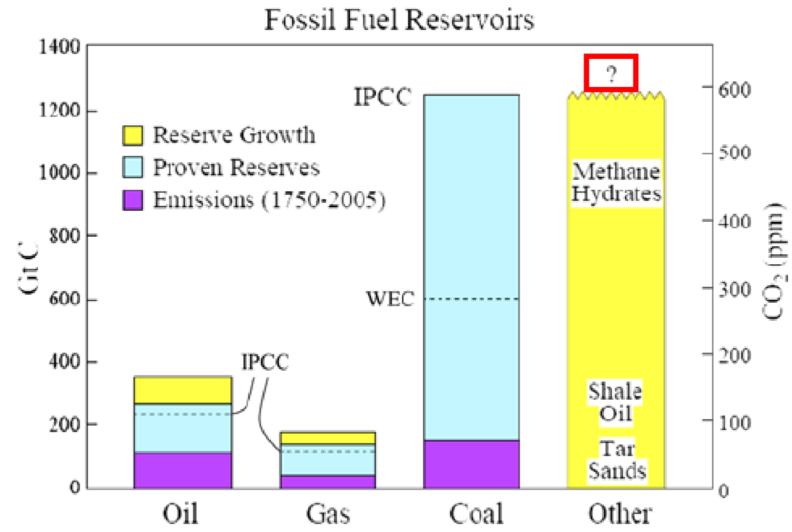


Figure 1. Fossil fuel-related estimates used in this study. Historical fossil fuel CO_2 emissions from the Carbon Dioxide Information Analysis Center [CDIAC; *Marland et al.*, 2006] and British Petroleum [*BP*, 2006]. Lower limits for current proven conventional reserve estimates for oil and gas from *IPCC* [2001a] (dashed lines), upper limits and reserve growth values from US Energy Information Administration [*EIA*, 2006]. Lower limit for conventional coal reserves from World Energy Council [*WEC*, 2007; dashed line], upper limit from *IPCC* [2001a]. Possible amounts of unconventional fossil resources from *IPCC* [2001a].

Kharecha and Hansen, *GBC*, 2008.
https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2007GB003142

See also https://www.sciencedirect.com/science/article/pii/S2666049022000524#s0135

Uptake of Atmospheric CO_2 by Oceans

Ocean sink: relatively long lived reservoir

In nearly all models, ocean uptake slows relative to rise in atmospheric CO_2

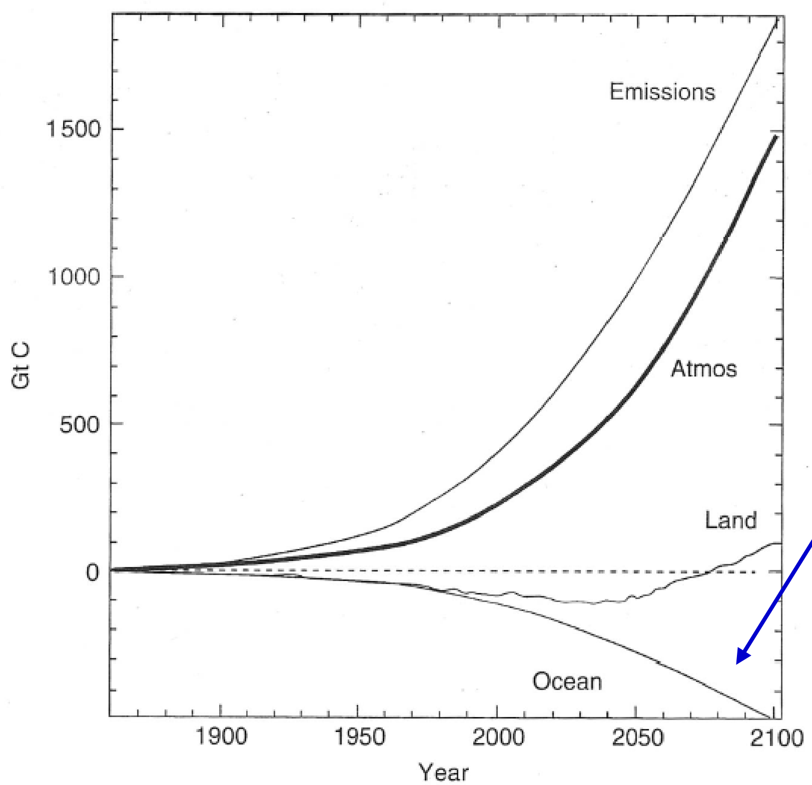


Figure 3.5 Illustrating the possible effects of climate feedbacks on the carbon cycle. Results are shown of the changing budgets of carbon

Figure 3.5, older (Third) edition of Houghton

Uptake of Atmospheric CO_2 by Oceans

– Solubility Pump:

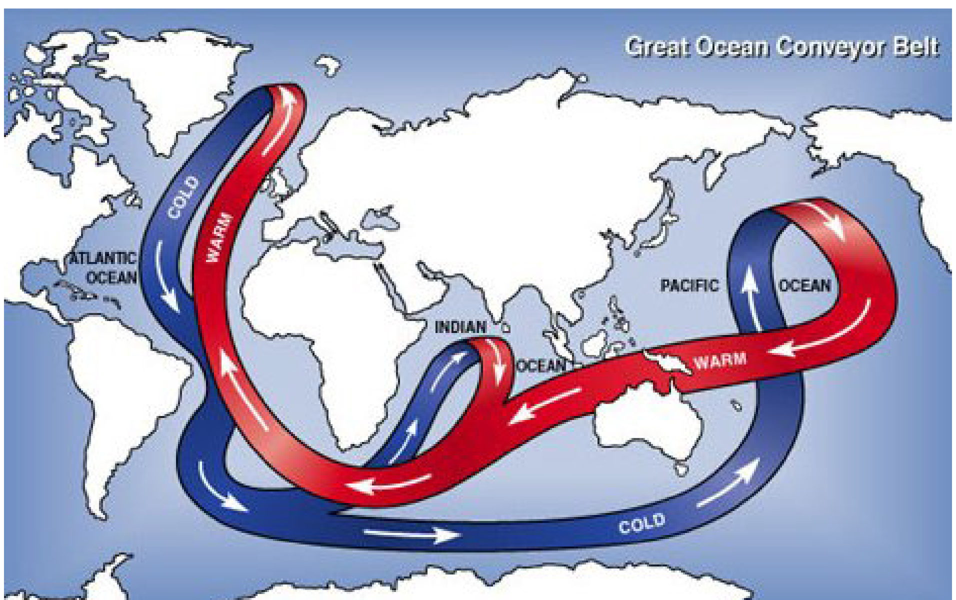
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

b) Deep water forms at high latitude. As deep water sinks, ocean carbon (ΣCO_2) accumulated at the surface is moved to the deep ocean interior.

– Biological Pump:

a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and $\mathbf{Fe^{2+}}$ & $\mathbf{Fe^{3+}}$. Ocean biology is never carbon limited.

b) Detrital material "rains" from surface to deep waters, contributing to higher CO_2 in intermediate and deep waters



http://science.nasa.gov/headlines/y2004/05mar_arctic.htm

Uptake of Atmospheric CO_2 by Oceans

– Solubility Pump:

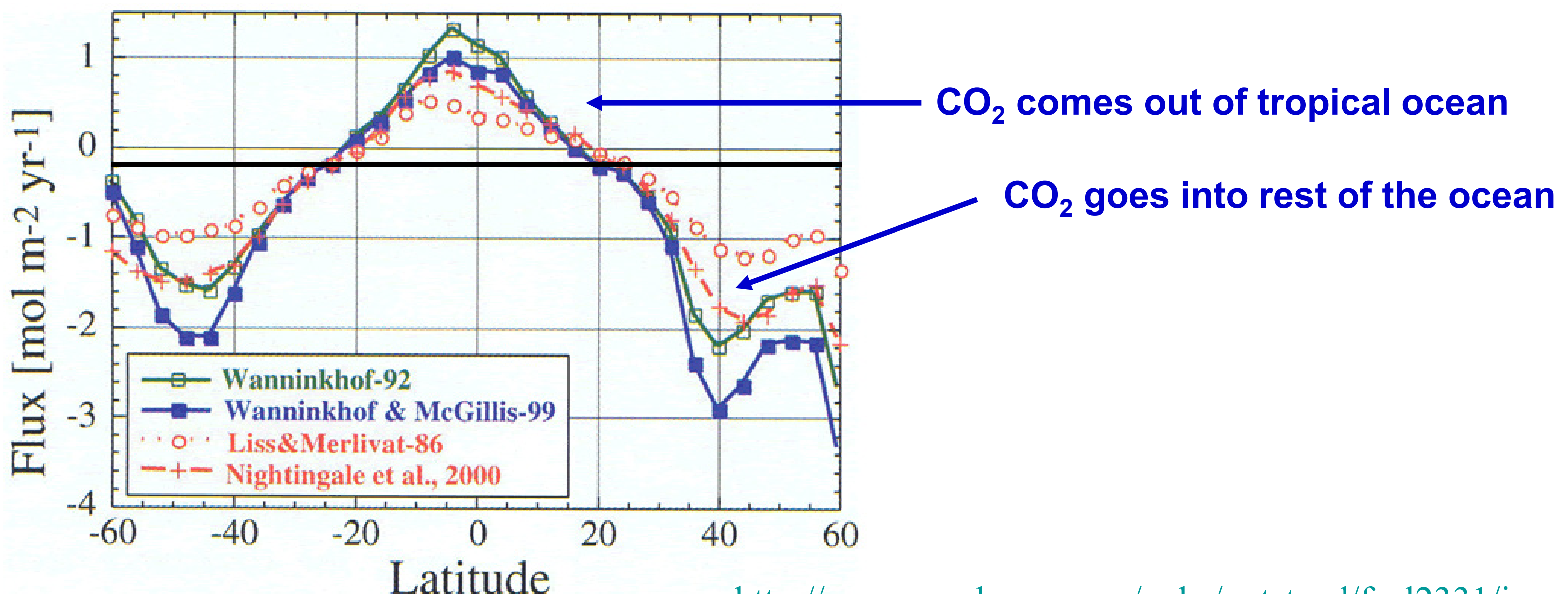
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

b) Deep water forms at high latitude. As deep water sinks, ocean carbon (ΣCO_2) accumulated at the surface is moved to the deep ocean interior.

– Biological Pump:

a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and $\mathbf{Fe^{2+}}$ & $\mathbf{Fe^{3+}}$. Ocean biology is never carbon limited.

b) Detrital material "rains" from surface to deep waters, contributing to higher CO_2 in intermediate and deep waters



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

Biology in Today’s Ocean

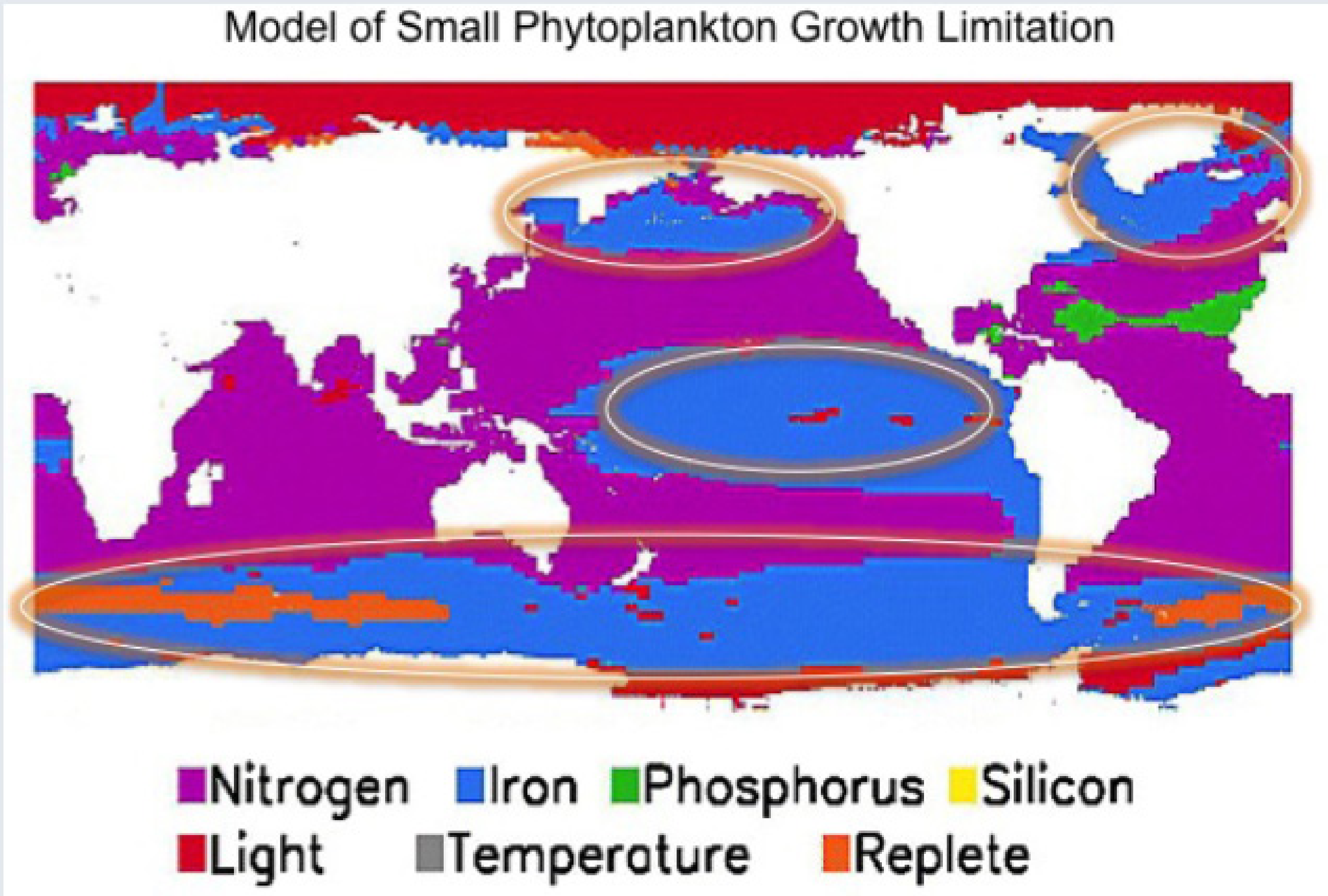


Figure 1. Results of a global model of small phytoplankton growth limitation by Moore et al. 2004 (*Global Biogeochemical Cycles*). Blue shaded areas denote regions that are potentially limited by iron availability. Iron is supplied by dust from continents and by upwelling of deep water. However, high iron demand in the euphotic zone quickly drives iron concentrations to nano- and picomolar levels that can be limiting to many phyto- and bacterioplankton.

Originally from http://www.whoi.edu/page.do?pid=130796
Similar image at https://journals.ametsoc.org/view/journals/clim/26/23/jcli-d-12-00566.1.xml

Sequestration of CO_2 from the Atmosphere: Ocean Biology

BOX 3.2
Historical Context of Ocean Iron Fertilization

"Give me half a tanker of iron, and I'll give you an ice age," biogeochemist John Martin reportedly quipped in a Dr. Strangelove accent at a conference at Woods Hole in 1988 (Fleming, 2010). Martin and his colleagues at Moss Landing Marine Laboratories proposed that iron was a limiting nutrient in certain ocean waters and that adding it stimulated explosive and widespread phytoplankton growth. They tested their iron deficiency, or "Geritol," hypothesis in bottles of ocean water, and subsequently experimenters added iron to the ocean in a dozen or so ship-borne "patch" experiments extending over hundreds of square miles (see text for discussion). OIF was shown to be effective at inducing phytoplankton growth, and the question became—was it possible that the blooming and die-off of phytoplankton, fertilized by the iron in natural dust, was the key factor in regulating atmospheric carbon dioxide concentrations during glacial-interglacial cycles? Dust bands in ancient ice cores encouraged this idea, as did the detection of natural plankton blooms by satellites.

This realization led to further questions. Could OIF speed up the biological carbon pump to sequester carbon dioxide? And could it be a solution to climate change? Because of this possibility, Martin's hypothesis received widespread public attention. What if entrepreneurs or governments could turn patches of ocean green and claim that the carbonaceous carcasses of the dead plankton sinking below the waves constituted biological "sequestration" of undesired atmospheric carbon? Several companies—Climos,[18] Planktos (now out of the business), GreenSea Ventures, and the Ocean Nourishment Corporation[19]—have proposed entering the carbon-trading market by dumping either iron or urea into the oceans to stimulate both plankton blooms and ocean fishing (Climos, 2007; Freestone and Rayfuse, 2008; Powell, 2008; Rickels et al., 2012; Schiermeier, 2003).

OIF projects could be undertaken unilaterally and without coordination by an actor out to make a point; in fact, one such incident took place off the coast of Canada in 2012 (Tollefson, 2012). However, as this section describes, there are still unresolved questions with respect to the effectiveness and potential unintended consequences of large-scale ocean iron fertilization.

NAS, 2015

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^{-}}$

Atmospheric CO_2	Pre-Industrial 280 ppm	Present Day 420 ppm	2 × Pre-Industrial 560 ppm
Ocean Carbon	2020×10^{-6} M	2083×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1888×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.7×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	181×10^{-6} M	146×10^{-6} M
pH	8.32	8.17	8.06

Ocean Carbon $[\Sigma\ CO_2] = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}]$

Notes:

$T = 293$ K; Alkalinity= 2.25×10^{-3} M

M ≡ mol/liter

Mathematics supporting this calculation on Extra Slides 1 to 3 of Class Notes.

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-}$

Atmospheric CO_2	Pre-Industrial 280 ppm	Present Day 420 ppm	2 × Pre-Industrial 560 ppm
Ocean Carbon	2020×10^{-6} M	2083×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1888×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.7×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	181×10^{-6} M	146×10^{-6} M
pH	8.32	8.17	8.06

Ocean is slightly basic

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-}$

Atmospheric CO_2	Pre-Industrial 280 ppm	Present Day 420 ppm	2 × Pre-Industrial 560 ppm
Ocean Carbon	2020×10^{-6} M	2083×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1888×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.7×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	181×10^{-6} M	146×10^{-6} M
pH	8.32	8.17	8.06

Ocean acidity rises as Atmospheric CO_2 increases

CC: "A decrease of 0.1 pH unit corresponds to a 26% increase in the amount of H+ in seawater"

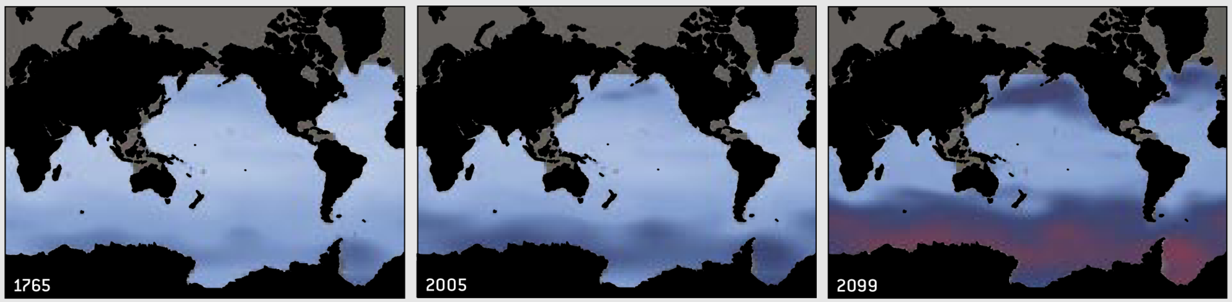
Uptake of Atmospheric CO_2 by Oceans

Oceanic uptake of atmospheric CO_2 leads to ***ocean acidification***

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

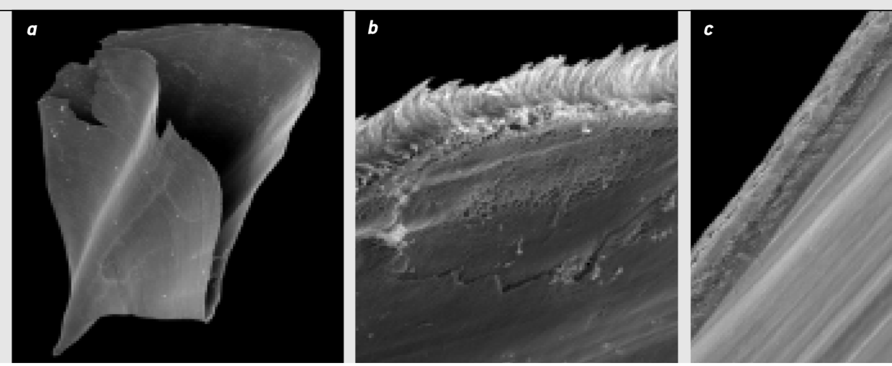
THE (RAGGED) FUTURE OF ARAGONITE

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

https://www2.atmos.umd.edu/~rjs/class/fall2024/supplemental_readings/doney_sci_am_2006.pdf

See also https://oceans.mit.edu/wp-content/uploads/doney_ann_rev_proof.pdf

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-}$

Atmospheric CO_2	Pre-Industrial 280 ppm	Present Day 420 ppm	2 × Pre-Industrial 560 ppm
Ocean Carbon	2020×10^{-6} M	2083×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1888×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.7×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	181×10^{-6} M	146×10^{-6} M
pH	8.32	8.17	8.06

Revelle Factor:

$$\frac{\Delta(\text{Atmospheric } CO_2)}{\langle \text{Atmospheric } CO_2 \rangle_{\text{Average}}} = \frac{140 \text{ ppm}}{0.5 \times (420 + 280)} = 0.40$$

$$\frac{\Delta(\text{Ocean Carbon})}{\langle \text{Ocean Carbon} \rangle_{\text{Average}}} = \frac{63 \times 10^{-6} \text{ M}}{0.5 \times (2020 + 2083) \times 10^{-6} \text{ M}} = 0.032$$

Pre-Industrial to Present: Ocean in the carbon rose by about 3% for a 40% increase in atmospheric CO_2

Uptake of Atmospheric CO_2 by Oceans

When CO_2 dissolves:

Net: $\mathbf{CO_2(aq) + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-}$

Atmospheric CO_2	Pre-Industrial 280 ppm	Present Day 420 ppm	2 × Pre-Industrial 560 ppm
Ocean Carbon	2020×10^{-6} M	2083×10^{-6} M	2122×10^{-6} M
$[HCO_3^-]$	1771×10^{-6} M	1888×10^{-6} M	1958×10^{-6} M
$[CO_2\,(aq)]$	9.13×10^{-6} M	13.7×10^{-6} M	18.3×10^{-6} M
$[CO_3^{2-}]$	239×10^{-6} M	181×10^{-6} M	146×10^{-6} M
pH	8.32	8.17	8.06

Revelle Factor:

$$\frac{\Delta(\text{Atmospheric } CO_2)}{\langle \text{Atmospheric } CO_2 \rangle_{\text{Average}}} = \frac{140\ \text{ppm}}{0.5 \times (560 + 420)} = 0.29$$

$$\frac{\Delta(\text{Ocean Carbon})}{\langle \text{Ocean Carbon} \rangle_{\text{Average}}} = \frac{39 \times 10^{-6}\ \text{M}}{0.5 \times (2083 + 2122) \times 10^{-6}\ \text{M}} = 0.018$$

Present to future we hope to avoid: Ocean carbon would rise by less than 2% for about a 30% further increase in atmospheric CO_2