

# The Perturbed Carbon Cycle

EES 2110

Introduction to Climate Change

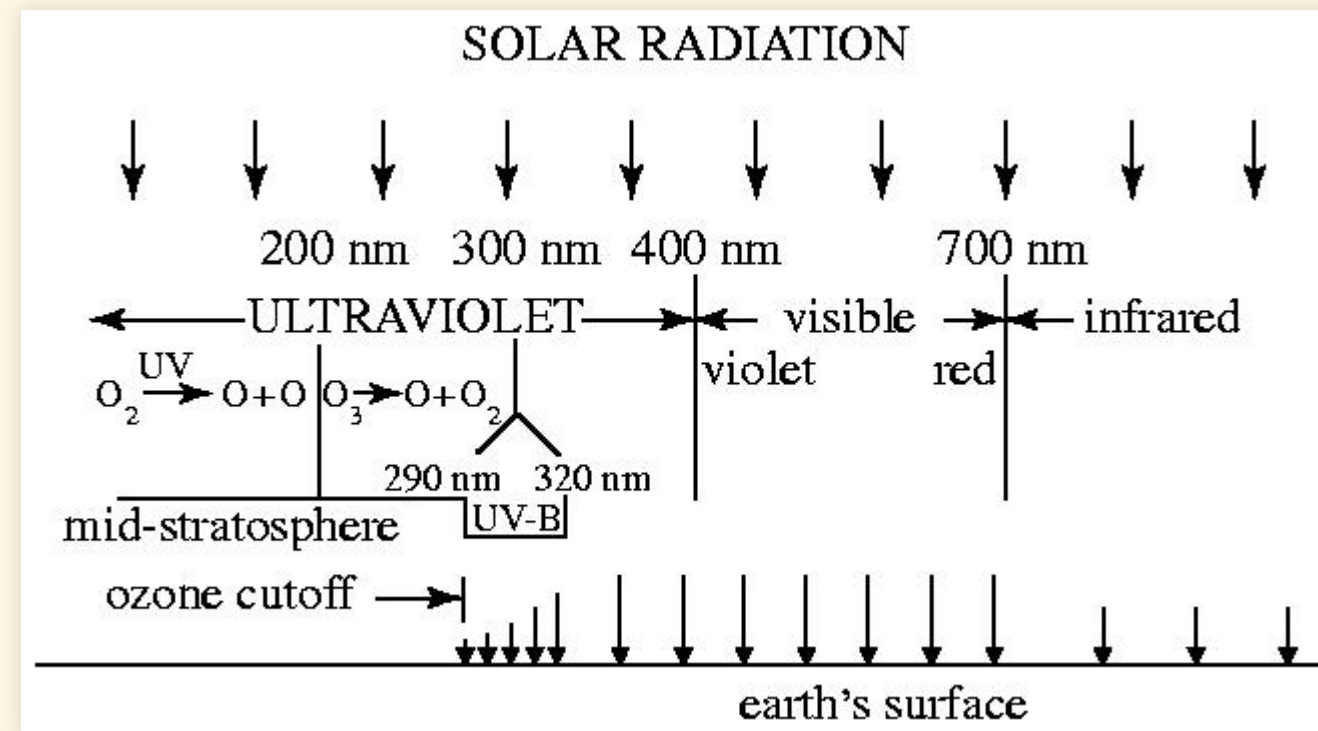
Jonathan Gilligan

Class #16: Wednesday, February 15 2023

# Ozone and Methane

Ozone

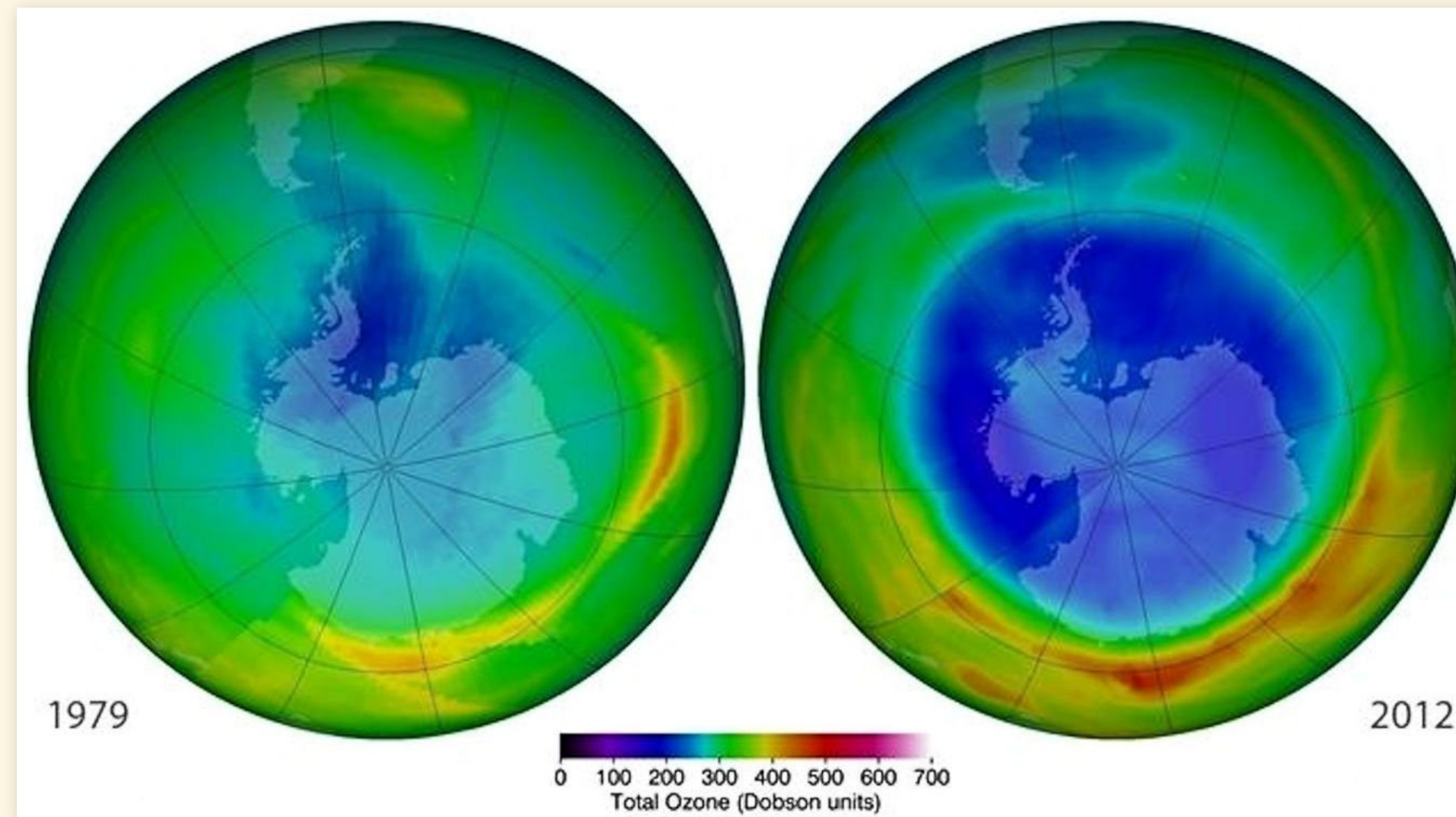
# Stratospheric Ozone



- Ozone is a naturally occurring molecule in the stratosphere
  - From 15–35 km altitude
- Blocks harmful ultraviolet (extreme shortwave) radiation
  - Disrupts DNA and proteins in the lens of the eye
  - Causes skin cancer
  - Causes blindness from cataracts
- Scientists have measured ozone from the ground since the 1920s
  - Useful for understanding winds and weather

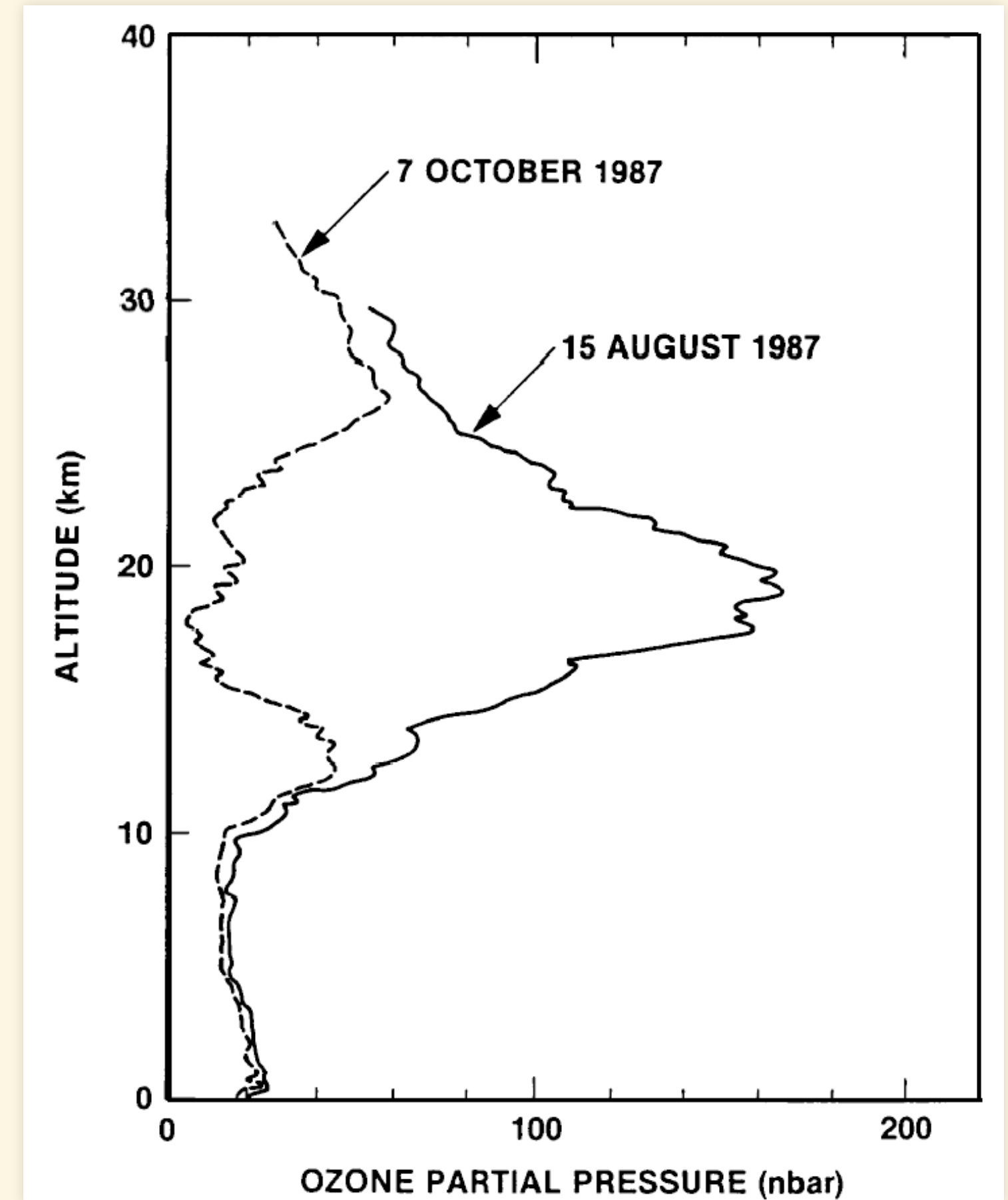
# Stratospheric Ozone Depletion

- 1974: Scientific prediction:
  - Chlorofluorocarbon chemicals will destroy ozone
  - Scientists believed ozone destruction would be gradual
- September 1980: Scientists in Antarctica see ozone go to zero in a matter of days
- 1985: Announcement: Discovery of a giant hole in the ozone layer over Antarctica every spring
- Tipping point:
  - Stratospheric chlorine < 2 parts per billion: No ozone hole
  - Stratospheric chlorine > 2 parts per billion: Ozone hole appears



# Discovery of the Ozone Hole

- Halley Bay Antarctica
  - British meteorological station
  - Measured ozone every month from 1958
- Antarctic Winter
  - June–September
  - No sun for months
- September 1980
  - Shortly after the sun rose, ozone disappeared
  - Ozone returned a few months later
  - Station head Joe Farman thought his instrument must be broken
    - Ordered a new instrument from England
    - The next September both instruments saw ozone disappear
  - 1984: Farman reports ozone hole
    - NASA had launched Total Ozone Mapping Spectrometer in 1979
      - Why hadn't it seen an ozone hole
    - NASA had programmed the computers to ignore crazy low ozone values



# What Causes the Ozone Hole?

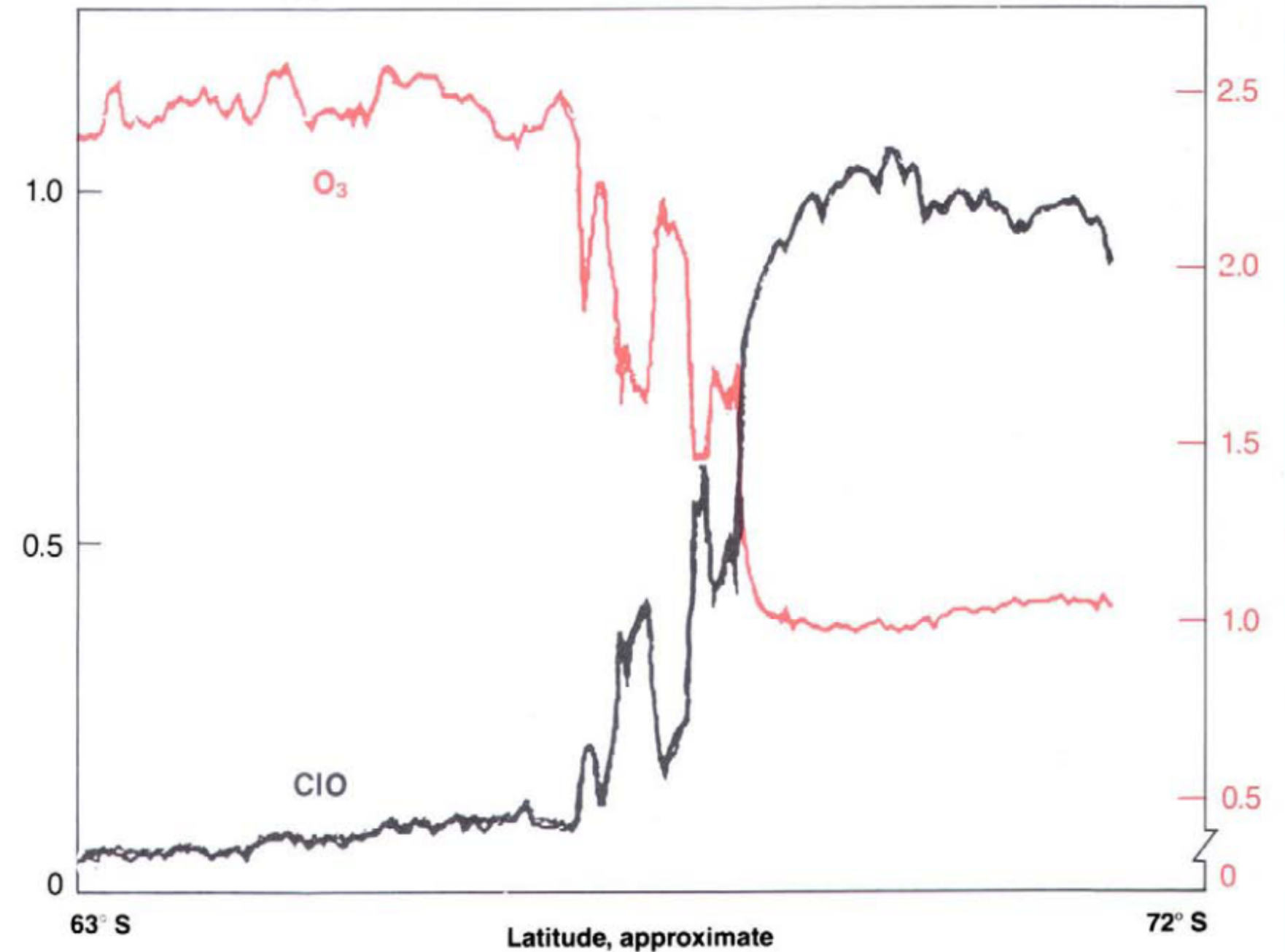


- 82% of Chlorine in the stratosphere is from human-made chemicals
- Sunlight breaks down chlorine-containing compounds
- Chlorine is activated on ice crystals in the stratosphere
- Activated chlorine destroys ozone
- Ozone is missing exactly where chlorine levels are high
- The “smoking gun”

### As reactive chlorine increases, Antarctic ozone decreases

Chlorine monoxide, ppb

Ozone, ppm

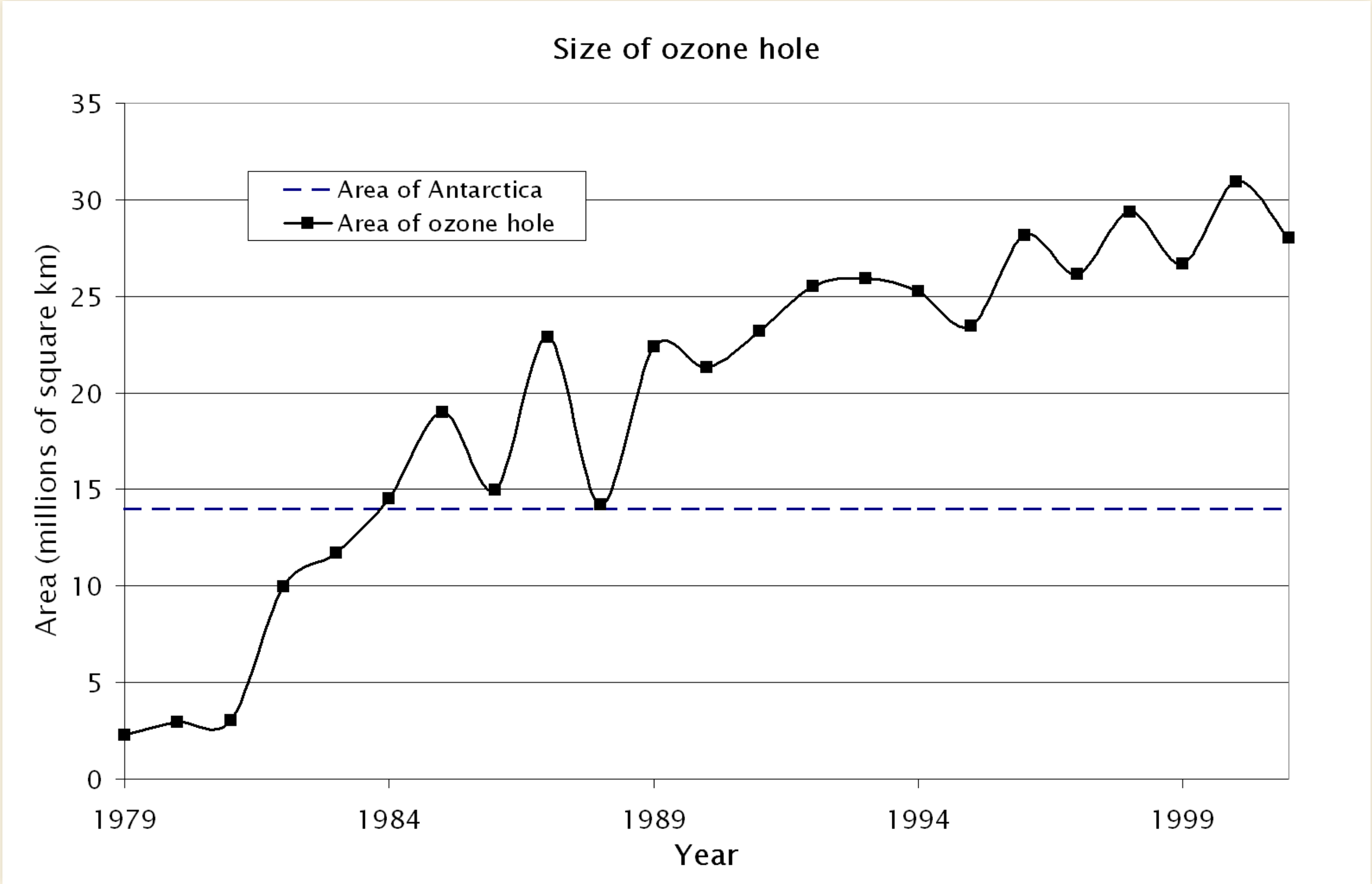


Instruments aboard NASA's ER-2 research airplane measured concentrations of chlorine monoxide and ozone simultaneously as the plane flew from Punta Arenas, Chile (53° S), to 72° S. The data shown above were collected on Sept. 16, 1987. As the plane entered the ozone hole, concentrations of chlorine monoxide increased to about 500 times normal levels while ozone plummeted.

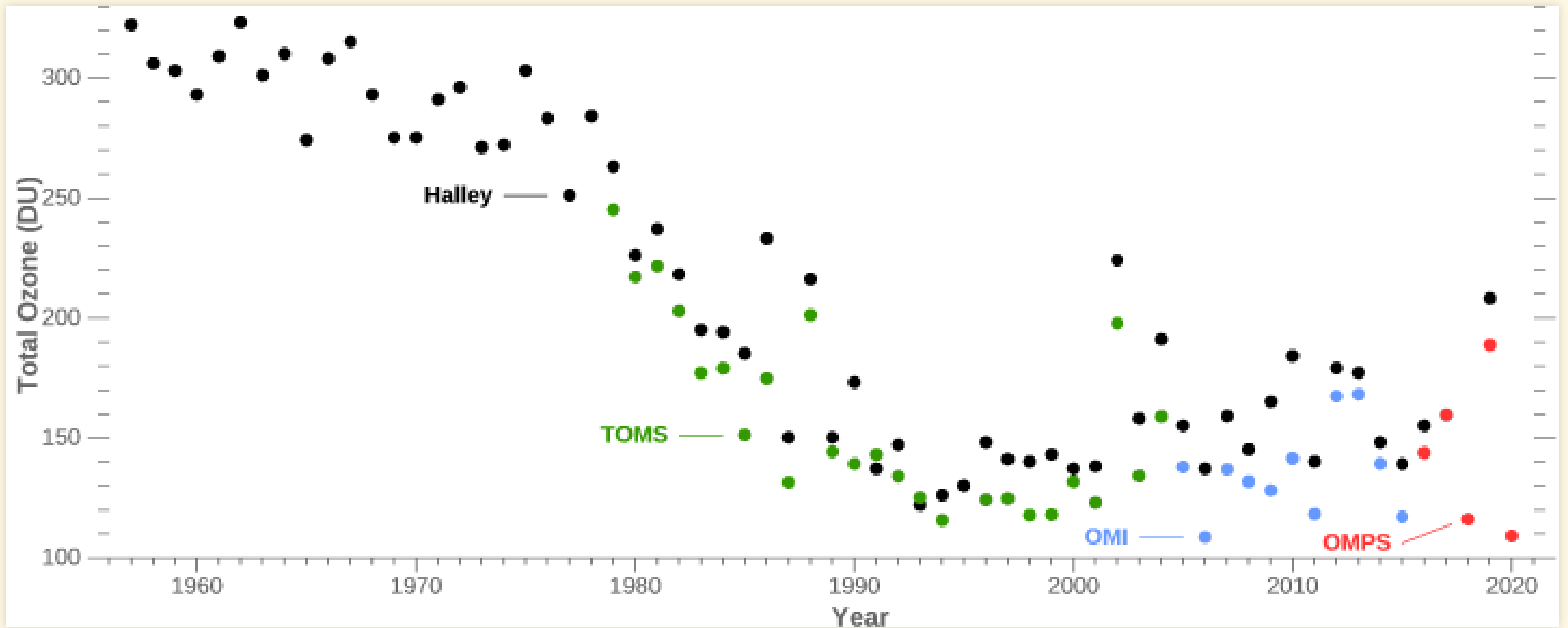
Source: James G. Anderson, Harvard University



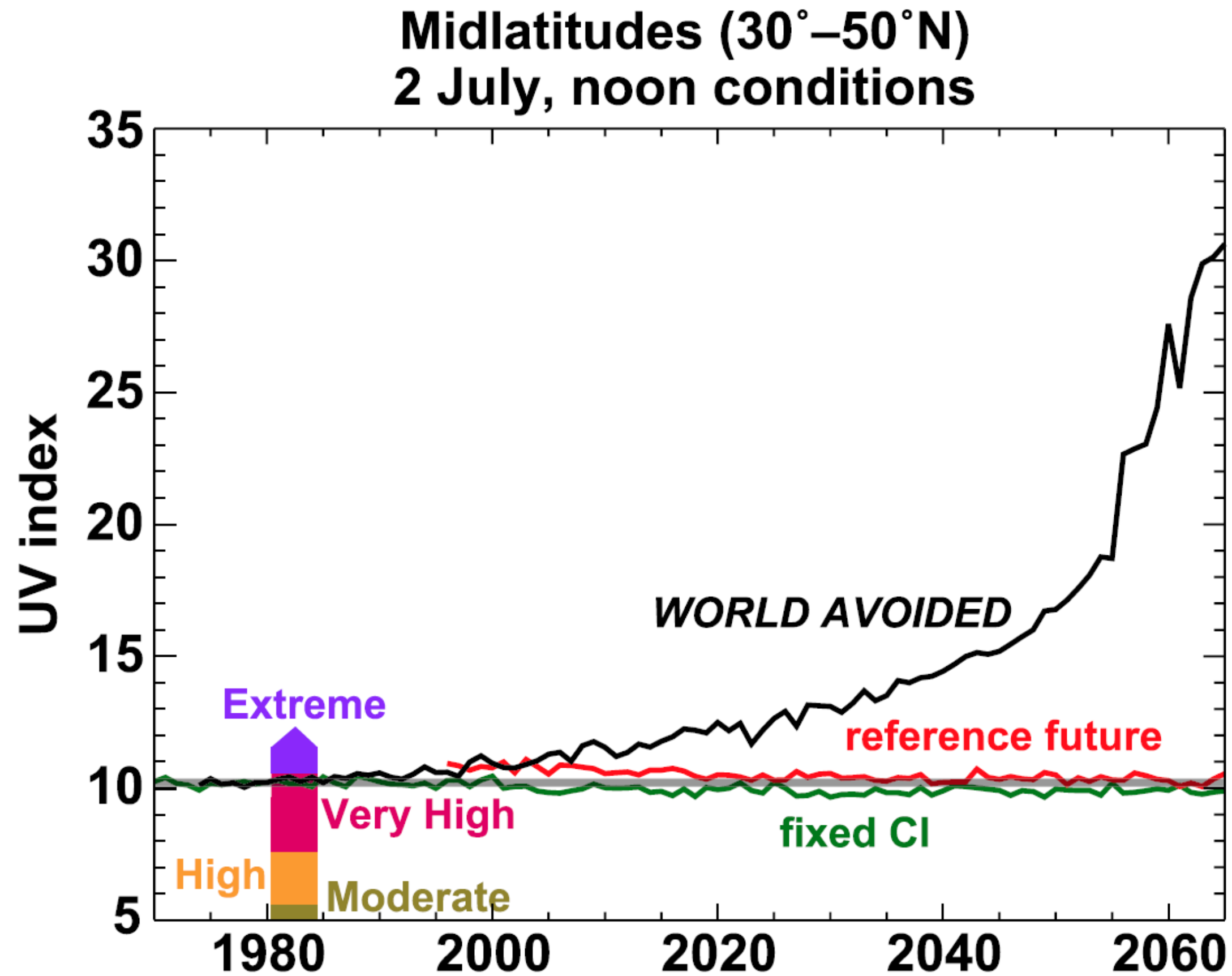
# Growth of Ozone Hole



# History of Ozone over Halley Bay



# Success: Avoided Futures



# Important Note:

- The ozone hole is completely different from global warming
- Caused by chemical reactions with chlorine atoms
- However:
  - CFC chemicals that destroy ozone are also powerful greenhouse gases
  - Ozone depletion is temperature-sensitive
    - Hole over Antarctica because of very cold stratosphere (much colder than arctic)
    - Global warming cools stratosphere
    - If we had not stopped production of CFC chemicals An ozone hole might have started over arctic too.
- Ozone in the stratosphere protects us from solar UV radiation
  - Ozone in the troposphere is a pollutant that damages our lungs

# Methane

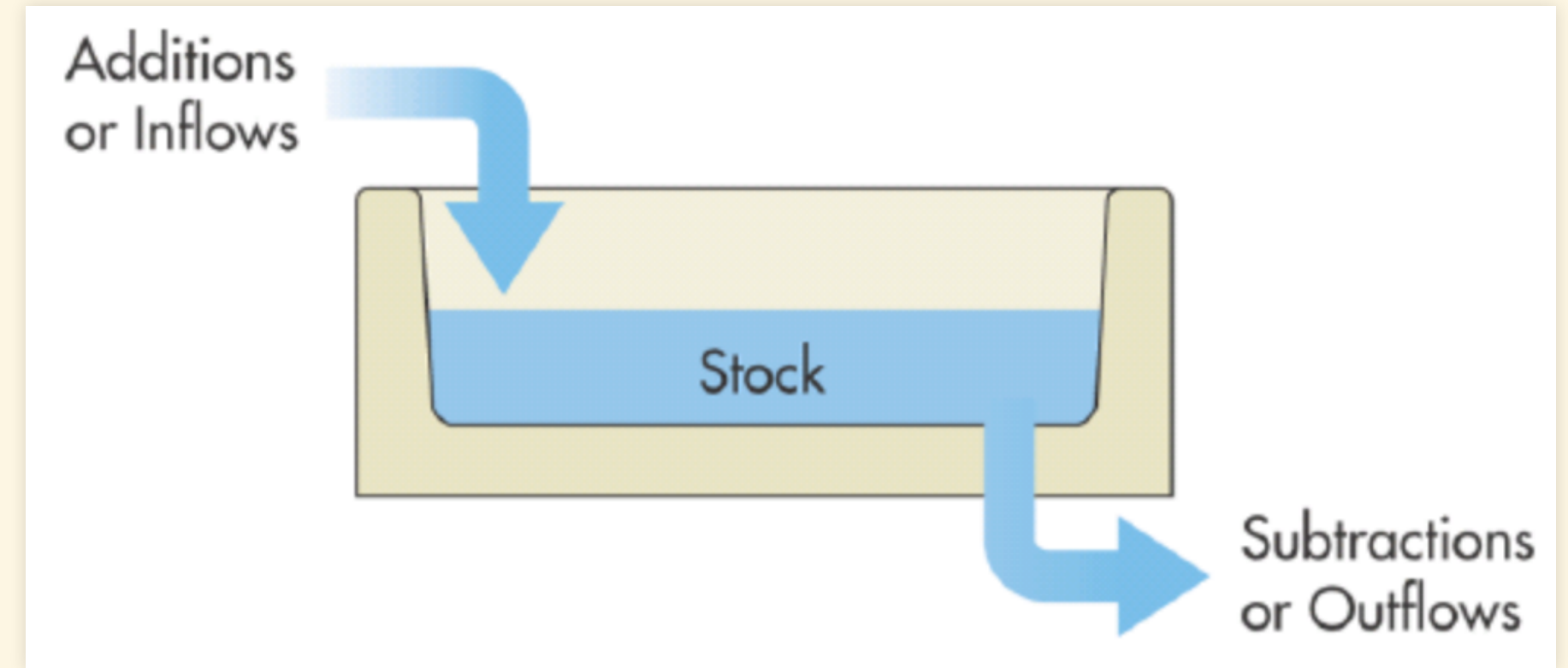
# Bathtub Model

- Level of water in the bathtub:
  - Rises when sources > sinks
  - Falls when sinks > sources
  - Equilibrium when sinks = sources

- Chemical equilibrium:

$$\begin{aligned} & \left[ \frac{\text{Gton C}}{\text{year}} \right] = \text{decomposition}; \\ & \left[ \frac{\text{Gton C}}{\text{year}} \right] \ll \text{decomposition}; \left[ \frac{\text{Gton C}}{\text{year}} \right] \\ & = \frac{\text{inventory}}{[\text{Gton C}]} \ll \text{inventory}; [\text{Gton C}] \\ & = \text{emission}; \left[ \frac{\text{Gton C}}{\text{year}} \right] \\ & \times \text{lifetime}; [\text{year}] \end{aligned}$$

- The lifetime of methane has been fairly constant, around 10 years.



- Ozone depletion is caused by decreasing lifetime
- Growing methane concentration is caused by increased emissions



# Methane vs. CO<sub>2</sub>

## Methane:

- Short lifetime (around 10 years)
- Simple outflow (decomposition)

## CO<sub>2</sub>

- Long, complicated lifetime (centuries to millennia)
- Multiple outflow paths
  - Photosynthesis
  - Dissolving in water
    - Complex pathways for dissolved CO<sub>2</sub>
  - Fast pathways can saturate
    - As fast pathways saturate, lifetime becomes longer
- The more CO<sub>2</sub> is in the atmosphere, the longer the lifetime becomes

# Saturation of Outflow Pathways

- Trees
  - Trees suck CO<sub>2</sub> from the atmosphere
  - Planting more trees could remove CO<sub>2</sub> faster
  - But there isn't enough land to plant all the trees we'd need
- Surface oceans
  - CO<sub>2</sub> dissolves rapidly into the surface oceans
    - But over time, the oceans become saturated
    - Dissolution of CO<sub>2</sub> slows down and then stops
- If people only put a little CO<sub>2</sub> into the atmosphere, it would be removed quickly
  - But when we put large amounts in
    - Fast removal paths become saturated
    - Removal slows down
    - Lifetime increases



# From atmosphere to rocks





# From atmosphere to rocks

- Carbonate vs. Silicate minerals
- Urey Reaction:  $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$ 
  - $\rightarrow$ : weathering (reactions near surface)
  - $\leftarrow$ : metamorphism (high temp./pressure deep beneath surface)
- Silicate minerals originate at high temperature (igneous)
- Carbonate minerals originate at low temperature (sedimentary)

# Connection to Climate

- Rain falls on silicate minerals
  - $\text{CO}_2$  dissolves into rainwater
  - Dissolved  $\text{CO}_2$  makes rainwater is acidic
- Acidic water dissolves silicate minerals
  - Dissolved ions ( $\text{Ca}^{+2}$ ),  $\text{SiO}_3^{-2}$ , etc.)
- In oceans, plankton convert dissolved  $\text{CO}_2$  & ions to calcite (calcium carbonate)
- Calcite ends up as limestone on sea floor
- **Bottom line:**
  - Weathering silicate minerals transforms atmospheric  $\text{CO}_2$  to rocks on sea floor.

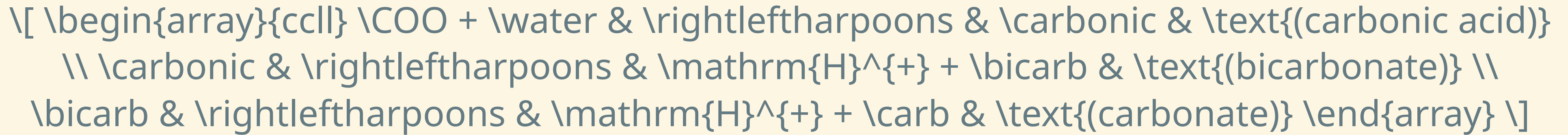
# Carbon Chemistry



# Carbon Chemistry

```
\[ \begin{array}{ccl} \text{COO} + \text{water} & \rightleftharpoons & \text{carbonic} \\ \text{carbonic acid} & & \\ \text{bicarb} & \rightleftharpoons & \text{bicarbonate} \\ \text{bicarbonate} & \rightleftharpoons & \text{bicarb} \\ \text{bicarb} & \rightleftharpoons & \text{bicarbonate} \\ \text{bicarbonate} & \rightleftharpoons & \text{bicarb} \end{array} \]
```

# Natural state of ocean



- Typical concentrations:
  - $\text{pH} \sim 8$ 
    - $[\text{H}^+] \sim 10^{-8} \text{ molar} = 10^{-5} \text{ moles/meter}^3$
  - Various forms of carbon: 2 moles/meter<sup>3</sup>
    - 88%  $\text{bicarb}^-$  ions
    - 11%  $\text{carb}^{2-}$  ions
    - 1%  $\text{COO}^-$  and  $\text{carbonic}$ .
  - Don't fret about detailed numbers
- **Why is it important that there is:**
  - **200,000 times more  $\text{bicarb}^-$  than  $[\text{H}^+]$ ?**
  - **10 times more  $\text{carb}^{2-}$  than  $\text{COO}^-$ ?**

Simple treatment:

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Add the three reactions

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\[ \def\scancel#1{\rlap{\smash{\cancel{#1}}}\phantom{#1}} \begin{aligned} & \{\color{black}\text{COO}\} + \{\color{black}\text{water}\} \& \rightleftharpoons \\ & \{\color{darkgreen}\text{carbonic}\} \& \rightleftharpoons \{\color{blue}\text{Hplus}\} + \{\color{darkred}\text{bicarb}\} \\ & \{\color{blue}\text{Hplus}\} + \{\color{purple}\text{carb}\} \& \rightleftharpoons \\ & \{\color{darkred}\text{bicarb}\} \end{aligned} \]
```

to get

```
\[ \begin{split} & \{\color{black}\text{COO}\} + \{\color{black}\text{water}\} \& \& + \\ & \{\color{darkgreen}\text{carbonic}\} + \{\color{blue}\text{Hplus}\} + \{\color{purple}\text{carb}\} \& \& \\ & \& \rightleftharpoons \{\color{darkgreen}\text{carbonic}\} + \{\color{blue}\text{Hplus}\} + 2\& , \\ & \{\color{darkred}\text{bicarb}\} \end{split} \]
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\[ \begin{split} {\color{black}\text{COO}} + {\color{black}\text{water}} {}&{} + \\ {\color{darkgreen}\text{scancel}\text{carbonic}} + {\color{blue}\text{scancel}\text{Hplus}} + \\ {\color{purple}\text{carb}} &\& \rightleftharpoons \\ {\color{darkgreen}\text{scancel}\text{carbonic}} + {\color{blue}\text{scancel}\text{Hplus}} + 2\, \\ {\color{darkred}\text{bicarb}} &\end{split} \]
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(Cancel common terms on both sides)

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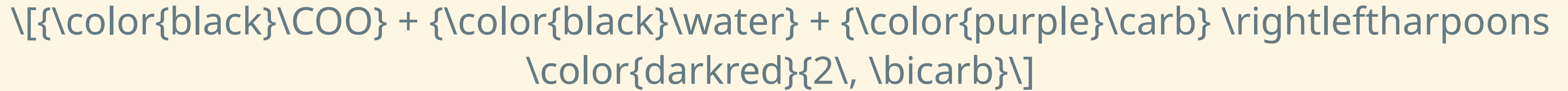
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```

**Now  $\color{black}\text{Hplus}$  doesn't matter.**

# Le Chatelier's Principle:

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- Add more  $\text{HCO}_3^-$  ... What happens?
  - Le Chatelier's principle:
    - Consume excess  $\text{HCO}_3^-$  by running reaction to right
- Why is this important?
  - Carbonate buffering means ocean can hold 10 times more  $\text{HCO}_3^-$ .
- But more dissolved  $\text{HCO}_3^-$  means less  $\text{CO}_2$ .
  - Why is decreased  $\text{CO}_2$  important?
    - Without  $\text{CO}_2$ , ocean can't absorb more  $\text{HCO}_3^-$ .

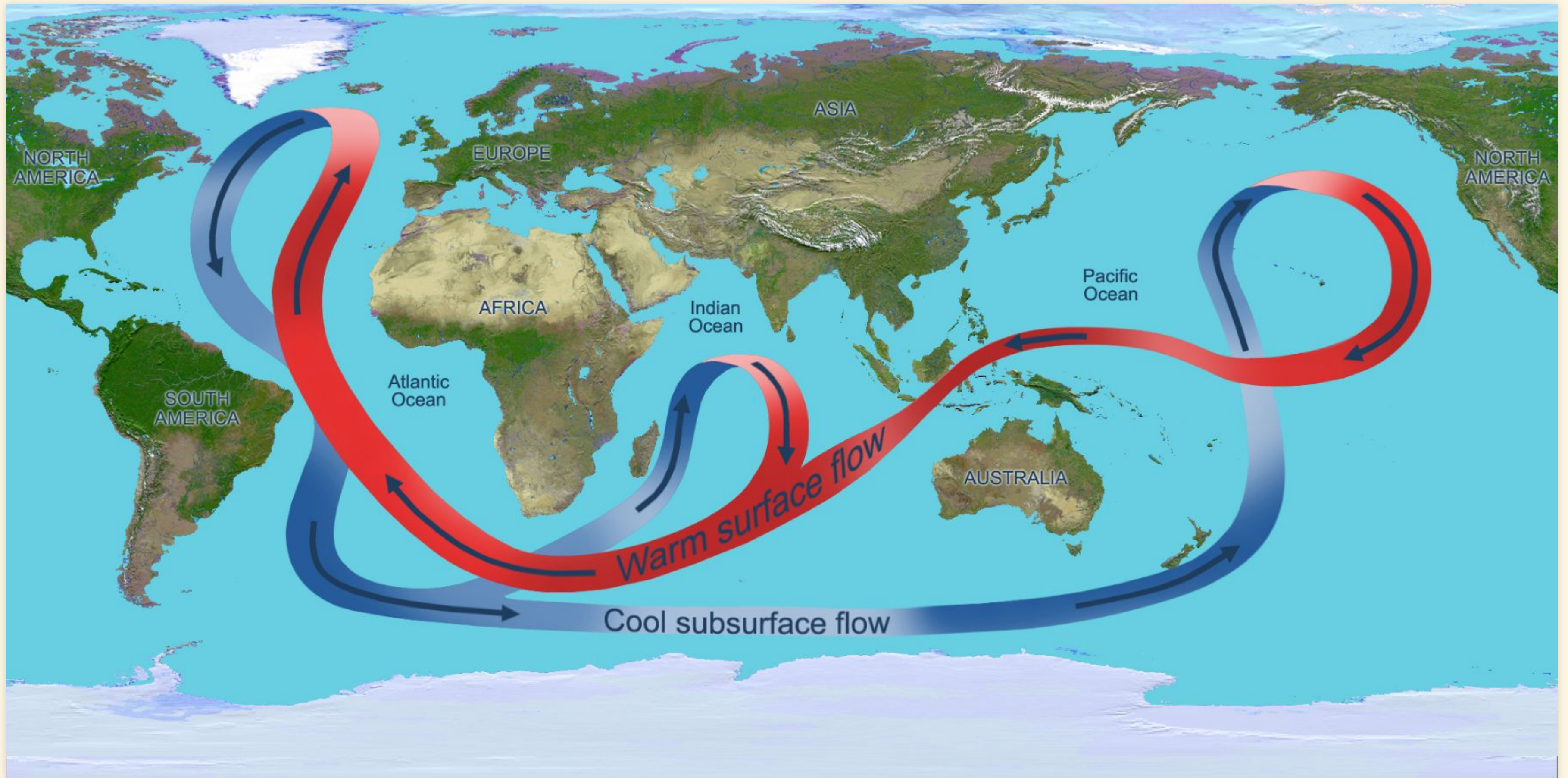
# Anthropogenic CO<sub>2</sub>

- **Sources:** ~11.5 GTC/year
  - 9.6 GTC from fossil fuels
  - 1.5 GTC from deforestation
  - 0.4 GTC from cement production
- **Sinks:** ~6.1 GTC/year
  - ~2.6 GTC into oceans (dissolving)
  - ~3.5 GTC into land (plants)
- **Remaining ~5.4 GTC/year stays in atmosphere.**
- Scale:  $(1 \sim \text{GTC} = 1 \sim \text{billion metric tons carbon} \approx 2 \text{ ppm})$ .
  - Numbers have changed since the textbook was published.
  - These are the latest.

Global conveyor belt



# Global conveyor belt





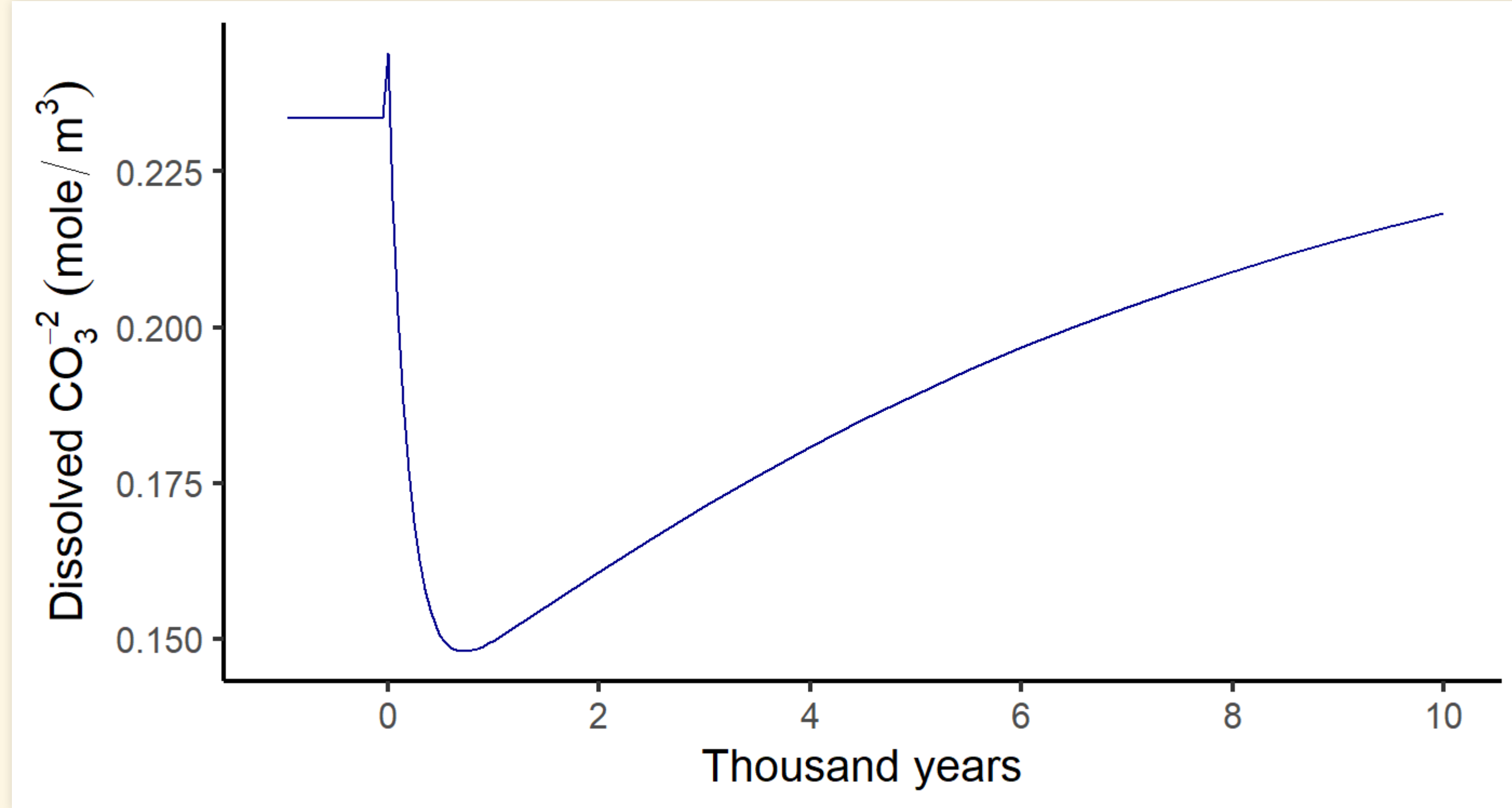
# Ocean Acidification

- More dissolved  $\text{HCO}_3^-$  means less  $\text{H}^+$
- Surface oceans saturate: can't absorb more  $\text{HCO}_3^-$ .
  - Thermocline means slow mixing with deep oceans.
  - $\text{HCO}_3^-$  absorption limited by conveyor bringing fresh carbonate from deep oceans.
  - Conveyor is slow (many centuries)
  - Warming oceans may slow conveyor
- **Decreasing carbonate = acidifying oceans**
  - $\text{CaCO}_3$  = bone, shells, teeth, etc.  $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$
  - Less  $\text{H}^+$  means the reaction moves to right:
    - Shells and coral dissolve
    - Damage or kill corals, shellfish, plankton, etc.

# Ocean Acidification

- More dissolved  $\text{CO}_2$  means less  $\text{pH}$
- Surface oceans saturate: can't absorb more  $\text{CO}_2$ .
  - Thermocline means slow mixing with deep oceans.
  - $\text{CO}_2$  absorption limited by conveyor bringing fresh carbonate from deep oceans.
  - Conveyor is slow (many centuries)
  - Warming oceans may slow conveyor
- **Deep ocean saturation:**
  - Deep oceans run out of carbonates (centuries)
  - Only source of new carbonate is dissolving limestone on sea floor
    - Thousands of years

# Carbonate after a big CO<sub>2</sub> release



GEOCARB model

# GEOCARB model

- <http://climatemodels.uchicago.edu/geocarb>  
or  
<https://climatemodels.jgilligan.org/geocarb>
- “Spin-up” establishes equilibrium
- Change at year zero
- Simulation shows how earth system responds to change over a million years
- Look at different time scales ...
- Look at different variables ...
  - [WeatS](#) = weathering of silicate minerals
  - [WeatC](#) = weathering of carbonate minerals
  - [BurC](#) = burial of carbon as limestone
  - [TCO2](#) = total dissolved carbon dioxide
  - [alk](#) = alkalinity ( $\backslash(\backslash\text{bicarb} + 2 \times \backslash\text{carb}\backslash)$ )

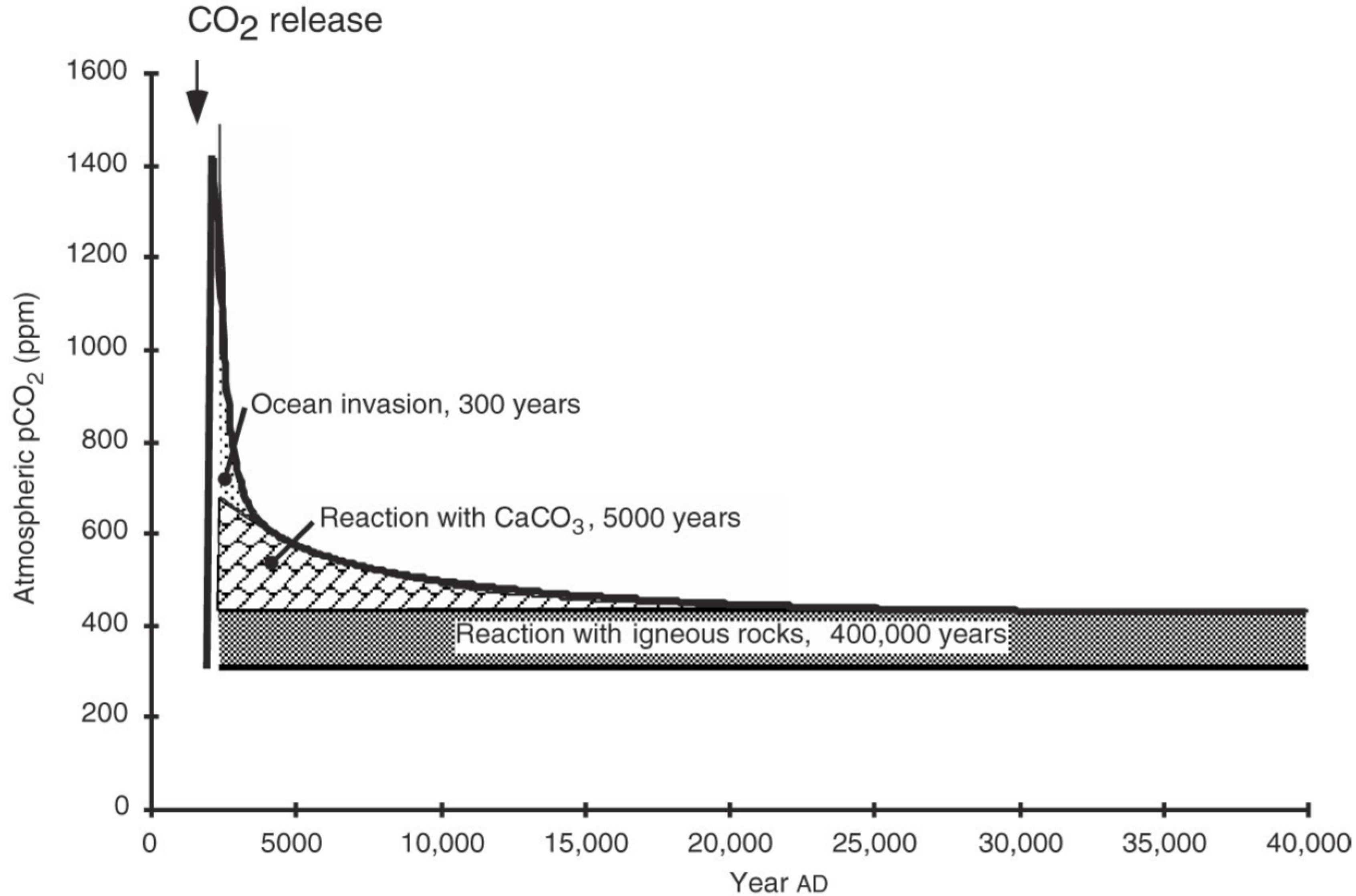
# Fate of CO<sub>2</sub> emissions

- By 2100 cumulative emissions may reach 3000 GTC
- Type 3000 into “Transition CO<sub>2</sub> spike”
- Switch to 1000 year time scale
  - What happens to  $p\text{CO}_2$ ?
  - What does the silicate thermostat do?
  - Look at calcite budget:
    - What happens to burial of carbonates?
      - What does it mean for carbonate burial to become negative?
      - Why is this happening?
      - **Clue:** look at Ocean  $\text{carb}$  concentration
    - What happens to the temperature over time?
- Switch to 10,000 year time scale
  - What happens to ocean  $\text{carb}$  & calcite budget?
    - Why?

# Prospects for future:

- **Oceanic sinks:**
  - A few centuries:
    - Around 50% of excess  $\text{CO}_2$  dissolves into oceans
    - Dissolution stops as oceans acidify
  - A few thousand years:
    - Reactions with limestone restore  $\text{pH}$ ,  $\text{CO}_2$  solubility
  - Hundreds of thousand of years
    - Silicate-mineral weathering removes and buries excess  $\text{CO}_2$ .
- **Bottom line:**
  - $\text{CO}_2$  stays in the atmosphere many thousands of years after we stop burning fossil fuels.





# CO<sub>2</sub> vs. Methane

- $\text{CO}_2$ :
  - After 1000 years, around 30% of excess  $\text{CO}_2$  remains in atmosphere
  - After 10,000 years, 13% remains
  - After 100,000 years, 6% remains
- Methane ( $\text{CH}_4$ ):
  - 31 times more powerful (molecule-for-molecule) than  $\text{CO}_2$
  - Reacts with  $\text{OH}$  (hydroxyl radicals) and oxidizes into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .
  - Atmospheric lifetime: 9.6 years:
    - After 25 years, 7% remains.
    - After 100 years, 0.003% remains.

# Weathering as Thermostat

# Weathering as Thermostat

CO<sub>2</sub> is balance of volcanic outgassing and chemical weathering

- **Higher temperatures:**
  - More rain, faster chemical reactions
  - Faster weathering
  - Atmospheric CO<sub>2</sub> falls
- **Lower temperatures**
  - Less rain, slower chemical reactions
  - Slower weathering
  - Atmospheric CO<sub>2</sub> rises
- Net effect:
  - Keeps temperature stable near some “set point”
  - Set-point is determined by geology

# Temperature of Earth

- Weathering acts as thermostat.
- Earth's temperature has been remarkably stable over time.
  - 4 billion years ago, sun was 30% dimmer...
  - But there has constantly been liquid water.
- Geologic change alters thermostat "setting":
  - Volcanic outgassing
  - Land surface (e.g., mountain ranges)
  - Vascular plants
- In the long run, silicate thermostat will fix global warming...
  - ...but it will take tens to hundreds of thousands of years.



