Ocean Acidification

EES 2110

Introduction to Climate Change

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Carbon Chemistry

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$$\begin{aligned} CO_2 + H_2O &\rightleftharpoons H_2CO_3 && \text{(carbonic acid)} \\ H_2CO_3 &\rightleftharpoons H^+ + HCO_3^- && \text{(bicarbonate)} \\ HCO_3^- &\rightleftharpoons H^+ + CO_3^{2-} && \text{(carbonate)} \end{aligned}$$

Natural state of ocean

$$\begin{aligned}
CO_2 + H_2O &\rightleftharpoons H_2CO_3 && \text{(carbonic acid)}\\
H_2CO_3 &\rightleftharpoons H^+ + HCO_3^- && \text{(bicarbonate)}\\
HCO_3^- &\rightleftharpoons H^+ + CO_3^{2-} && \text{(carbonate)}
\end{aligned}$$

- Typical concentrations:
  - $\mathrm{pH} \sim 8$:
    - $H^+ \sim 10^{-8}\,\mathrm{molar} = 10^{-5}\,\mathrm{moles/meter}^3$
  - Various forms of carbon: 2 moles/meter^3
    - 88% HCO_3^- ions
    - 11% CO_3^{2-} ions
    - 1% CO_2 and H_2CO_3.
  - Don't fret about detailed numbers
- **Why is it important that there is:**
  - **200,000 times more HCO_3^- than H^+?**
  - **10 times more CO_3^{2-} than CO_2?**

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Add the three reactions

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$

to get

$$CO_2 + H_2O + H_2CO_3 + H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3 + H^+ + 2\,HCO_3^-$$

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$$CO_2 + H_2O + \cancel{H_2CO_3} + \cancel{H^+} + CO_3^{2-} \rightleftharpoons \cancel{H_2CO_3} + \cancel{H^+} + 2\,HCO_3^-$$

(Cancel common terms on both sides)

Simple treatment:

Add the three reactions

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$

to get

$$CO_2 + H_2O + \qquad + CO_3^{2-}$$

$$\rightleftharpoons \qquad 2\,HCO_3^-$$

(Cancel common terms on both sides)

Simple treatment:

Add the three reactions

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$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
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to get

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2\,HCO_3^-$$

Now H^+ doesn't matter.

Le Chatelier’s Principle:

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$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2\,HCO_3^-$$

- Add more CO_2 … What happens?
  - Le Chatelier's principle:
    - Consume excess CO_2 by running reaction to right
- Why is this important?
  - Carbonate buffering means
    ocean can hold 10 times more CO_2.
- But more dissolved CO_2 means less CO_3^{2-}.
  - Why is decreased CO_3^{2-} important?
    - Without CO_3^{2-}, ocean can't absorb more CO_2.

Anthropogenic CO_2

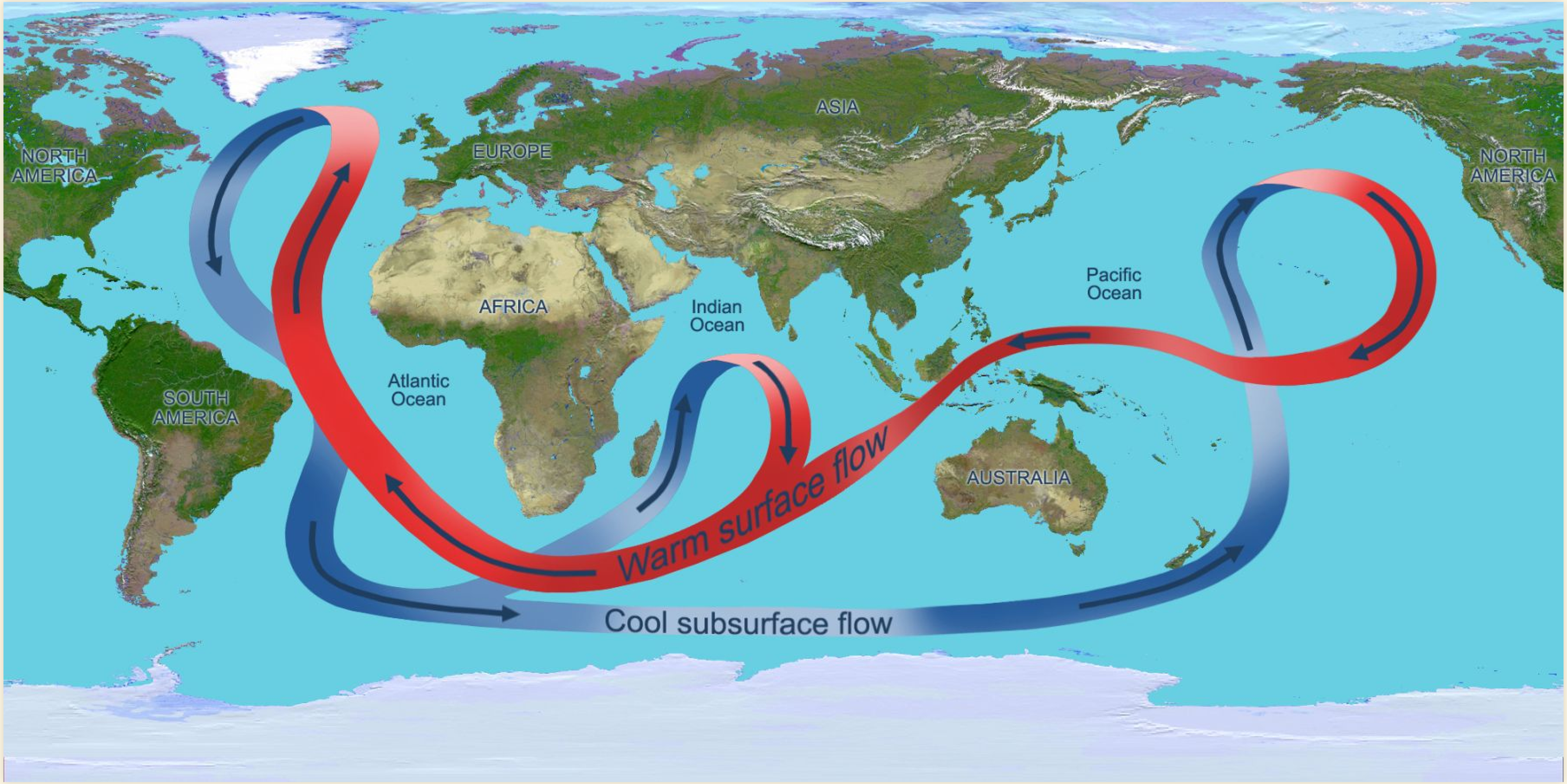
- **Sources:** ~11.5 GTC/year
  - 9.6 GTC from fossil fuels
  - 1.5 GTC from deforestation
  - 0.4 GTC from cement production
- **Sinks:** ~6.1 GTC/year
  - ~2.6 GTC into oceans (dissolving)
  - ~3.5 GTC into land (plants)
- **Remaining ~5.4 GTC/year stays in atmosphere.**

- Scale: $1\ \text{GTC} = 1$ 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 CO_2 means less CO_3^{2-}
- Surface oceans saturate: can't absorb more CO_2.
  - Thermocline means slow mixing with deep oceans.
  - CO_2 absorption limited by conveyor bringing fresh carbonate from deep oceans.
  - Conveyor is slow (many centuries)
  - Warming oceans may slow conveyor
- **Decreasing carbonate = acidifying oceans**
  - $CaCO_3$ = bone, shells, teeth, etc.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

  - Less CO_3^{2-} means the reaction moves to right:
    - Shells and coral dissolve
    - Damage or kill corals, shellfish, plankton, etc.

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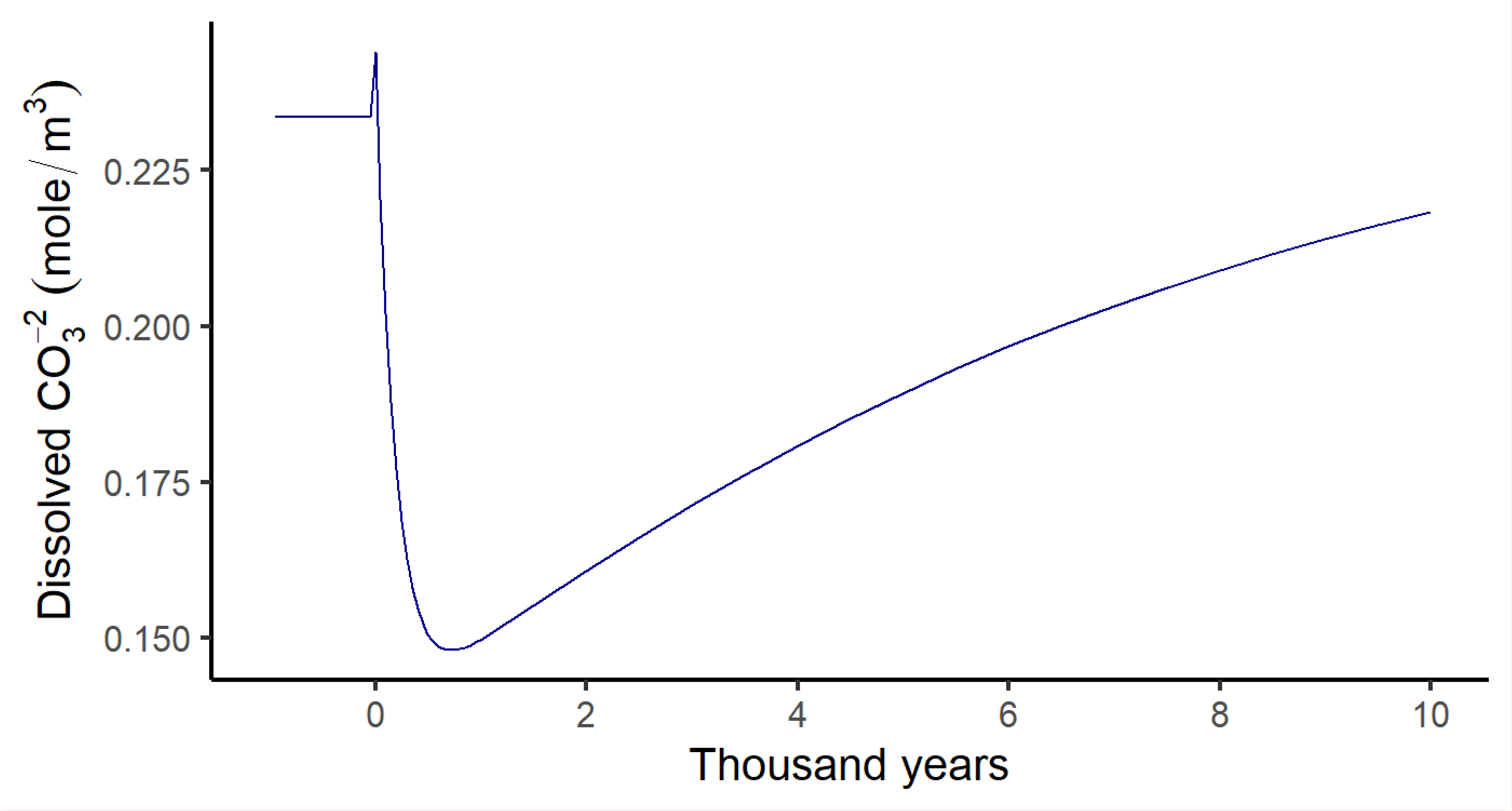
  - Warming oceans may slow conveyor
- **Deep ocean saturation:**
  - Deep oceans run out of carbonates (centuries)
  - Only source of new carbonate is dissolving limestone on sea floor
    - Thousands of years

Carbonate after a big CO_2 release



GEOCARB model

GEOCARB model

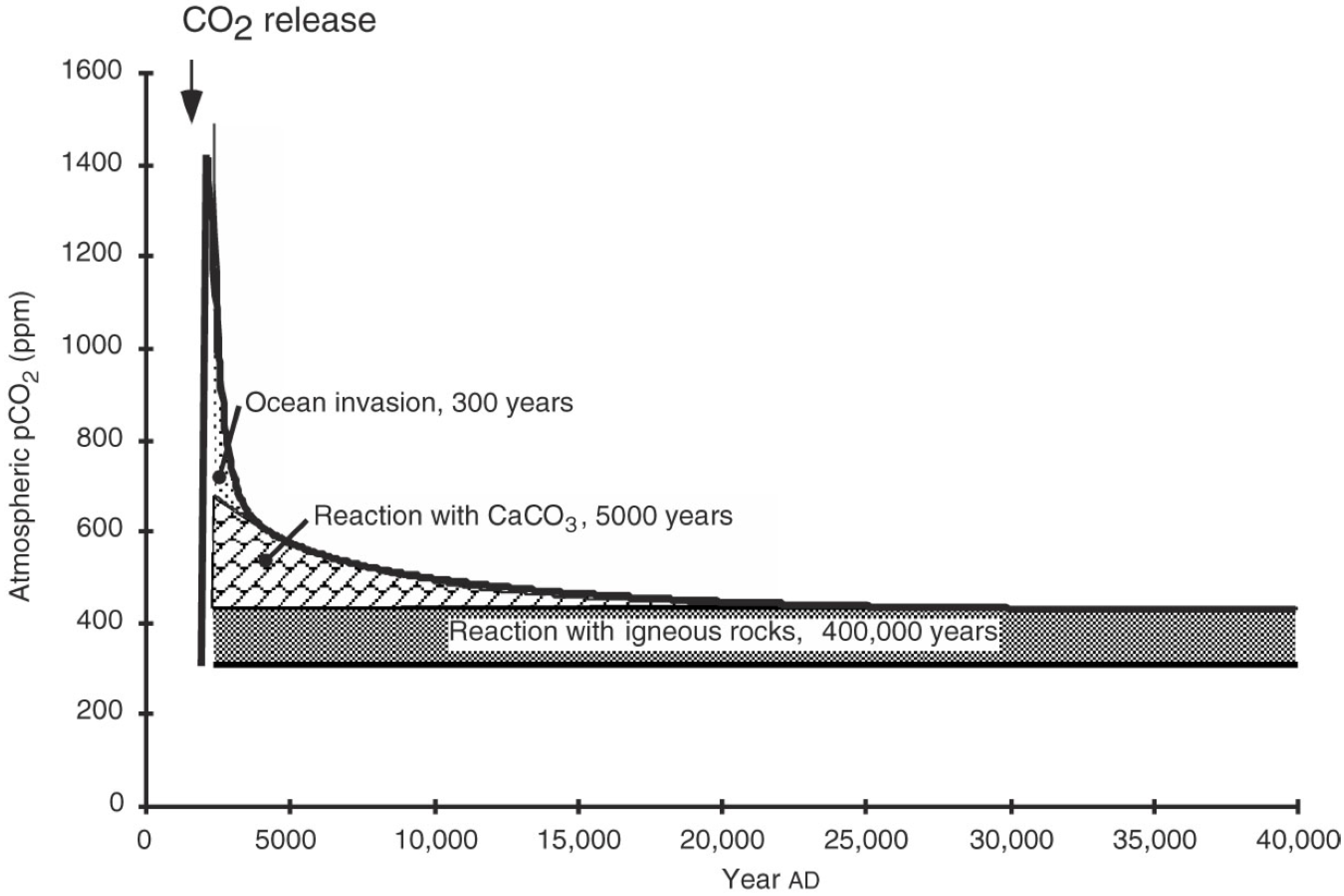
- http://climatemodels.uchicago.edu/geocarb
  or
  https://climatemodels.jgilligan.org/geocarb
- “Spin-up” establishes equilibrium
- Change at year zero
- Simulation shows how earth system responds to change over a million years
- Look at different time scales …
- Look at different variables …
  - `WeatS` = weathering of silicate minerals
  - `WeatC` = weathering of carbonate minerals
  - `BurC` = burial of carbon as limestone
  - `TCO2` = total dissolved carbon dioxide
  - `alk` = alkalinity ($HCO_3^- + 2 \times CO_3^{2-}$)

Fate of CO_2 emissions

- By 2100 cumulative emissions may reach 3000 GTC
- Type 3000 into "`Transition CO2 spike`"
- Switch to 1000 year time scale
  - What happens to pCO_2?
  - What does the silicate thermostat do?
  - Look at $CaCO_3$ 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 CO_3^{2-} concentration
    - What happens to the temperature over time?
- Switch to 10,000 year time scale
  - What happens to ocean CO_3^{2-} & $CaCO_3$ budget?
    - Why?

Prospects for future:

- **Oceanic sinks:**
  - A few centuries:
    - Around 50% of excess CO_2 dissolves into oceans
    - Dissolution stops as oceans acidify
  - A few thousand years:
    - Reactions with limestone restore pH, CO_2 solubility
  - Hundreds of thousand of years
    - Silicate-mineral weathering removes and buries excess CO_2.
- **Bottom line:**
  - CO_2 stays in the atmosphere many thousands of years after we stop burning fossil fuels.



CO_2 release
1600
1400
1200
1000
800
600
400
200
0
Atmospheric pCO_2 (ppm)
Ocean invasion, 300 years
Reaction with $CaCO_3$, 5000 years
Reaction with igneous rocks, 400,000 years
0
5000
10,000
15,000
20,000
25,000
30,000
35,000
40,000
Year AD

CO_2 vs. Methane

- CO_2:
  - After 1000 years, around 30% of excess CO_2 remains in atmosphere
  - After 10,000 years, 13% remains
  - After 100,000 years, 6% remains
- Methane (CH_4):
  - 31 times more powerful (molecule-for-molecule) than CO_2
  - Reacts with OH^- (hydoxyl radicals) and oxidizes into H_2O and 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_2 is balance of volcanic outgassing and chemical weathering

- **Higher temperatures:**
  - More rain, faster chemical reactions
  - Faster weathering
  - Atmospheric CO_2 falls
- **Lower temperatures**
  - Less rain, slower chemical reactions
  - Slower weathering
  - Atmospheric CO_2 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.