The Perturbed Carbon Cycle

EES 3310/5310
Global Climate Change
Jonathan Gilligan

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From atmosphere to rocks

- Carbonate vs. Silicate minerals
- Urey Reaction:

$$CaSiO_3 + CO_2 \Leftrightarrow CaCO_3 + SiO_2$$

- \Rightarrow : weathering (reactions near surface)
- 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
 - CO₂ dissolves into rainwater
 - Dissolved CO₂ makes rainwater is acidic
- Acidic water dissolves silicate minerals
 - Dissolved ions (Ca^{+2} , SiO_3^{-2} , etc.)
- In oceans, plankton convert dissolved CO₂ & ions to calcite (calcium carbonate)
- Calcite ends up as limestone on sea floor
- Bottom line:
 - Weathering silicate minerals transforms atmospheric CO₂ to rocks on sea floor.

Carbon Chemistry

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$$CO_2 + H_2O \implies H_2CO_3$$
 (carbonic acid)
 $H_2CO_3 \implies H^+ + HCO_3^-$ (bicarbonate)
 $HCO_3^- \implies H^+ + CO_3^{2-}$ (carbonate)

Natural state of ocean

$$CO_2 + H_2O \implies H_2CO_3$$
 (carbonic acid)
 $H_2CO_3 \implies H^+ + HCO_3^-$ (bicarbonate)
 $HCO_3^- \implies H^+ + CO_3^{2-}$ (carbonate)

- Typical concentrations:
 - pH ~ 8:
 - \circ H $^+$ \sim 10 $^{-8}$ molar = 10 $^{-5}$ moles/meter 3
 - Various forms of carbon: 2 moles/meter³
 - 88% HCO₃ ions
 - 11% CO₃²⁻ ions
 - 1% CO₂ and H₂CO₃.
 - 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 ?

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

$$CO_2 + H_2O + H_2CO_3 + H^+ + CO_3^{2-}$$

 $\Rightarrow H_2CO_3 + H^+ + 2HCO_3^-$

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(Cancel common terms on both sides)

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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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$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^{-1}$$

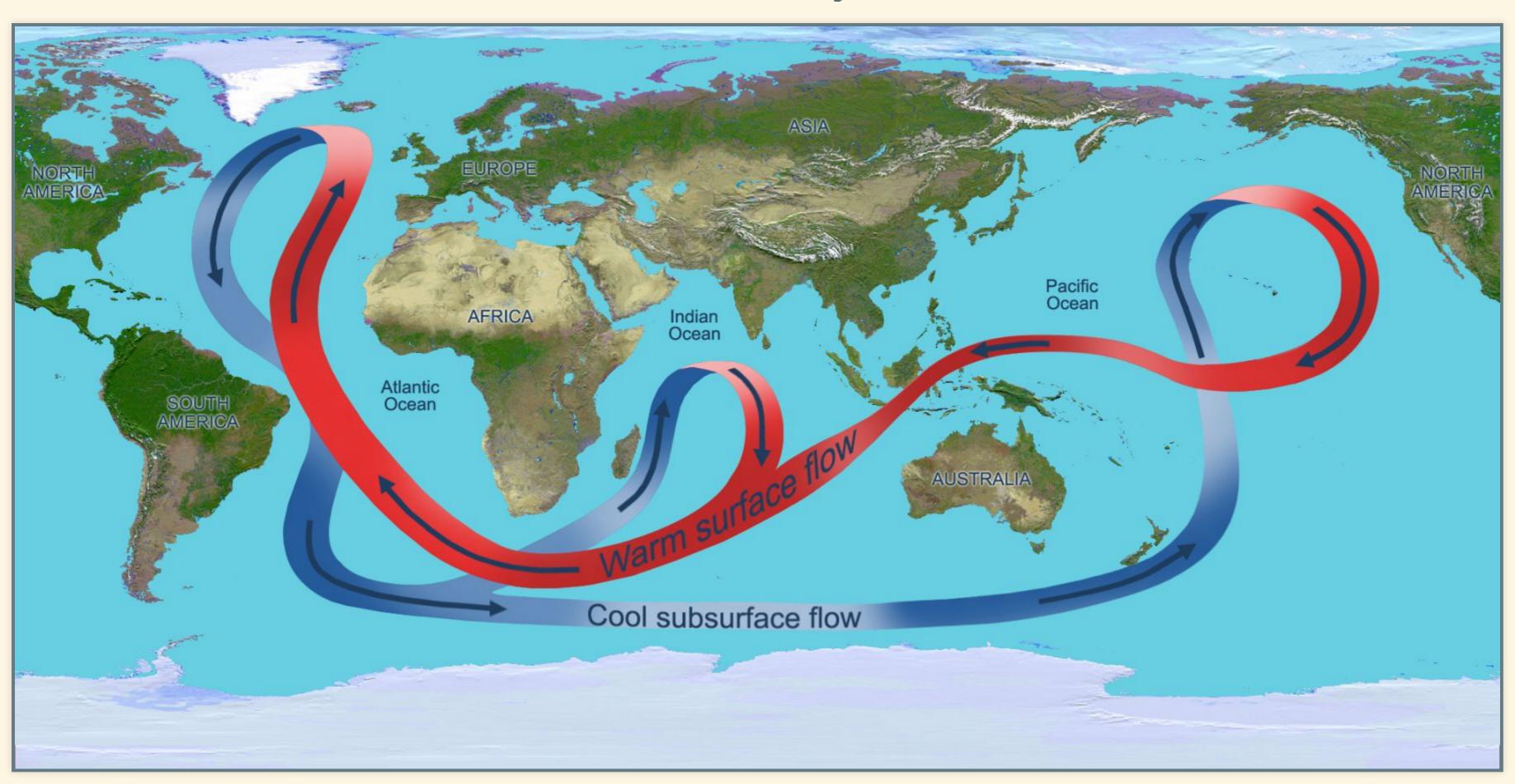
- Add more CO₂ ... What happens?
 - Le Chatelier's principle:
 - Consume excess CO₂ by running reaction to right
- Why is this important?
 - Carbonate buffering means ocean can hold 10 times more CO₂.
- But more dissolved CO_2 means less CO_3^{2-} .
 - Why is decreased CO_3^{2-} important?
 - Without CO_3^{2-} , ocean can't absorb more CO_2 .

Anthropogenic CO₂

- 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: $1 \text{ GTC} = 1 \text{ billion metric tons carbon} \approx 2 \text{ppm}$.
- Numbers have changed since the textbook was published.
- These are the latest.

Global conveyor belt

Global conveyor belt



Ocean Acidification

- More dissolved CO₂ means less CO₃²⁻
- Surface oceans saturate: can't absorb more CO_2 .
 - Thermocline means slow mixing with deep oceans.
 - \bullet CO₂ 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.

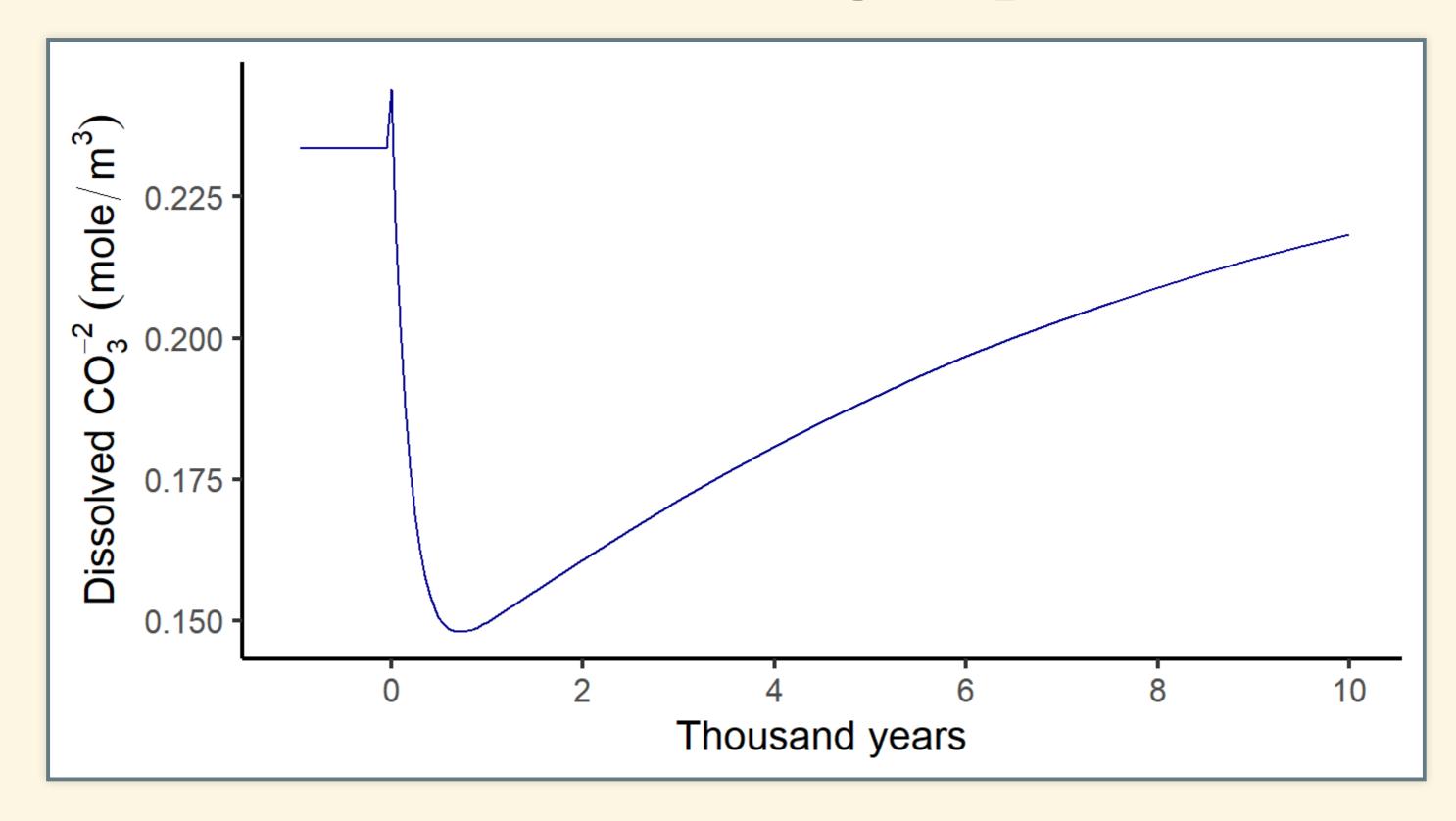
$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

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

Ocean Acidification

- More dissolved CO₂ means less CO₃²⁻
- Surface oceans saturate: can't absorb more CO_2 .
 - Thermocline means slow mixing with deep oceans.
 - CO₂ 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 CO₂ release



GEOCARB model

GEOCARB model

- http://climatemodels.uchicago.edu/geocarb or https://climatemodels.ees3310.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 CO₂ emissions

- By 2100 cumulative emissions may reach 3000 GTC
- Type 3000 into "Transition CO2 spike"
- Switch to 1000 year time scale
 - What happens to pCO₂?
 - What does the silicate thermostat do?
 - Look at CaCO₃ budget:
 - What happens to burial of carbonates?
 - What does it mean for carbonate burial to become negative?
 - Why is this happening?
 - \circ 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?

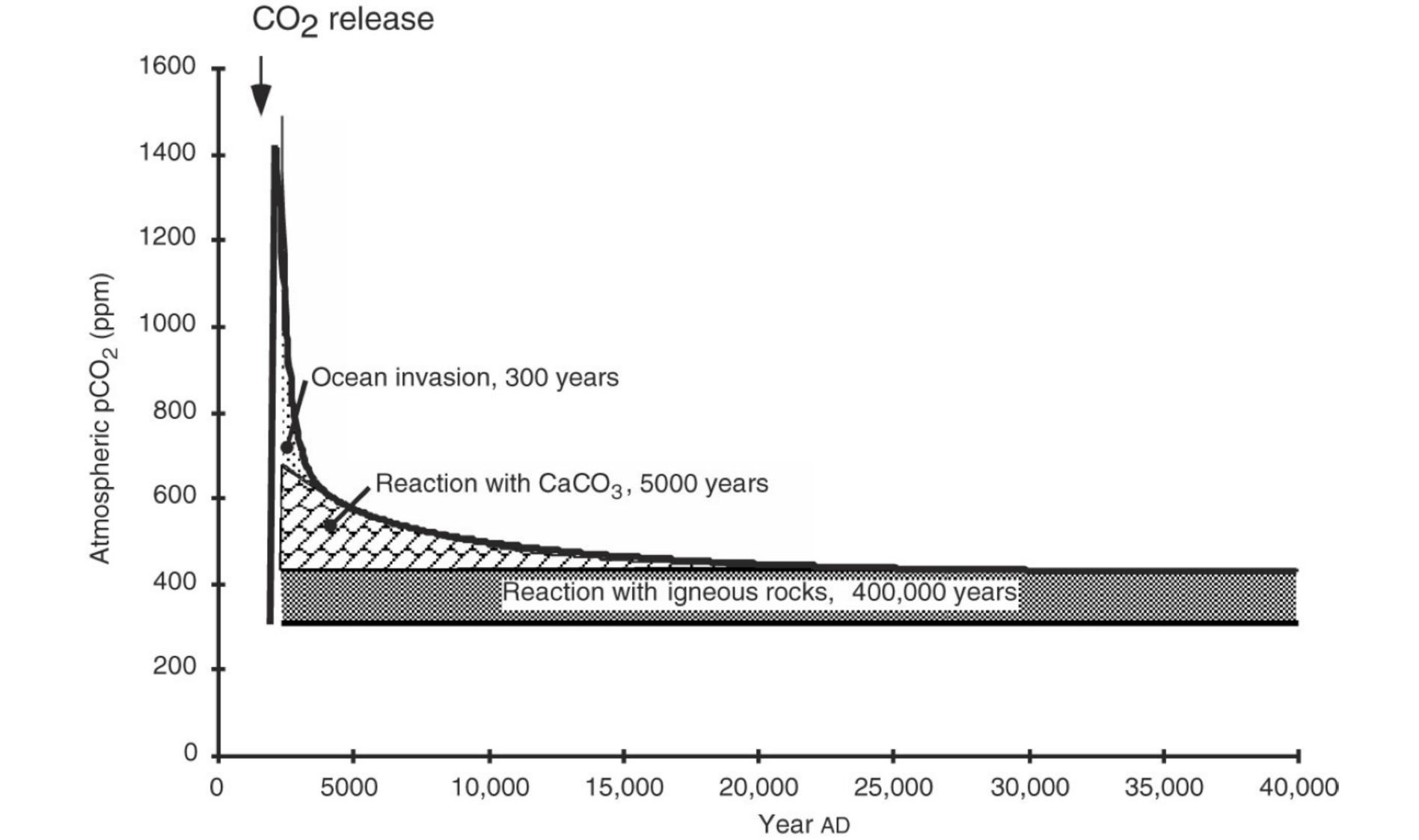
Prospects for future:

Oceanic sinks:

- A few centuries:
 - Around 50% of excess CO₂ dissolves into oceans
 - Dissolution stops as oceans acidify
- A few thousand years:
 - Reactions with limestone restore pH, CO₂ solubility
- Hundreds of thousand of years
 - \circ Silicate-mineral weathering removes and buries excess CO_2 .

Bottom line:

■ CO₂ stays in the atmosphere many thousands of years after we stop burning fossil fuels.



CO₂ vs. Methane

- CO₂:
 - After 1000 years, around 30% of excess CO₂ remains in atmosphere
 - After 10,000 years, 13% remains
 - After 100,000 years, 6% remains
- Methane (CH₄):
 - 31 times more powerful (molecule-for-molecule) than CO₂
 - Reacts with OH^- (hydoxyl radicals) and oxydizes 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

CO₂ is balance of volcanic outgassing and chemical weathering

• Higher temperatures:

- More rain, faster chemical reactions
- Faster weathering
- Atmospheric CO₂ falls

• Lower temperatures

- Less rain, slower chemical reactions
- Slower weathering
- Atmospheric CO₂ 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.