Global Carbon Cycle Change

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Origin and Evolution of Earth: Research Questions for a Changing Planet

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Basis for documentary film

“Earth – the Inside Story”

Funded by the Department of Energy and National Science Foundation

Produced by Earth Images Foundation, Oakland, CA

Doug Prose Cinematographer

Starring (among others) Wendy Mao and Simon Klemperer
7. What causes climate to change; how much can it change?

What processes govern climate change?
Why has climate stayed in a hospitable range?
What caused exceptionally warm and cold periods?
What triggers abrupt climate change?
Can the atmospheric CO₂ history be determined?
Climate change is driven by

**Carbon Cycle Change**

Just how messed up are Earth’s Carbon Cycles? Where are we headed?
Major points

• The current rate of transfer of C from geologic storage (as coal, oil, gas, limestone) to the atmosphere is approaching **10 Gigaton C/yr** \((1 \text{ ton} = 1000\text{kg})\)

• The components of the Earth’s system we interact with (atmosphere, land biosphere, soils, surface ocean) can be considered to be **one unit (Earth Surface)** because they exchange C rapidly (up 100 Gt C/yr).

• The normal (pre-industrial/pre-agriculture) rate of transfer of C from geologic storage to the Earth Surface is slightly uncertain but roughly **0.03 Gt C/yr**

• We have a problem because **10 >> 0.03**. The other large fluxes between surface reservoirs are distractions.
Major points

• Over the next 400 years (let’s say), we will transfer another 1000 to 5000 Gt C to the Earth Surface reservoir

• The main questions are:
  • Will it be closer to 1000 or 5000 Gt (or a larger number)
  • How will the extra C be partitioned between the Earth Surface reservoirs (atmosphere versus the others)
What is normal operating procedure for the Earth?

and why does it matter?

Let’s start with the planetary picture
Overview of Planetary Points

• Earth has had liquid water at its surface for almost all time (ca. 4.4 out of 4.55 Gyr). Water is the critical requirement for having a “carbon cycle”
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• The Earth’s atmosphere contains only about 1-2 part in $10^6$ of the planet’s “accessible carbon,” a small fraction, but well regulated.
Earth Started Hot…

Canup (2008)
Artist's depiction of the Earth a few hundred years after the Moon-forming impact at about 4.53 billion years ago.

- Silicate vapor atmosphere
- Molten silicate surface
By 4.4 Gyr, Earth has cooled to temperatures similar to modern.
Transition from Hot to modern Earth-like?*

With a molten Earth (viscosity $\approx 0.1$ Pa-sec) mantle convects vigorously and all the gases (including carbon) are expelled into the atmosphere.

$\Rightarrow$ All the C and H$_2$O in the Earth started out in the atmosphere!

*Story from Abe (1993) and Zahnle et al. (2007)
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As magma oceans cool enough to crust over with solid rock, atmospheric H$_2$O can condense and start to form oceans.

--- the hot rock will react with hot water + CO$_2$ and make carbonate. Somehow that carbonate needs to be mixed back into the mantle otherwise the mantle would have no water + CO$_2$ today

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Once the mantle becomes solid (about 4 b.y. ago, viscosity ≈ 10²² Pa-sec), things slow down in the deep Earth, more similar to the present

--- Now we need to get C back out of the mantle, but keep the right amount in the atmosphere to maintain the Goldilocks temperature

*Story from Abe (1993) and Zahnle et al. (2007)*
Planetary Carbon budget

(where is it; how fast does it move; evidence that it moves in and out of the deep Earth)
Where is the carbon?

$M_{\text{Earth}} = 6 \times 10^{12}$ Gt

$M_{\text{Atmos}} = 2 \times 10^6$ Gt

Liquid H$_2$O at surface since 4.4 Gyr ago
Continents (CaCO$_3$) + Organic: $6.5 \times 10^7$ Gt C

Core: $4 \times 10^9$ Gt C

Mantle: $3 \pm 1 \times 10^8$ Gt C

Ocean dissolved: 38,000 Gt C

$M_{Earth} = 6 \times 10^{12}$ Gt
Continents (CaCO₃) + Organic  
6.5 x 10⁷ Gt C

Coal 5000 Gt C  
Hydrates 5000 Gt C

Mₐₐₜₐₜ = 6 x 10¹² Gt

Atmosphere  
780 Gt C  
(was 600 Gt C)

Land Biosphere  
600 Gt C

Soil  
1,500 Gt C

Ocean dissolved  
38,000 Gt C  
(Surface 1000 Gt C)
Kilauea volcano has erupted constantly since 1983; about 3 Gt/yr of lava and about 0.001 Gt C/yr

Global volcanic emission rate about 50x Kilauea?

Lava contains gas (H₂O, CO₂, SO₂, ...)

CO₂ outgassing from deep Earth probably tracks global heat flow

From Zhang & Zindler, 1993

Total C outgassed from mantle ≈ 2-3 x 10⁸ Gt

Total currently at surface ≈ 0.65 x 10⁸ Gt
Earth’s Carbon Cycle - volcanoes

Global volcanic outgassing rate
\[ \approx 0.06 \text{ Gt C/yr} \]

Time to outgas mantle carbon:
\[ t_{\text{mantle}} = \frac{3 \times 10^8 \text{ GtC}}{0.06 \text{ GtC/yr}} = 5 \text{ Gyr} \]

Time to accumulate all crustal carbon:
\[ t_{\text{crust}} = \frac{6 \times 10^7 \text{ GtC}}{0.06 \text{ GtC/yr}} = 1 \text{ Gyr} \]
Water and regulation of Earth’s surface temperature
Atmospheric carbon $\approx 0.00015\%$ of accessible carbon (not core C)

600 Gt atmospheric C (pre-Industrial)
0.65 x $10^8$ Gt C in crust

Atmospheric carbon $\approx 40\%$ of accessible carbon

1.26 x $10^8$ Gt atmospheric C

**Why is Venus so different from Earth?** - it is too close to the Sun
If too hot, all surface $\text{H}_2\text{O}$ in atmosphere, no liquid water, lose H from top.

All outgassed C is then oxidized to $\text{CO}_2$, no way to return $\text{CO}_2$ to solid form or to mantle.

Atmosphere becomes mostly $\text{CO}_2$, strong greenhouse, temperature is very high.

Venus - No surface $\text{H}_2\text{O}$
If radiant heating is just right, almost all H$_2$O is liquid water (99.9999%), negligible loss of H from top of atmosphere.

Outgassed CO$_2$ can be removed from atmosphere by rock weathering.

Atmosphere becomes mostly N$_2$, weak greenhouse, T is between 0 and 60°C.
Venus absorbs less energy from the Sun but has a strong greenhouse effect.

Venus could have been more like Earth during its first 1 Gyr, because Sun was weaker.
Conditions in the Solar System were different in the past relative to the present – strong solar wind and UV; Sun less bright

From Zahnle et al (2007)
Earth lies within the Planetary “Habitable Zone”
The weathering regulator
Geologic Carbon Cycle regulates Earth surface temperature

**Atmosphere**

- CO$_2$ dissolves in the ocean
- Injection of CO$_2$ into the atmosphere tends to acidify the oceans

**Continent**

- "Acidic" rain
- Acidic rain partially dissolves exposed rock, which tends to de-acidify the oceans
- Subduction provides a mechanism to return carbon to the deep mantle
- And causes (Ca,Mg)CO$_3$ to precipitate

**Volcanic Arc**

- Short circuit

**Mantle**
Earth’s climate-regulating carbon cycle

$\text{CO}_2$ is degassed from the deep Earth and added to the atmosphere; it combines with water to make carbonic acid ($\text{H}_2\text{CO}_3$)

$\text{CO}_2$ is removed from the atmosphere* by reaction of carbonic acid with silicate minerals and then fixed in limestone ($\text{CaCO}_3$), which can also be subducted into the mantle

\[
\begin{align*}
2\text{CO}_2 + 2\text{H}_2\text{O} & \iff 2\text{H}^+ + 2\text{HCO}_3^- \\
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}^+ + \text{H}_2\text{O} & \iff \text{Ca}^{2+} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \\
\text{Ca}^{2+} + 2\text{HCO}_3^- & \iff \text{CaCO}_3 + \text{CO}_2
\end{align*}
\]

$\text{CO}_2 + \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} \iff \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{CaCO}_3$

Igneous Rock \quad Clays \quad Limestone

*Typical rate = 0.1 Gt C/yr, probably faster in early Earth, slower now
Dissolving rocks – it can be fast with strong acids

Can be done in the lab in an hour to a day; but requires using concentrated acids like HF, HClO₄, HNO₃ – crushing the rock to powder and warming to ca. 100°C!

It happens at relatively fast rates (years to decades) in geothermal systems where fluids are acidic – HCl and H₂SO₄ – and hot (100° to 300°C)
Dissolving rocks – it is **slow** with weak, dilute acids like $\text{H}_2\text{CO}_3$

($\text{H}_2\text{CO}_3$ dissociates in rain water to $\text{H}^+$ and $\text{HCO}_3^-$)

For a 0.5 mm diameter grain; this rate is $\approx$ 1 molecule/sec per grain

A 1 nanometer-thick layer is dissolved from the grain surface every 1000 years*

*This is what could be called “ultra-slow” chemistry; which we are still learning about.
Aqueous ions to the oceans:
- $\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$
- $\text{SiO}_2$ (quartz)
- $\text{AlSi}_2\text{O}_5(\text{OH})_4$ kaolinite
- $(\text{CO}_3^{2-})_{\text{aq}}$ to oceans

Add weak acid ($\text{H}_2\text{CO}_3$) (rain)
CO₂ – atmospheric temperature feedback

- Increase CO₂
  - Increase T, acidify waters
  - Decrease weathering
- Decrease CO₂
  - Decrease T, de-acidify waters
  - Decrease weathering

Volcanoes

Solar Luminosity

Mountain Building + Weathering
CO₂ – atmospheric temperature feedback

\[ \frac{d[CO_2]_{atm}}{dt} = P_{\text{volcanic}} - k_{\text{weathering}}[CO_2]_{atm}^{n} \]

"steady-state" approximate solution

\[ [CO_2]_{atm} = \left( \frac{P_{\text{volcanic}}}{k_{\text{weathering}}} \right)^{1/n} \]

\( k_{\text{weathering}} \) varies with time due to “mountain building” and solar luminosity

\( P_{\text{volcanic}} \) decreases with time as the Earth cools
Simple Models for CO$_2$ versus Age

Models and data for last 600 million years
To compensate the faint Sun, need stronger greenhouse (more CO₂ ± CH₄)

Graph showing the relationship between CO₂ partial pressure and time before present, with markers for today's CO₂ and other historical data points.
There is more detail to the story for the past 65 million years. From Zachos et al. 2000ff.
How high was \( \text{CO}_2 \) during the past 70 Myr? When there was no polar ice?

**Figure from McCauley & DePaolo, 1997**
Model for growth of East Antarctic Ice Sheet (≈ 38 to 35 Ma)

Pre-Ice Topography

DeConto & Pollard, 2003

EAIS forms only when CO$_2$ drops below 560 – 700ppm
Peak SST (°C) during the PETM

Proxies: $\delta^{18}$O, TEX86, Mg/Ca

ACEX - Lomonosov Ridge; New Jersey Margin, Bass River; California, Lodo; Maud Rise, Sites 689 and 690; Allison Guyot, Site 865

Approximately 1500 ppm CO$_2$

55 Mya

Courtesy of Jim Zachos
What is happening now?
Geologic Carbon Cycle regulates Earth surface temperature

- **Fossil fuel burning**: 8.5 Gt C/yr
- **0.03 Gt C/yr**

**CO₂**

- **Injection of CO₂ into the atmosphere** tends to acidify the oceans
- **“Acidic” rain**
- **Calcining for cement production**: 0.5 Gt C/yr
- Subduction provides a mechanism to return carbon to the deep mantle
- Acidic rain partially dissolves exposed rock, which tends to de-acidify the oceans
- And causes (Ca,Mg)CO₃ to precipitate

**Continent**

**Mantle**

**Volcanic Arc**

**Subduction**

**Short circuit**

**CO₂** dissolves in the ocean

**Fossil fuel burning**

8.5 Gt C/yr

0.03 Gt C/yr

**Volcanic Arc**

**Subduction**

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**Mantle**
The Carbon Cycle 1.x:
A seriously perturbed system

Emissions 9 Gt/yr
“Natural” processes sequester 5 Gt/yr

“Normal” background geological flux ≈0.03 Gt/yr
The Carbon Cycle 1.0: The natural carbon cycle

- Emissions: 0.03 Gt/yr
- Natural processes sequester 0.03 Gt/yr
- Current fluxes are ca. 200-300x natural
Carbon Cycle 2.0:
Abundant Energy with near-zero C emissions

Emissions ca. 1-3 Gt/yr

Natural processes sequester ca. 3 Gt/yr

Global carbon dioxide budget (gigatonnes of carbon per year)

Energy production 1 to 3

0 to -2

2100 ff ??????

Ocean sink -3

Geological reservoirs

Credit: IGBP I GCP
Box model version of global carbon cycle

Atmosphere
600 Gt

Terrestrial Biosphere
600 Gt

Terrestrial Soils
1500 Gt

Surface ocean
1000 Gt

Total Surface Reservoirs
3700 Gt

Deep Earth Reservoirs

Ocean carbonate sediment

Volcanoes (0.03 Gt C/yr)

Shells (0.03 Gt C/yr)

*Fluxes in Gt C/yr
Box model version of global carbon cycle

So far we have added 500 Gt C
By 2200 AD we will add another 1000 to 4000 Gt C
Where will it go?

*Fluxes in Gt C/yr
Atmosphere: 600 Gt
Terrestrial Biosphere: 600 Gt
Terrestrial Soils: 1500 Gt
Surface ocean: 1000 Gt
Total Surface Reservoirs: 3700 Gt
Deep Earth Reservoirs

Normal Net Fluxes vs. 2010 Emissions

Volcanoes: 0.03
2011 – 9 Gt/yr
Ocean carbonate sediment: 0.03
Shells: 0.1
Carbon has never before been transferred as fast as today’s 9 Gt/yr….

Last Glacial-to-interglacial transition: 17 to 11 ka

150 Gt C in 6000 yr (0.025 Gt/yr)
How long will it take to return to “normal” atmospheric CO$_2$?

Fig. 2  A response of CLIMBER-2 model (Brovkin et al. 2002; Brovkin et al. 2007; Ganopolski et al. 1998) to Moderate (1,000 Gton C) and Large (5,000 Gton C) fossil fuel slugs. The equilibrium climate sensitivity of the model is 2.6°C. Temperatures were smoothed with a 250 filter to eliminate a spurious fluctuation of Antarctic sea ice caused by the low model resolution. The land carbon cycle was neglected in these simulations while deep sea sediments were explicitly simulated using a sediment diagenesis model (Archer 1991). a Emissions scenarios and reference IPCC SRES scenarios (B1 and A2). b Simulated atmospheric CO$_2$ (ppmv). c Simulated changes in global annual mean air surface temperature (°C)

Archer and Brovkin, 2008.
Three removal mechanisms, three time scales

Table 1  Carbon sink reactions

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction Equation</th>
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<tbody>
<tr>
<td>Seawater buffer</td>
<td>$\text{CO}_2 + \text{CO}_3^- + \text{H}_2\text{O} \leftrightarrow 2 \text{HCO}_3^-$ (dissolved in the ocean)</td>
</tr>
<tr>
<td>CaCO$_3$ neutralization</td>
<td>$\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^-$ (ocean)</td>
</tr>
<tr>
<td>Silicate weathering</td>
<td>$\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$ (ocean sediments)</td>
</tr>
</tbody>
</table>

![Graph showing removal mechanisms over time]
1000 Gt C
Total emissions

Ice-free Earth?
5000 Gt C
Total emissions

Ice-free Earth?

Uncertainty in response
Projections of integrated carbon emissions

- '+2°C': 500 Gt C, 1000 Gt C, 1500 Gt C
- '+3°C': 1000 Gt C
- '+4°C':

**Conserv& Efficiency**

**Coal -> Gas**

**Nuc**

**Renew**

**CCS**

Emissions to the atmosphere

- 1000 Gt C
- 1500 Gt C

Gt C/yr Emitted

2005 2020 2035 2050 2065 2080 2095

IPCC
Global Organic Carbon & Gas Hydrates

5000 Gton C total emissions may not be the worst case

Units = $10^{15}$ g carbon
30% of global C emissions are taken up by terrestrial ecosystems and stored mostly in soil.
We are not certain where the emitted carbon will go in the future....
Current open-ended C cycle
Carbon Cycle 1.x (2011 AD)

Transfer rate from geologic reservoirs = 9 Gt C/yr in 2010

Future balanced C cycle
Carbon Cycle 2.0 (2100 AD?)

Need 2x to 3x more energy production with <0.3 of 2010 C emissions
Comment on uncertainty of prediction……..
Comment on uncertainty of prediction……

Machta had these data for the 1972 paper

*Machta* (1972)

**Fig. 12.** Mean monthly atmospheric carbon dioxide concentrations at Mauna Loa.
Comment on uncertainty of prediction……..

Model for surficial carbon cycles

Machta (1972)
Machta (1972)

Measured
Conclusions

• The major perturbation that mankind has caused in the carbon cycle is in transferring C from deep Earth reservoirs to the atmosphere at a rate that has grown from about 2.5 Gt C/yr in 1960 to 9 Gt C/yr in 2011.

• The current transfer rate of 9 Gt C/yr and growing is ca. 200 times greater than what is “normal” and about 20 times greater than the most catastrophic C release that has occurred in the last 65 million years.

• There is no question about and no significant uncertainty in the size of mankind’s contribution to the change in the carbon cycle – it is all of it!
The End