CO$_2$ reconstructions and processes during the last 65 Myr

Summer School: Climate Change on Tectonic Time-Scales: Marrying Data and Earth System Models
University of Bremen

Peter Köhler

Alfred Wegener Institute for Polar and Marine Research, Bremerhaven
peter.koehler@awi.de

22 June 2010
1. Basics on the Carbon Cycle

2. CO$_2$ reconstructions
   - $\delta^{11}$B
   - B/Ca
   - Alkenones, $\delta^{13}$C$_{\text{org}}$
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3. Processes
   - The Faint young sun Paradox
   - CO$_2$ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4. Summary
Outline

1. Basics on the Carbon Cycle
2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C_{org}
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Basics on the Carbon Cycle

C Pools and C fluxes

Reservoir sizes in GtC
Fluxes and Rates in GtC yr\(^{-1}\)

IPCC 2007

Peter Köhler (AWI Bremerhaven)
CO₂ in seawater reacts with water and dissociates immediately after:

\[ \text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+ \]

Only the part of CO₂, which get dissolved after Henry’s Law can exchange with the atmosphere.

**Figure 1.1.1:** Schematic illustration of the carbonate system in the ocean. CO₂ is exchanged between atmosphere and ocean via equilibration of CO₂(g) and dissolved CO₂. Dissolved CO₂ is part of the carbonate system in seawater that includes bicarbonate, HCO₃⁻, and carbonate ion, CO₃²⁻.

Zeebe & Wolf-Gladrow 2001
Chemical System in Equilibrium

\[
\text{DIC} \equiv \sum \text{CO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

DIC, \(\sum\text{CO}_2\) also sometimes called PCO\(_2\)

Equilibrium constants:

\[K_1^*, K_2^* = f(\text{temperature } T, \text{ salinity } S, \text{ pressure } P).\]
Present day conditions and $S = 35$, $T = 25^\circ C$:

$[CO_2] = 10 \mu\text{mol kg}^{-1}$; $[HCO_3^-] = 1818 \mu\text{mol kg}^{-1}$; $[CO_3^{2-}] = 272 \mu\text{mol kg}^{-1}$

$[CO_2] : [HCO_3^-] : [CO_3^{2-}] \sim 1\% : 90\% : 10\%$

Zeebe & Wolf-Gladrow 2001
Total Alkalinity (TA or ALK) is the excess of proton (H\(^+\) ion) acceptors over proton donators (with respect to a zero level of protons).

Or even simpler:
Proton acceptor: negative charged ion
Proton donator: H\(^+\) or ion/molecule that can spend one H\(^+\) ion

Roughly:

\[ TA \sim 1 \times [HCO_3^-] + 2 \times [CO_3^{2-}] \]
also called carbonate alkalinity

Or in detail:

\[ TA = 1 \times [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \text{minors} \]
Total Alkalinity and DIC are conservative quantities, meaning, their concentrations are unaffected by changes in pH, pressure, temperature, or salinity.

\[
\text{CO}_2, \ \text{HCO}_3^-, \ \text{or} \ \text{CO}_3^{2-} \ \text{are not conservative!}
\]

With two variables (out of DIC, TA, CO\textsubscript{2}, HCO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, pH) together with T, S, P the carbonate system is fully described, the other four quantities can be calculated out of them.
Basics on the Carbon Cycle

C Pools and C fluxes

Atmosphere: $\text{CO}_2 = 600 \text{ Pg C}$
$\tau_{(\text{atm.-surf.)}} = 10 \text{ yr}$; $\tau_{(\text{atm.-terr.)}} = 6 \text{ yr}$

Terrestrial: $C_{\text{org}} = 2,100 \text{ Pg C}$
$\tau_{(\text{atm.-terr.)}} = 18 \text{ yr}$

Surface ocean: DIC = 700 Pg C
$\tau_{(\text{surf.-deep})} = 25 \text{ yr}$

Export: $C_{\text{org}} = 4 \text{ Pg C yr}^{-1}$
$\text{CaCO}_3 = 1 \text{ Pg C yr}^{-1}$

Deep ocean: DIC = 38,000 Pg C
$\tau_{(\text{surf.-deep})} = 1,250 \text{ yr}$

$\text{CaCO}_3$ burial: $0.2 \text{ Pg C yr}^{-1}$

River input of dissolved $\text{CaCO}_3$: $0.2 \text{ Pg C yr}^{-1}$

Sediments and crust:
$(\text{Ca,Mg})\text{CO}_3 = 48,000,000 \text{ Pg C}$
$\tau_{(\text{weathering})} = 240 \text{ Myr}$
$C_{\text{org}} = 15,000,000 \text{ Pg C}$
$\tau_{(\text{weathering})} = 300 \text{ Myr}$

Sigman and Boyle 2000 N
Outline

1 Basics on the Carbon Cycle

2 CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C_{org}
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3 Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4 Summary
CO₂ Reconstructions, 65,000,000 yr (IPCC 2007)

Peter Köhler (AWI Bremerhaven)

CO₂ during last 65 Myr

22/06/2010, Uni HB 12 / 103
Outline

1. Basics on the Carbon Cycle

2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C₉-org
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4. Summary
δ¹¹B, pH—δ¹¹B, pH—B

G. sacculifer: shell size effect

Yu et al., 2010 EPSL; Hönisch 2004, P
General approach:

- Calculate surface water pH out of $\delta^{11}$B.
- Determine independently another parameter of the carbonate system ($CO_2$, $HCO_3^-$, $CO_3^{2-}$, pH, DIC, alkalinity), mostly alkalinity is estimated.
- Surface water $pCO_2$ can be calculated out of pH and 2nd parameter.
- Under the assumption that surface water $pCO_2$ and atmospheric $pCO_2$ stays (and stayed so in the past) in equilibrium this surface water $pCO_2$ is a proxy for atmospheric $pCO_2$.

**Advantage:** Based on well understood marine chemistry

**Disadvantage:** 2nd parameter needed, atm-surf-equilibrium might have changed over time, seems to work only for mono-specific selections
δ^11B example I, single species, last 2 Myr

Hönisch et al 2009, S
$\delta^{11}$B example II, multi-species, last 60 Myr

<table>
<thead>
<tr>
<th>Neogene</th>
<th>Palaeogene</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPli</td>
<td>Miocene</td>
</tr>
<tr>
<td>late</td>
<td>middle</td>
</tr>
<tr>
<td>late</td>
<td>middle</td>
</tr>
</tbody>
</table>

Atmosphere $p_{CO_2}$ (p.p.m.)

Age (Myr ago)

Pearson and Palmer 2000 N
Outline

1. Basics on the Carbon Cycle
2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C<sub>org</sub>
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
**δ¹¹B, pH—δ¹¹B, pH—B**

_G. sacculifer: shell size effect_

- **O** empirical calibration data (Sanyal et al., 2001)
- **●** shell size data (this study)

---

**Fig. 1**

- B(OH)$_3$
- B(OH)$_4^-$

**Fig. 2**

- δ¹¹B (‰)
- pH (SWS)

---

Yu et al., 2010 EPSL; Hönsisch 2004, P
General approach:

- Planktic foraminiferal B/Ca ratios = f (seawater borate/bicarbonate ratios [B(OH)\(_4^-\)/HCO\(_3^-\)]) = f(pH).
- similar to the \(\delta^{11}\)B approach.

**Advantage:** Based on well understood marine chemistry

**Disadvantage:** 2nd parameter needed, atm-surf-equilibrium might have changed over time.
B/Ca example I, last 20 Myr

Tripathi et al 2009, S
Outline

1 Basics on the Carbon Cycle

2 CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³Cₗₒᵣᵍ
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3 Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4 Summary
Alkenones, or $\delta^{13}C_{\text{org}}$

General approach:
Paleoatmospheric CO$_2$ concentrations can be estimated from the stable carbon isotopic compositions of sedimentary organic molecules known as alkenones. Alkenones are long-chained (C37-C39) unsaturated ethyl and methyl ketones produced by a few species of Haptophyte algae in the modern ocean. Alkenone-based $p$CO$_2$ estimates derive from records of the carbon isotopic fractionation that occurred during marine photosynthetic carbon fixation ($\epsilon_p$). Chemostat experiments conducted under nitrate-limited conditions indicate that alkenone-based $\epsilon_p$ values ($\epsilon_{p37:2}$) vary as a function of the concentration of aqueous CO$_2$ (CO$_2$$_{aq}$) and specific growth rate. These experiments also provide evidence that cell geometry accounts for differences in $\epsilon_p$ among marine microalgae cultured under similar conditions.

**Disadvantage:** Based on analogue, not on chemistry, atm-surf-equilibrium might have changed over time
Alkenones, example I, last 60 Myr

Pagani et al., 2005 S
Involving uncertainties in haptophyte depth habitats, changes in subtropical Pacific site fgema where some enhanced vertical mixing increased nutrient delivery. Higher nutrients and associated growth rates would reduce the tropics were reduced and vertical ocean mixing rates enhanced. However, expansion of the tropical warm pool alone would act. SST gradient implies enhanced poleward ocean heat transport was reduced with a deeper tropical thermocline and a poleward shift.

As climate cooled, the CO2 slope intersected CO2v when strong water column stratification developed. Our estimates are linear regressions of maximum and minimum CO2 concentrations at 3.3–3.0 Myr, the time intervals.

The precisions of NwSbfn and an inhouse standard were better than εvrootbmeanbsquare errorVa based on an calibration. The gas concentrations in the range of preindustrial and early Pliocene CO2 estimates as the result of probable changes in physical oceanography and growth rates. Note the different scales for x and the magnitude of CO2. The gas concentration during the earliest Pliocene is only slightly smaller and predicts that CO2 was reduced.

In summary, xO450–375 climate cooling has been an important in the interpretation of CO2 records. Supplementary Information are consistent with other estimates. 

The Micropalaeontological Society

Haywooda vc Mc S Valdesa Pc Jc Modelling Pliocene warmtho xontribution of atmospherea oceans and cryospherec

Glob. Planet. Change

References

The precisions of NwSbfn and an inhouse standard were better than εvrootbmeanbsquare errorVa based on an calibration. The gas concentrations in the range of preindustrial and early Pliocene CO2 estimates as the result of probable changes in physical oceanography and growth rates. Note the different scales for x and the magnitude of CO2. The gas concentration during the earliest Pliocene is only slightly smaller and predicts that CO2 was reduced.

In summary, xO450–375 climate cooling has been an important in the interpretation of CO2 records. Supplementary Information are consistent with other estimates. 

The Micropalaeontological Society

Haywooda vc Mc S Valdesa Pc Jc Modelling Pliocene warmtho xontribution of atmospherea oceans and cryospherec

Glob. Planet. Change

References
Alkenones mixed with $\delta^{11}$B, example III, last 5 Myr

Seki et al., 2010 EPSL
Outline

1 Basics on the Carbon Cycle

2 CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C org
   - Stomata
     - Validation of different approaches
     - Greenhouse Effect

3 Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4 Summary
**Stomata**

**Figure 1. Stomata and CO₂**

(a) Effects of climate on leaf stomatal density (SD) and stomatal index (SI). Under droughted conditions, leaf epidermal cells are small and the stomata tightly packed. Under non-droughted conditions, leaf epidermal cells are fully expanded forcing the spacing of the stomatal pores further apart, thereby decreasing SD.

(b) Comparison of a Holocene terrestrial reconstruction of atmospheric CO₂ concentration (ppmv) with the highest needle concentrations coincide with already in the lower part of unit 2. The samples identified in two samples in the mid part of the sequence (1.99–1.90 m) and this occurrence is consistent with the pollen record. Also needles of Pinus and Betula pendula were only found in unit 3, although a few leaves were found in samples corresponding to the peaks in pollen percentages. This may reflect less favourable conditions for preservation of pollen. As for Pinus, no needles were found in unit 4.

(c) Comparison of Lateglacial CO₂ concentrations, with 95% confidence intervals, based on stomatal index data obtained from fossil leaves of three species of dwarf shrubs, each independently calibrated, for the Lateglacial (LIA) are indicated. (c) Comparison of Lateglacial CO₂ reconstruction of past CO₂ concentrations, with 95% confidence intervals, based on stomatal index data obtained from fossil leaves of three species of dwarf shrubs, each independently calibrated, for the Lateglacial (LIA) are indicated.

Rundgren 2003 GGG, Rundgren 2005 GPC

**CO₂ reconstructions**

**Stomata**
Our data confirm modeling experiments that show that Cenozoic CO₂ must decline below a threshold of 500 ppmv to induce glacial ice buildup (2). Kürschner et al. PNAS January 15, 2008 vol. 105 no. 2 451

Fig. 3. Predicted CO₂ mixing ratios and global air temperature inferred from climate–CO₂ relations for the past 65 Myr. Also indicated are the major Miocene climate key events and the position of the Miocene cooling events Mi1/1a, Mi2, and Mi3/4 known from the marine oxygen isotope record (1). The effects of pCO₂ variations may have directly impacted the structure and productivity of terrestrial biomes by affecting plant photosynthetic performance. In sensitivity tests at 280 and 560 ppmv for Miocene global vegetation models (36), the expansion of Miocene grasslands (2, 37, 38), and evidence for C3–C4 transitions in terrestrial herbivore communities (3–5), the expansion of Miocene grasslands (2, 37, 38), and evidence for C3–C4 transitions in terrestrial herbivore communities (3–5) were characterized by a mix of C3 grasses and C4 herbs (39). The marked Miocene CO₂ variations show pronounced changes related to vegetation distribution (40). The early Eocene to mid-Miocene transition was the warmest period of the past 35 Ma. Our results demonstrate that this climate optimum was forced significantly by increased C3–C4 biomass from paleosols (43).

Fig. 4. Stomatal index of fossil leaf samples between 25 and 12 Ma (late Oligocene until late middle Miocene) from terrestrial ecosystems. (A) Early Miocene glaciation. The gray band indicates the envelope as determined by the minimum and maximum CO₂ levels in individual fossil leaf samples. The error bars of the species-specific CO₂ levels contributed to the middle Miocene climatic optimum (3). The mid-Miocene CO₂ climate optimum was the warmest period of the past 35 Ma. Our results demonstrate that this climate optimum was forced significantly by increased C3–C4 biomass from paleosols (43).

Kuershner 2008 PNAS
Outline

1 Basics on the Carbon Cycle

2 CO₂ reconstructions
   - $\delta^{11}$B
   - B/Ca
   - Alkenones, $\delta^{13}$C$_{org}$
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3 Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4 Summary
Compilation of CO₂ proxies over last 20 Myr

Van de Wal et al., 2011, CPD
Benthic $\delta^{18}$O: A sea level and deep ocean temperature

![Graph showing deep ocean temperature and atmospheric CO2 levels over time](image)

- Deep Ocean Temperature (°C)
- Atmospheric CO2 (ppm)
- Time (Ma)

**Validation of different approaches**

**CO2 reconstructions**

Further information and source: Peter Köhler (AWI Bremerhaven)
Validation of different approaches

Deconvolve sea level and deep ocean $\Delta T$ out of $\delta^{18}O$

Fraction of sea level and deep ocean $\Delta T$ in $\delta^{18}O$ changes over time!

A

B

C

D

Siddall et al., 2010 QSR
Deconvolve sea level and deep ocean $\Delta T$ out of $\delta^{18}O$

Bintanja et al., 2005 N
Modelling ice sheets over last 20 Myr out of $\delta^{18}O$

Van de Wal et al., 2011, CPD
Van de Wal et al., 2011, CPD
Develop relationship atmospheric $\Delta T$–$CO_2$

\[
\Delta T_{NH40-80} = C \cdot \ln \frac{CO_2}{CO_{2,ref}} \quad \text{with} \quad C = \frac{\alpha \beta \gamma S}{1-f}
\]

$\alpha$: ratio $\Delta T_{NH40-80}/\Delta T_{global}$

$\beta$: radiative forcing of $CO_2$

$\gamma$: enhancement factor for non-$CO_2$ GHG

$S$: (Charney) climate sensitivity (fast feedbacks: Planck, water vapour, lapse rate, clouds, sea ice albedo)

$f$: feedbacks of slow processes (land ice, dust, vegetation)

Van de Wal et al., 2011, CPD
Outline

1. Basics on the Carbon Cycle

2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C_{org}
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect

3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr

4. Summary
Planck’s Law:

Radiation of every black body as function of temperature and wavelength.

- Birth of Quantum Mechanics: Light (photons) have discrete energies
- Plancks Constant $h \sim 6.6 \cdot 10^{-34}$ Js
- $E = h \cdot \nu$. $\nu$: frequency
- Planck’s Law brought together 2 approximations (Wien; Rayleigh-Jeans)
- Wien’s displacement law: $\lambda_{\text{max}} \cdot T = 2.9 \cdot 10^{-3}$ m K.
- Sun ($T = 5500$ K): $\lambda_{\text{max}} = 527$nm (VIS)
- Earth ($T = 255$ K): $\lambda_{\text{max}} = 11\mu$m (IR)

Integration over all wavelength: Energy emission $= f(T) 
\Rightarrow$ Stefan-Bolzmann-Law: $R = \sigma T^4$
Radiation at Earth

Incoming solar radiation

1368 W/m²

Non-rotating disk surface area = $\pi r^2$

average radiation at surface:
1368 W/m²

Rotating sphere surface area = $4\pi r^2$

average radiation at surface:
342 W/m²

Ruddiman 2001
Black Body Radiation

Stefan-Bolzmann-Law: \( R = \sigma T^4 \)
Stefan-Bolzmann-Constant: \( \sigma = 5.67 \times 10^{-8} \text{W/(m}^2 \cdot \text{K}^4) \)
Solarconstant: \( S = 1367 \text{W/m}^2 \); average radiation: \( S_M = 342 \text{W/m}^2 \).
Albedo: \( \alpha = 0.3 \)

\[
\text{Steady state:} \\
\text{Incoming} = \text{Outgoing} \\
S(1 - \alpha)\pi r^2 = R4\pi r^2 \\
\text{or} \\
S_M(1 - \alpha)4\pi r^2 = R4\pi r^2 \\
T_{e,0} = \left( \frac{S(1 - \alpha)}{4\sigma} \right)^{1/4} \\
T_{e,0} = 255K(-18^\circ C)
\]

Measured:
Land: \( 9.84^\circ C (1.077 \times 10^{14} \text{m}^2) \) [Leemans and Cramer(1991)]
1931–1960 Ocean: \( 18.1^\circ C (3.578 \times 10^{14} \text{m}^2) \) [Levitus and Boyer(1994)]
Global Mean: \( 16^\circ C \)
Difference (\( \Delta T = 34 \text{ K} \)) has to be explained by radiative forcing
CO₂ reconstructions

Greenhouse Effect

Simplified Energy Budget (Köhler et al., 2010, QSR)

\[ \alpha_p = 0.30 \]

\[ \alpha_A = 0.212 \]

\[ \alpha_S = 0.15 \]

\[ a = 0.20 \]

\[ \varepsilon = 0.60 \]

\[ R_0 = \sigma T_E^4 \]

\[ \alpha_S: 0.10 \quad 0.55 \quad 0.75 \quad 0.20 \]

SW

LW

Peter Köhler (AWI Bremerhaven)

CO₂ during last 65 Myr

22/06/2010, Uni HB

43 / 103
Develop relationship atmospheric $\Delta T$–$\text{CO}_2$

$$\Delta T_{\text{NH}40-80} = C \cdot \ln \frac{\text{CO}_2}{\text{CO}_2, \text{ref}} \quad \text{with} \quad C = \frac{\alpha \beta \gamma S}{1-f}$$

$\alpha$: ratio $\Delta T_{\text{NH}40-80}/\Delta T_{\text{global}}$

$\beta$: radiative forcing of $\text{CO}_2$

$\gamma$: enhancement factor for non-$\text{CO}_2$ GHG

$S$: (Charney) climate sensitivity (fast feedbacks: Planck, water vapour, lapse rate, clouds, sea ice albedo)

$f$: feedbacks of slow processes (land ice, dust, vegetation)

Van de Wal et al., 2011, CPD
Model-based CO₂ reconstructed from benthic δ¹⁸O

Van de Wal et al., 2011, CPD
Validation Summary

- Calculate sea level, $\Delta T$ within one modelling framework leads to self-consistent results.
- Evaluate proxy-based CO$_2$ with modelling $\Delta T$ shows inconsistencies in some of the proxies (stomata, alkenones, multi-species $\delta^{11}$B)
- Regression of $\Delta T$ and best proxy-CO$_2$ can be understood based on theoretical background of radiative forcings
- Reconstructed CO$_2$ declines from 450 ppmv (20 Myr BP) to 280 ppmv at pre-industrial times.

Van de Wal et al., 2011, CPD
Outline

1. Basics on the Carbon Cycle
2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³C_{org}
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Outline

1. Basics on the Carbon Cycle
2. CO₂ reconstructions
   - δ¹¹B
   - B/Ca
   - Alkenones, δ¹³Cₐ₉g
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO₂ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Solar luminosity increased over earth’s history: Early sun was about 30% weaker than today.

At present-day atmospheric composition, temperature should have been below freezing point of water for most of earth’s history.
Solar luminosity increased over earth’s history: Early sun was about 30% weaker than today.

At present-day atmospheric composition, temperature should have been below freezing point of water for most of earth’s history.
But:

- Geologic evidence for liquid ocean over at least 3.5 billion years: Sediment rocks, microfossils showing presence of life
- Something must have prevented earth from freezing
- But if there is a heating process, it must be less active today
- Earth seems to possess a thermostat
Greenhouse Effect

The main candidate: A stronger greenhouse effect in early earth

Weaker solar radiation

Stronger greenhouse

CO₂ in atmosphere

A

Early Earth

Stronger solar radiation

Weaker greenhouse

CO₂ in rocks

B

Modern Earth
This requires more CO$_2$ in the early atmosphere. Where did it come from? The largest reservoir nowadays is in rocks.

How can CO$_2$ exchange between atmosphere and rocks?
This requires more CO$_2$ in the early atmosphere. Where did it come from? The largest reservoir nowadays is in rocks.

**Major carbon reservoirs (gigatons; 1 gigaton = 10$^{15}$ grams)**

- Atmosphere: 600 (pre-industrial)
- Ocean mixed layer: 1000
- Deep ocean: 38,000
- Sediments and rocks: 66,000,000
- Soils: 1560
- Vegetation: 610

How can CO$_2$ exchange between atmosphere and rocks?
Outline

1. Basics on the Carbon Cycle
2. \( \text{CO}_2 \) reconstructions
   - \( \delta^{11}\text{B} \)
   - B/Ca
   - Alkenones, \( \delta^{13}\text{C}_{\text{org}} \)
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - \( \text{CO}_2 \) outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Volcanoes presently emit ca. 0.15 Pg C a$^{-1}$, mostly in the form of CO$_2$ (also some emission of CH$_4$). This activity might have been stronger.
Residence time of C in A/O/B with respect to volcanic outgassing:

\[ \tau = \frac{41700 \text{PgC}}{0.15 \text{PgC yr}^{-1}} \approx 278000 \text{yr}. \]
But:
- Volcanic emissions may be drivers of a changed CO$_2$ content, but they don’t react to changes in climate.
- A thermostat requires some form of feedback.
- Some other process required!
Outline

1. Basics on the Carbon Cycle
2. \( \text{CO}_2 \) reconstructions
   - \( \delta^{11}\text{B} \)
   - \( \text{B/Ca} \)
   - Alkenones, \( \delta^{13}\text{C}_\text{org} \)
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - \( \text{CO}_2 \) outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Atmosphere to Rock Flux: Weathering

The process opposing the long-term build-up of CO$_2$ through volcanic outgassing is **continental weathering**. Continental weathering is the chemical transformation of exposed rocks with rainwater and dissolved reactive gases CO$_2$ and O$_2$.
weathering reactions with carbonic acid in rainwater
Limestone
Limestone (CaCO$_3$) is easily broken down in the dissolution reaction

$$H_2O + CO_2 \Rightarrow H_2CO_3$$  \hspace{1cm} (1)

rain + atmosphere ⇒ carbonic acid

$$CaCO_3 + H_2CO_3 \Rightarrow Ca^{2+} + 2HCO_3^-$$  \hspace{1cm} (2)

limestone + carbonic acid ⇒ continental weathering
Silicate Minerals

Typical silicate minerals: Olivine, feldspar and quartz
Typical silicate weathering reaction: Na-feldspar is converted to secondary mineral kaolinite

$$\text{H}_2\text{O} + \text{CO}_2 \Rightarrow \text{H}_2\text{CO}_3$$  \hspace{1cm} (3)

$$\text{rain} + \text{atmosphere} \Rightarrow \text{carbonic acid}$$

$$2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} \Rightarrow 2\text{Na}^{2+} + 2\text{HCO}_3^- + 4\text{H}_2\text{SiO}_4 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$$

All C in silicate weathering comes from the atmosphere!
After Weathering

What happens with the dissolved minerals? They are precipitated inorganically or organically.

\[
\text{CaSiO}_3 + \text{H}_2\text{CO}_3 \\
\text{Silicate bedrock} + \text{Carbonic acid in soils} \\
\text{Weathering on land}
\]

\[
\text{Ca}^{+2} \text{Si}^{+4} \text{HCO}_3^- \\
\text{Ions dissolved in river water} \\
\text{Transport in rivers}
\]

\[
\text{SiO}_2 + \text{CaCO}_3 \\
\text{Shells of ocean plankton} \\
\text{Deposition in ocean}
\]
carbonate Precipitation: done by several groups, e.g. coccolithophorids
Organic production of CaCO₃ in the ocean:

Net reaction formula:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \iff \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (4)

- 1 mol CaCO₃ reduced DIC by 1 mol
- 1 mol CaCO₃ reduced alkalinity by 2 mol

It is not that each mol CaCO₃ produces 1 mol CO₂ as might be suggested from this equation and the illustrations. Most of the CO₂ is immediately transformed into HCO₃⁻. However, the asynchronous changes in alkalinity and DIC change the carbonate system.
Carbonate Cycle

- CO$_2$ gas exchange:
  $\Delta(TA) = 0$
  $\Rightarrow$: CO$_2$ uptake reduces pH + increases [CO$_2$]

- CaCO$_3$ cycle:
  $\Delta(ALK) = 2 \times \Delta(DIC)$
  $\Rightarrow$: CaCO$_3$ production reduces pH + increases [CO$_2$]

- Org C cycle:
  $\Delta(ALK) = -1.14 \times \Delta(DIC)$
  $\Rightarrow$: Org C production increases pH + decreases [CO$_2$]

Zeebe & Wolf-Gladrow 2001
Silicate precipitation: today mostly done by diatoms
The net effect of weathering can be summarized into the basic equation:

\[ \text{igneous rocks} + \text{acid volatiles} \Rightarrow \text{sedimentary rocks} + \text{salty ocean} \]

Silicate weathering and precipitation removes CO$_2$ from atmosphere!

Carbonate weathering and subsequent precipitation has no net effect on CO$_2$.

But both weathering processes introduce alkalinity into the ocean. So long-term effects of weathering might exist via chemical reaction of the oceanic sediment.
The net effect of weathering can be summarized into the basic equation:

\[
\text{igneous rocks} + \text{acid volatiles} \Rightarrow \text{sedimentary rocks} + \text{salty ocean}
\]

**Silicate weathering** and precipitation removes \( \text{CO}_2 \) from atmosphere!

**Carbonate weathering** and subsequent precipitation has no net effect on \( \text{CO}_2 \).

But both weathering processes introduce alkalinity into the ocean. So long-term effects of weathering might exist via chemical reaction of the oceanic sediment.
The net effect of weathering can be summarized into the basic equation:

\[
\text{igneous rocks + acid volatiles} \Rightarrow \text{sedimentary rocks + salty ocean}
\]

**Silicate weathering** and precipitation removes CO$_2$ from atmosphere!

**Carbonate weathering** and subsequent precipitation has no net effect on CO$_2$.

But both weathering processes introduce alkalinity into the ocean. So long-term effects of weathering might exist via chemical reaction of the oceanic sediment.
Rate of chemical weathering depends on:

- surface to volume ratio of rock: mechanical weathering increases chemical weathering!
- temperature: reactions proceed faster in warmer climate
- precipitation: water is needed
- acidity of ground water: atmospheric CO$_2$ and organics have an influence
Weathering Feedback

Temperature: higher weathering in warmer regions
Precipitation: highest weathering in tropics
Weathering Feedback

Plant growth: increases with temperature

![Graph showing the relationship between temperature and plant growth. The x-axis represents temperature in °C, ranging from -10 to 30. The y-axis represents production in g/m²/yr, ranging from 0 to 3000. The graph shows that plant growth increases with temperature.]
Weathering Feedback

Warmer and wetter climate leads to increased weathering
Sediment yield is a measure for intensity of weathering.
Over long timescales, greenhouse strength is driven by the balance between

- source of CO₂ from volcanism
- sink of CO₂ from silicate weathering

Important to notice:

- Changes in climate driven e.g. by CO₂ changes from volcanism.
- Negative weathering feedback dampens climate changes.
- But that does not mean that climate does not change at all!
Outline

1. Basics on the Carbon Cycle
2. \( \text{CO}_2 \) reconstructions
   - \( \delta^{11}\text{B} \)
   - B/Ca
   - Alkenones, \( \delta^{13}\text{C}_{\text{org}} \)
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - \( \text{CO}_2 \) outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
For earth’s early history only weak constraints exist on how stable climate really was:

- an ocean was present: $0^\circ C < T < 100^\circ C$
- life could evolve: $T \approx 40^\circ C$? (degradation of most proteins; however thermophiles exist)

Much more information on climate over the last 545 million years, the Phanerozoic
This is a time of rapid biological change: Evolution of land plants.

Many new species appeared, but also some mass extinctions.

![Biodiversity during the Phanerozoic](chart.png)
Ice sheets present on land: 430 or 325–240 or 35 Myr BP till now.
Warm-loving species (broadleaf plants, crocodiles, etc) present at high latitudes: 430–325 or 240–35 Myr BP (interrupted by somewhat cooler time)
The Phanerozoic — last 545 Myr

The Phanerozoic V

Peter Köhler (AWI Bremerhaven)

CO₂ during last 65 Myr
CO\textsubscript{2} model reconstructions generally agree with proxy data and show some relation to sequence of warm/cold climates.

What are the mechanisms?
Most explanations focus on role of plate tectonics
Plate Tectonics

The Phanerozoic — last 545 Myr

Late Cambrian 514 Ma

Early Devonian 390 Ma

Late Permian 255 Ma

Late Jurassic 152 Ma

Middle Eocene 50.2 Ma

Modern World

Peter Köhler (AWI Bremerhaven)

CO₂ during last 65 Myr

22/06/2010, Uni HB

85 / 103
How do plate tectonics relate to changes in climate/CO$_2$? Three basic hypotheses have been put forward:

- polar landmass hypothesis
- spreading-rate hypothesis
- uplift/weathering hypothesis
Polar Landmass Hypothesis

One of the oldest hypotheses: Glaciation occurs when there is a landmass at sufficiently high latitude, so that a continental ice sheet can evolve.

Location of the south pole in relation to supercontinental Gondwana.
### Polar Landmass Hypothesis

#### TABLE 5-1 Evaluation of the Polar Position Hypothesis of Glaciation

<table>
<thead>
<tr>
<th>Time (Myr ago)</th>
<th>Ice sheets present?</th>
<th>Continents in polar position?</th>
<th>Hypothesis supported?</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>425–325</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>325–240</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>240–125</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>125–35</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>35–0</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Hypothesis only for some times supported by data
Spreading Rate Hypothesis

More active plate tectonics leads to higher outgassing of CO$_2$, driving warmer climate.
age of seafloor: decrease of spreading over last 100 mya
Spreading Rate Hypothesis

Weathering acts to dampen, but not to eliminate climate change
Spreading Rate Hypothesis

<table>
<thead>
<tr>
<th>Time (Myr ago)</th>
<th>Ice sheets present?</th>
<th>Spreading rates</th>
<th>Hypothesis supported?</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>No</td>
<td>Fast</td>
<td>Yes (high CO₂)</td>
</tr>
<tr>
<td>0</td>
<td>Yes</td>
<td>Slow</td>
<td>Yes (low CO₂)</td>
</tr>
</tbody>
</table>

Hypothesis supported by data
Uplift/Weathering Hypothesis

Collision of continental plates leads to formation of large mountain ranges
Higher mountains lead to stronger weathering, CO$_2$ removal and colder climate
### Uplift/Weathering Hypothesis

TABLE 5-3 Evaluation of the Uplift Weathering [CO$_2$ Removal] Hypothesis

<table>
<thead>
<tr>
<th>Time (Myr ago)</th>
<th>Ice sheets present?</th>
<th>Continents colliding?</th>
<th>Hypothesis supported?</th>
</tr>
</thead>
<tbody>
<tr>
<td>325–240</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes (low CO$_2$)</td>
</tr>
<tr>
<td>240–35</td>
<td>No</td>
<td>No</td>
<td>Yes (high CO$_2$)</td>
</tr>
<tr>
<td>35–0</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes (low CO$_2$)</td>
</tr>
</tbody>
</table>

Hypothesis supported by data
Tectonics and CO$_2$

- Both spreading-rate hypothesis and uplift/weathering hypothesis roughly consistent with timing of warm/cold climates.

- But both make contrasting inferences about weathering:
  - Spreading-rate hypothesis: weathering is dampening atmospheric CO$_2$ and climate change which is introduced by volcanic CO$_2$ outgassing.
  - Uplift/weathering hypothesis: CO$_2$ and climate change introduced by weathering.

- Newest evidence on Weathering and Faint Young Sun Paradox.
Long-term stability of global erosion rates and weathering during late-Cenozoic cooling

Jane K. Willenbring\textsuperscript{1} & Friedhelm von Blanckenburg\textsuperscript{1}

Willenbring 2010 N
Stable Cenozoic Weathering?

Left: Increased sedimentation rate indicate increase in weathering
Right: 10Be/9Be ratio as weathering proxy (only 10 Myr!!!)

Willenbring 2010 N
LETTERS

No climate paradox under the faint early Sun

Minik T. Rosing¹,²,⁴, Dennis K. Bird¹,⁴, Norman H. Sleep⁵ & Christian J. Bjerrum¹,³

Rosing 2010 N
No Faint Young Sun Paradox???

Existence of Fe(II-III) oxides (magnetite) in banded iron formations is inconsistent with high CO$_2$ necessary under the faint young sun paradox. Their solution: Lower albedo of early Earth sufficient for above freezing point.

Rosing 2010 N
Outline

1. Basics on the Carbon Cycle
2. CO$_2$ reconstructions
   - $\delta^{11}$B
   - B/Ca
   - Alkenones, $\delta^{13}$C$_{\text{org}}$
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO$_2$ outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary
Pre-ice core CO\(_2\) is estimated from different proxies (\(\delta^{11}\)B, B/Ca, stomata, \(\delta^{13}\)C \(_{\text{ORG}}\)) which rather low resolution and large uncertainties.

Validation with model-based \(\Delta T = f(\delta^{18}\)O) and theory on radiative forcing highlights “good” and “weak” CO\(_2\) proxies.

Faint Young Sun Paradox can be explained if continental weathering acts as a thermostat, which dampens climate change.

Silicate weathering extracts CO\(_2\) from the atmosphere and puts it in the ocean sediments.

Carbonate weathering does not extract CO\(_2\) from the atmosphere.

From 3 hypothesis (Spreading-rate, Uplift/weathering, Polar Landmass) two are consistent with timing of Earth’s cooling.

New data weakens weathering hypothesis and Faint Young Sun Paradox.


Summary


