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

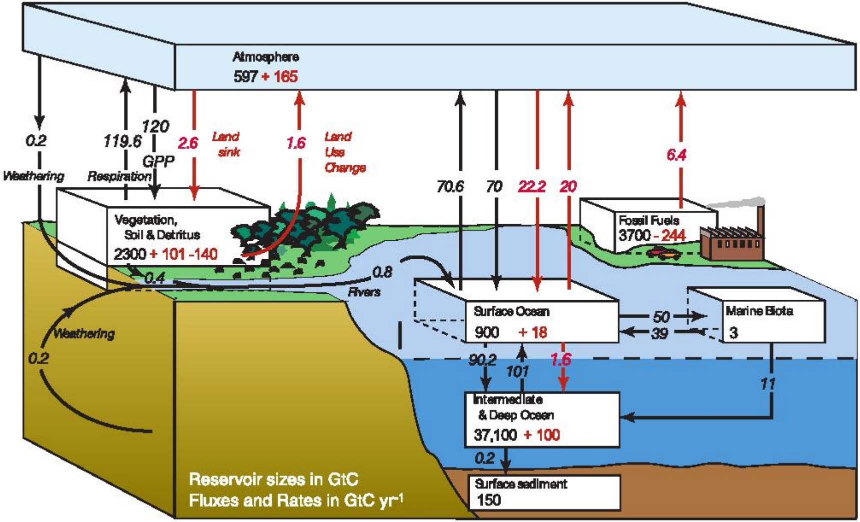
Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
    - δ^{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. CO_2 reconstructions
   - δ^{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

C Pools and C fluxes



IPCC 2007

CO_2 in Seawater

CO_2 in seawater reacts with water and dissociates immediately after:

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$$

Only the part of CO_2, which get dissolved after Henry's Law can exchange with the atmosphere.

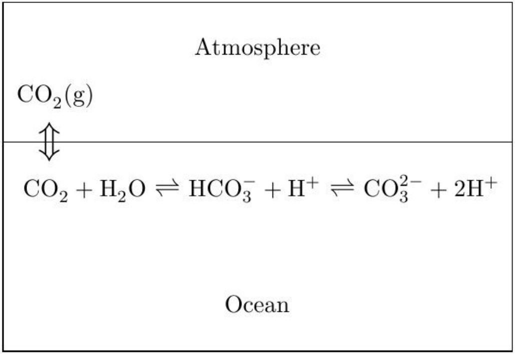


Figure 1.1.1: Schematic illustration of the carbonate system in the ocean. CO_2 is exchanged between atmosphere and ocean via equilibration of $CO_2(g)$ and dissolved CO_2. Dissolved CO_2 is part of the carbonate system in seawater that includes bicarbonate, HCO_3^-, and carbonate ion, CO_3^{2-}.

Zeebe & Wolf-Gladrow 2001

Chemical System in Equilibrium

$$\mathrm{CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+}$$

[H_2CO_3] is negligible and the equation reduced to

$$\mathrm{CO_2 + H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{HCO_3^- + H^+} \overset{K_2}{\rightleftharpoons} \mathrm{CO_3^{2-} + 2H^+}$$

Dissolved Inorganic Carbon — DIC

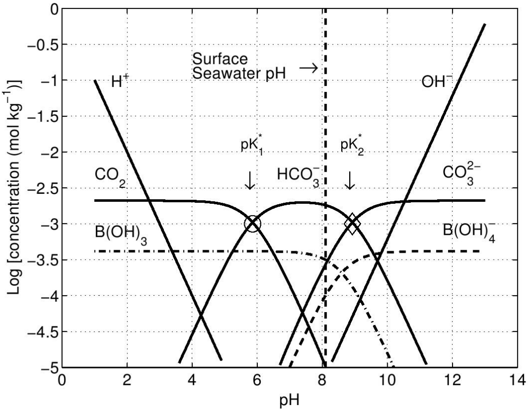
$$\mathrm{DIC} \equiv \Sigma\mathrm{CO_2} = [\mathrm{CO_2}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]$$

DIC, $\sum CO_2$ also sometimes called PCO_2

Equilibrium constants:

$K_1^*, K_2^* = f$(temperature T, salinity S, pressure P).

Bjerrum Plot



Present day conditions and $S = 35$, $T = 25^\circ$ C:

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

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

Zeebe & Wolf-Gladrow 2001

Total Alkalinity

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:

$$TA = 1 \times [HCO_3^-] + 2 \times [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \text{ minors}$$

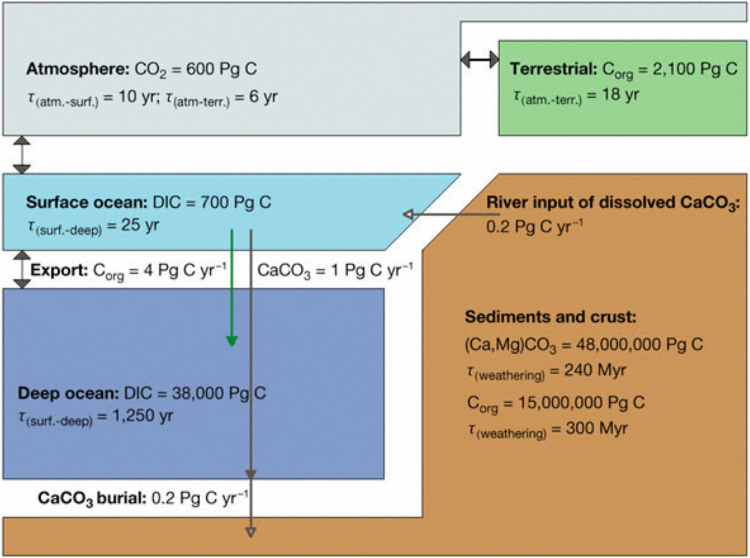
Carbonate System

Total Alkalinity and DIC are conservative quantities, meaning, their concentrations are unaffected by changes in *p*H, pressure, temperature, or salinity

CO_2, HCO_3^-, or CO_3^{2-} are not conservative!

With two variables (out of DIC, TA, CO_2,HCO_3^-, CO_3^{2-}, *p*H) together with T, S, P the carbonate system is fully described, the other four quantities can be calculated out of them.

C Pools and C fluxes

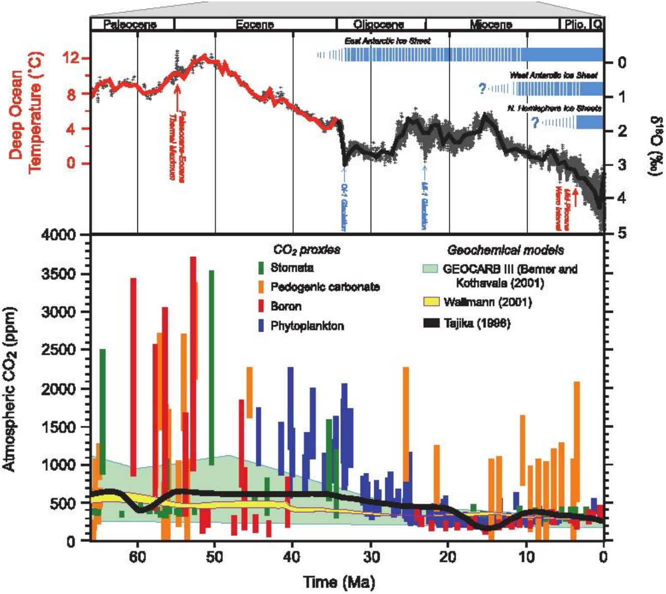


Sigman and Boyle 2000 N

Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, $\delta^{13}C_{\mathrm{org}}$
   - 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

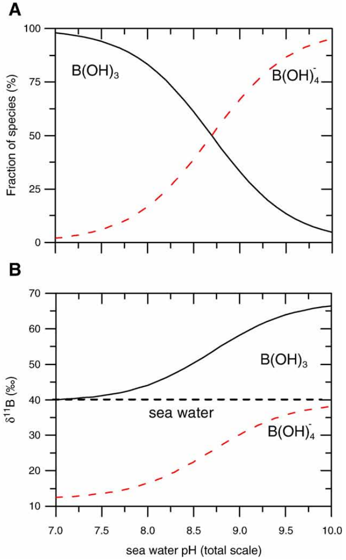
CO_2 Reconstructions, 65,000,000 yr (IPCC 2007)

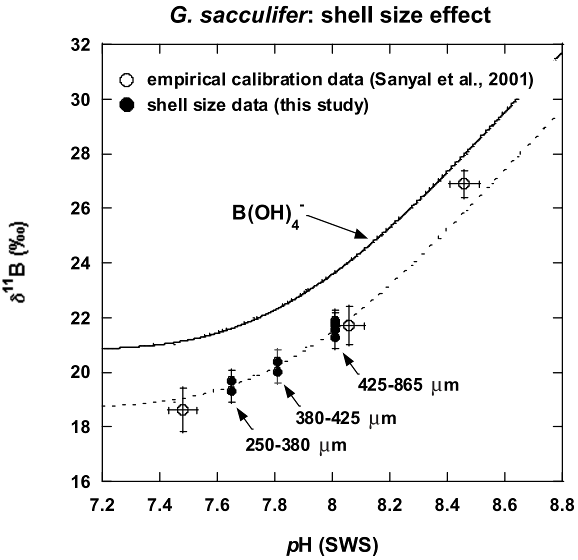


Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, $\delta^{13}C_{\mathrm{org}}$
   - 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

δ^{11}B, *p*H—δ^{11}B, *p*H—B





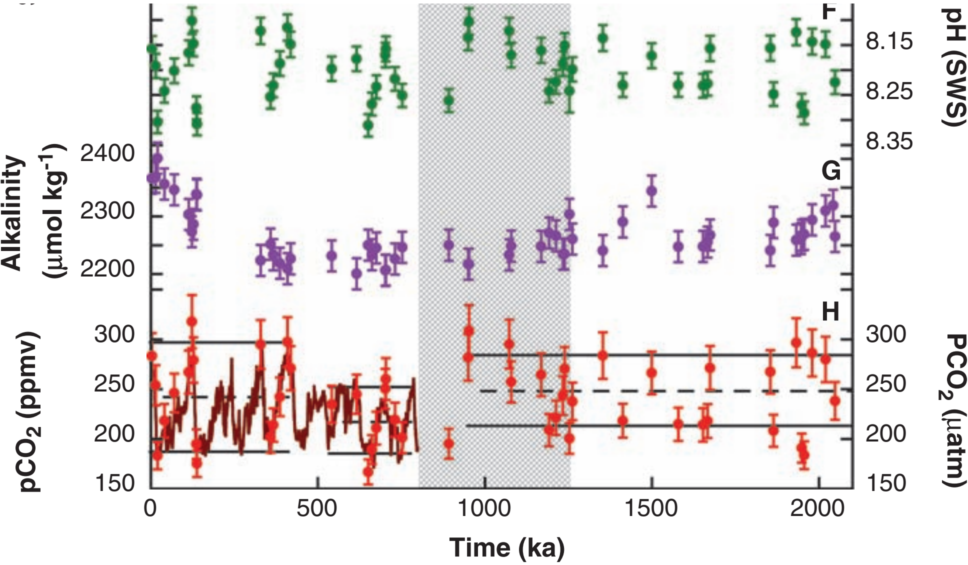
Yu et al., 2010 EPSL; Hönisch 2004, P

δ^{11}B, boron isotopes

General approach:

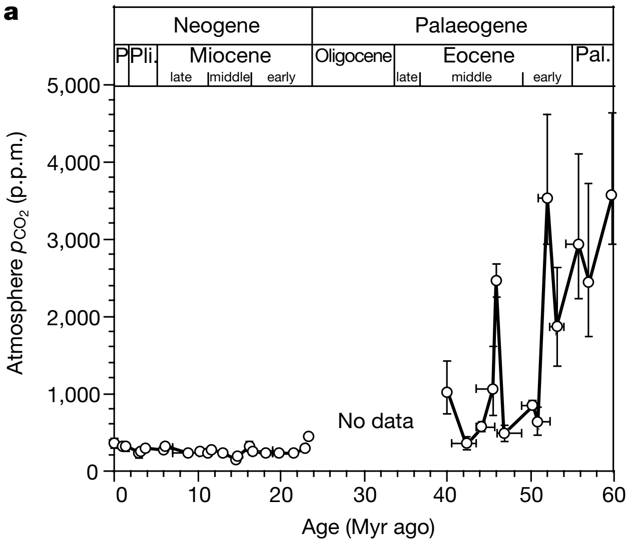
- Calculate surface water pH out of δ^{11}B.
- Determine independently another parameter of the carbonate system (CO_2, HCO_3^-, CO_3^{2-}, pH, DIC, alkalinity), mostly alkalinity is estimated.
- Surface water pCO_2 can be calcuated out of pH and 2nd parameter.
- Under the assumption that surface water 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^{11}B example I, single species, last 2 Myr



Hönisch et al 2009, S

δ^{11}B example II, multi-species, last 60 Myr

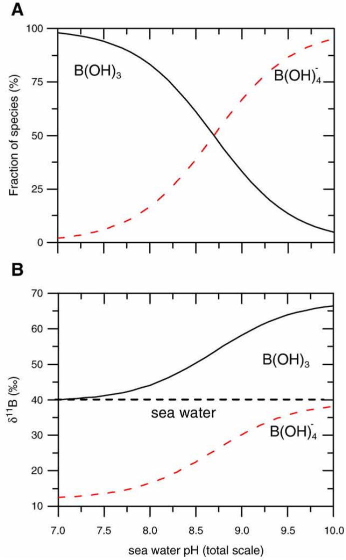


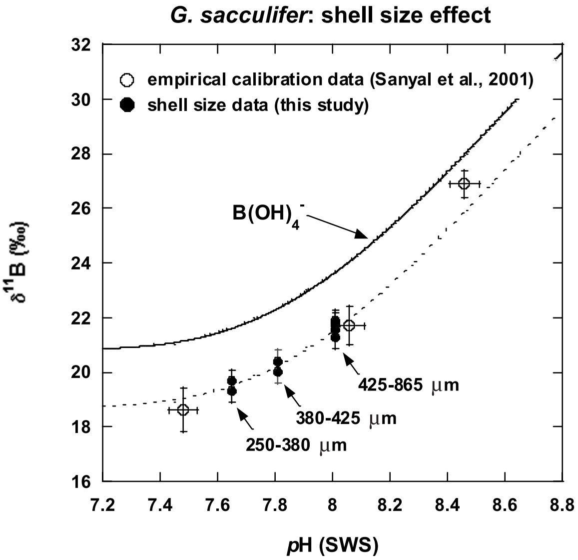
Pearson and Palmer 2000 N

Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, $\delta^{13}C_{\rm org}$
   - 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

δ^{11}B, *p*H—δ^{11}B, *p*H—B





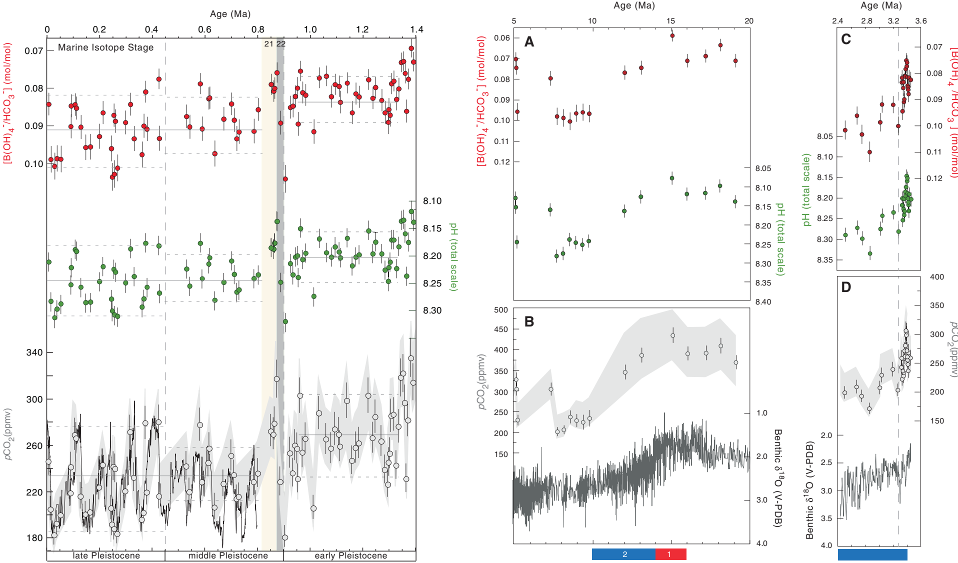
Yu et al., 2010 EPSL; Hönisch 2004, P

B/Ca

General approach:

- Planktic foraminiferal B/Ca ratios = f (seawater borate/bicarbonate ratios [B(OH)4-/HCO3-]) = f(pH).
- similar to the δ^{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



Tripati et al 2009, S

Outline

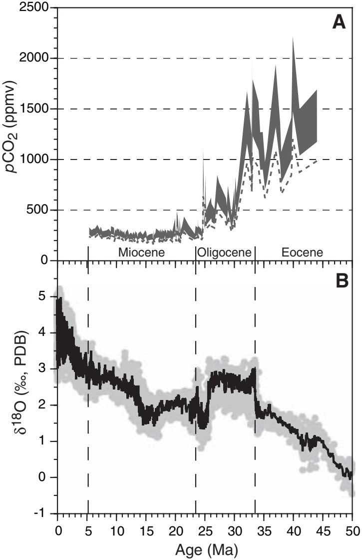
1. Basics on the Carbon Cycle
2. CO_2 reconstructions
    - $\delta^{11}B$
    - B/Ca
    - Alkenones, $\delta^{13}C_{\text{org}}$
    - Stomata
    - Validation of different approaches
    - Greenhouse Effect
3. Processes
    - The Faint young sun Paradox
    - CO_2 outgassing
    - Weathering
    - The Phanerozoic — last 545 Myr
4. Summary

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

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 pCO_2 estimates derive from records of the carbon isotopic fractionation that occurred during marine photosynthetic carbon fixation (ϵ_p). Chemostat experiments conducted under nitrate-limited conditions indicate that alkenone-based ϵ_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 ϵ_p among marine microalgae cultured under similar conditions.

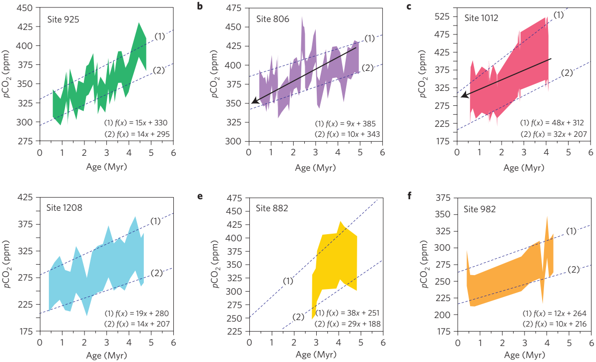
- **Disadvantage:** Based on analogue, not on chemistry, atm-surf-equilibrium might have changed over time

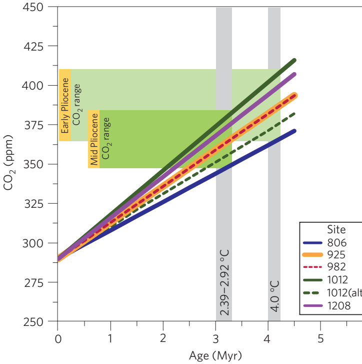
Alkenones, example I, last 60 Myr



Pagani et al., 2005 S

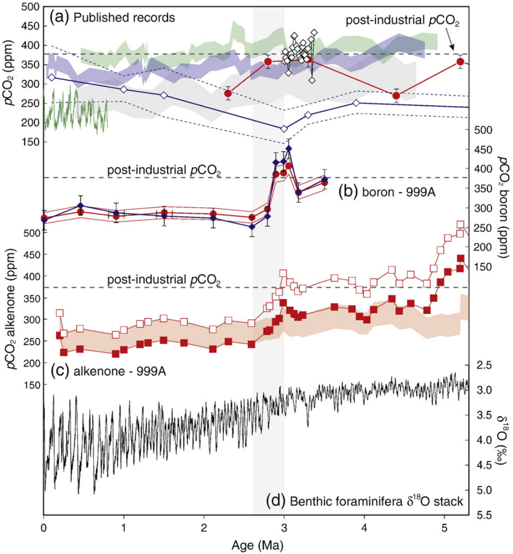
Alkenones, example II, last 6 Myr





Pagani et al., 2010 NG

Alkenones mixed with δ^{11}B, example III, last 5 Myr

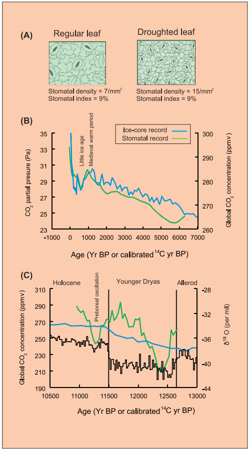


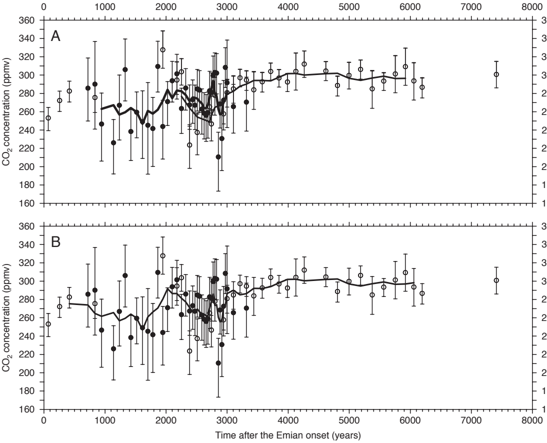
Seki et al., 2010 EPSL

Outline

1. Basics on the Carbon Cycle
2. CO_2 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
   - CO_2 outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary

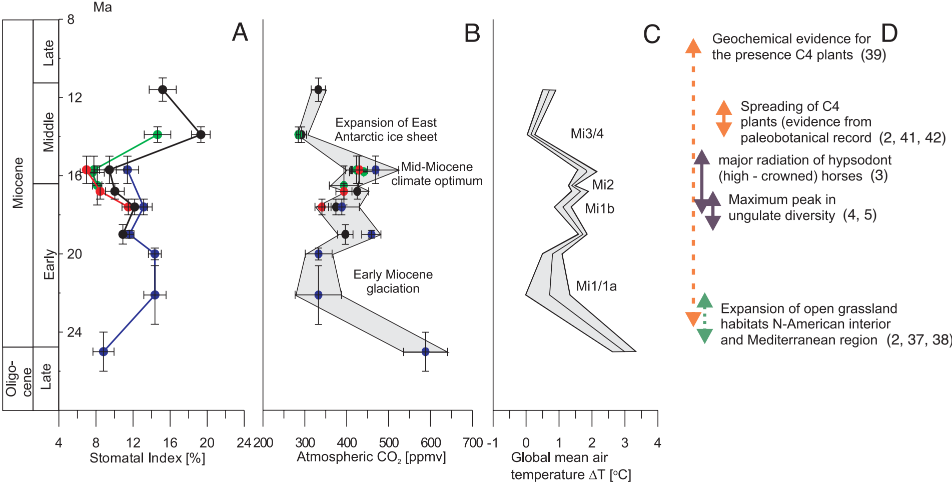
Stomata





Rundgren 2003 GGG, Rundgren 2005 GPC

Stomata



Kuerschner 2008 PNAS

Outline

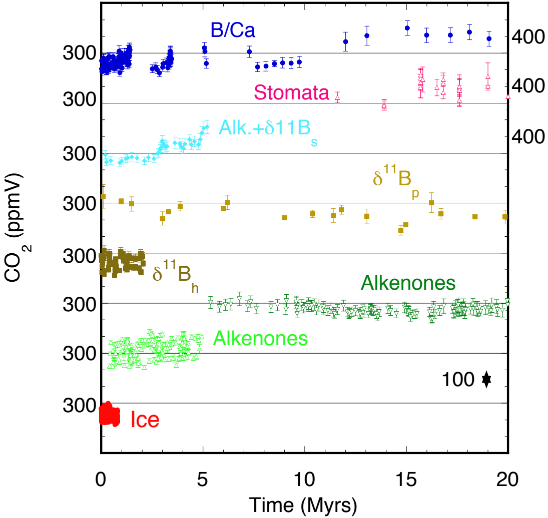
1 Basics on the Carbon Cycle

2 CO_2 reconstructions
- δ^{11}B
- B/Ca
- Alkenones, $\delta^{13}C_{\mathrm{org}}$
- Stomata
- Validation of different approaches
- Greenhouse Effect

3 Processes
- The Faint young sun Paradox
- CO_2 outgassing
- Weathering
- The Phanerozoic — last 545 Myr

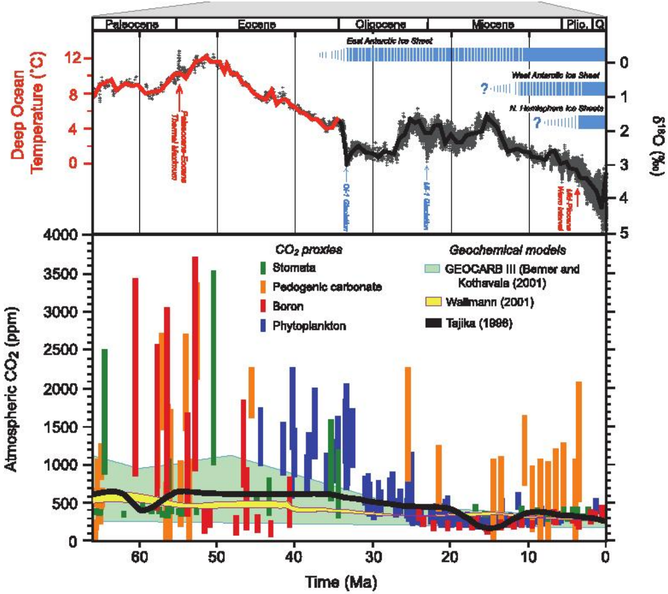
4 Summary

Compilation of CO_2 proxies over last 20 Myr



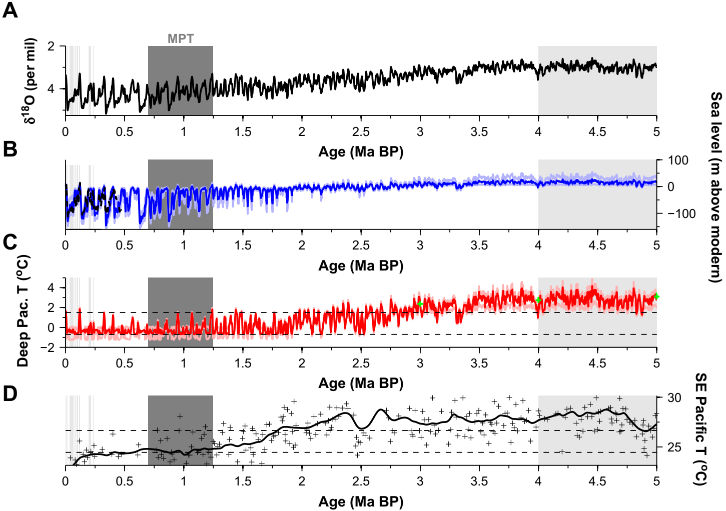
Van de Wal et al., 2011, CPD

Benthic δ^{18}O: A sea level and deep ocean temperature



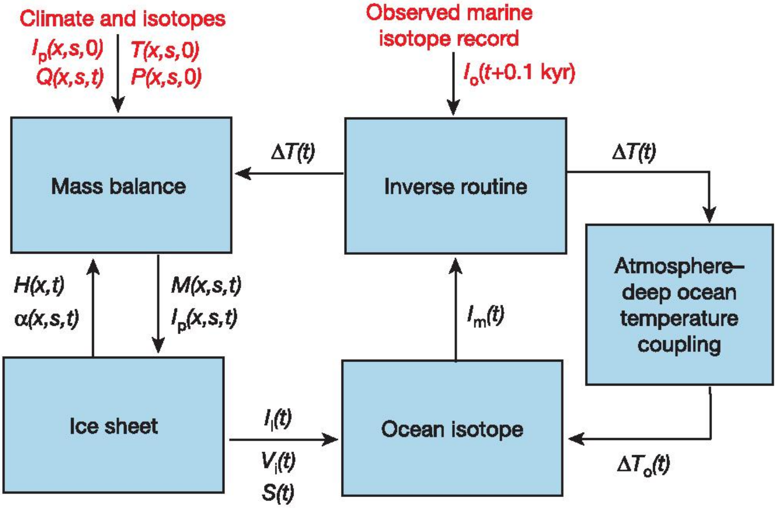
Deconvolve sea level and deep ocean ΔT out of δ^{18}O

Fraction of sea level and deep ocean ΔT in δ^{18}O changes over time!



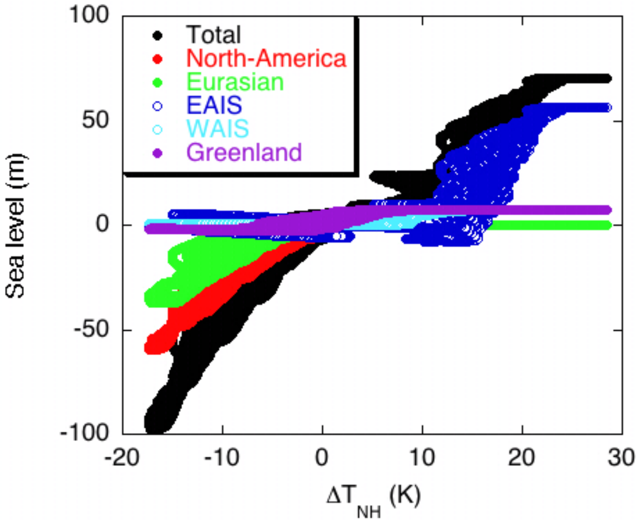
Siddall et al., 2010 QSR

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



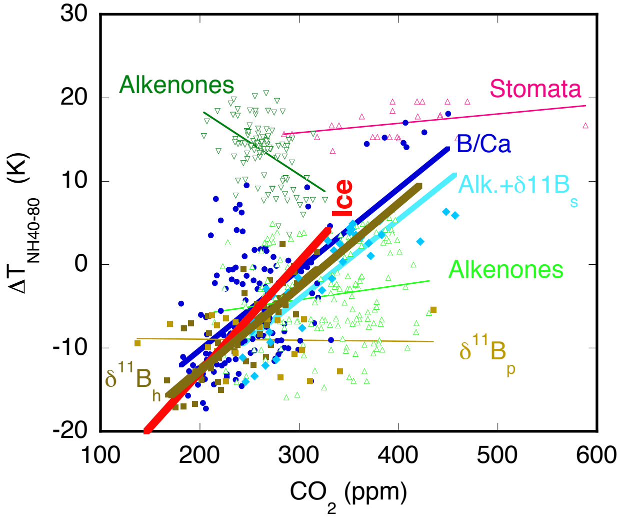
Bintanja et al., 2005 N

Modelling ice sheets over last 20 Myr out of $\delta^{18}O$



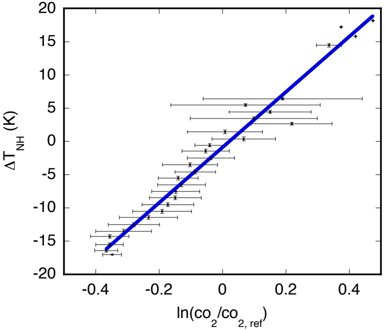
Van de Wal et al., 2011, CPD

Compare modelled atmospheric ΔT with proxy CO_2



Van de Wal et al., 2011, CPD

Develop relationship atmospheric ΔT—CO$_2$



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

α: ratio $\Delta T_{NH40-80}/\Delta T_{global}$
β: radiative forcing of CO$_2$
γ: 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

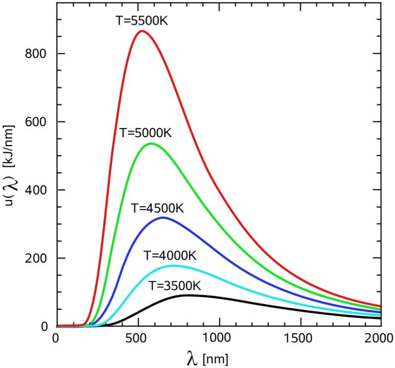
Outline

1. Basics on the Carbon Cycle
2. 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

Planck's Law

Planck's Law: $$I(\nu,T) = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}}-1}.$$

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

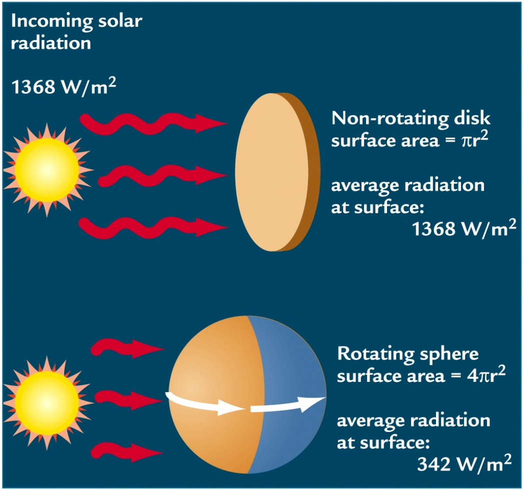


- Birth of Quantum Mechanics: Light (photons) have discrete energies
- Plancks Constant $h \sim 6.6 \cdot 10^{-34}$Js
- $E = h \cdot \nu$. ν: frequency
- Planck's Law brought together 2 approximations (Wien; Rayleigh-Jeans)
- Wien's displacement law: $\lambda_{\max} \cdot T = 2.9 \cdot 10^{-3}$ m K.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

Integration over all wavelength: Energy emission $= f(T)$

$\Rightarrow$ Stefan-Bolzmann-Law: $R = \sigma T^4$

Radiation at Earth



Ruddiman 2001

Black Body Radiation

Stefan-Bolzmann-Law: $R = \sigma T^4$

Stefan-Bolzmann-Constant: $\sigma = 5.6710^{-8} W/(m^2 \cdot K^4)$

Solarconstant: $S = 1367 W/m^2$; average radiation: $S_M = 342 W/m^2$.

Albedo: $\alpha = 0.3$

Steady state:

Incoming $=$ Outgoing

$$S(1-\alpha)\pi r^2 = R 4\pi r^2$$

or

$$S_M(1-\alpha)4\pi r^2 = R 4\pi r^2$$

$$T_{e,0} = \left(\frac{S(1-\alpha)}{4\sigma}\right)^{(1/4)}$$

$$T_{e,0} = 255K(-18^\circ C)$$

Measured:

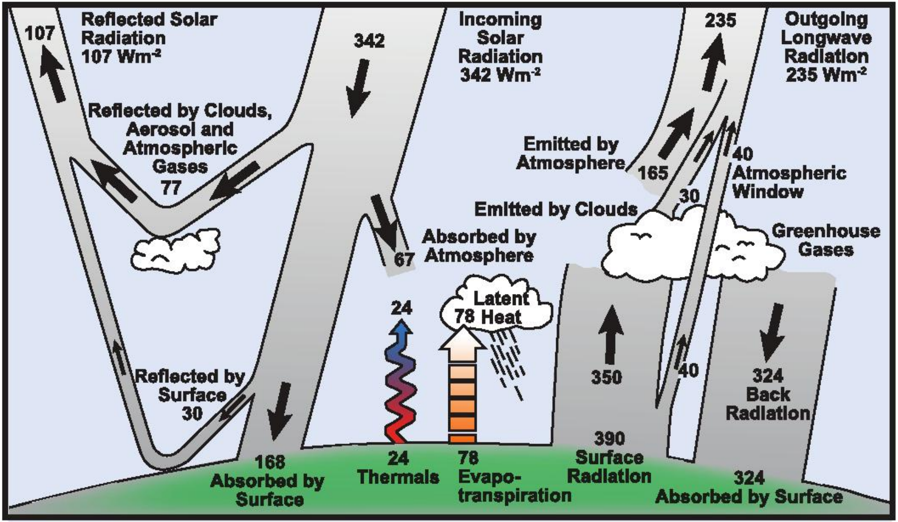
Land: $9.84^\circ C(1.077 \times 10^{14} m^2)$ [Leemans and Cramer(1991)]

1931–1960 Ocean: $18.1^\circ C(3.578 \times 10^{14} m^2)$ [Levitus and Boyer(1994)]

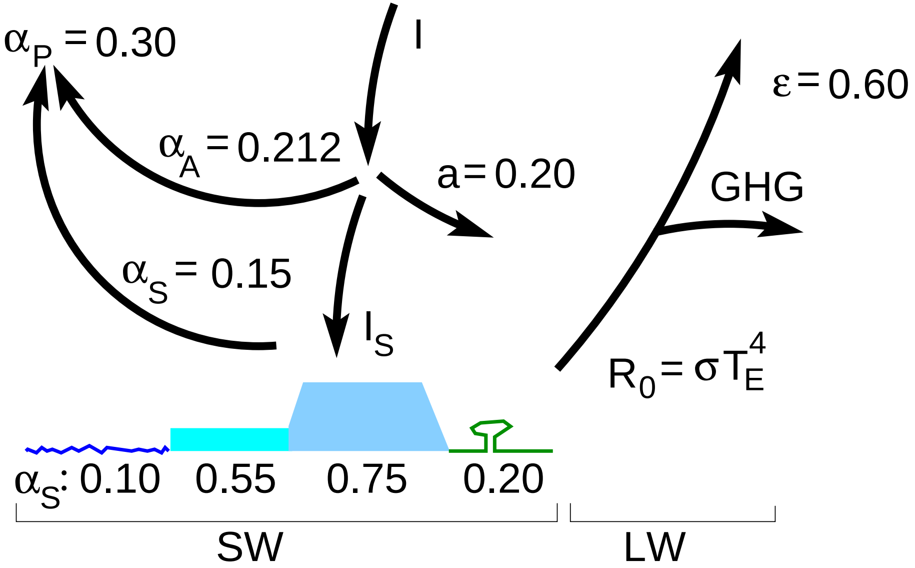
Global Mean: 16° C

Difference (ΔT = 34 K) has to be explained by radiative forcing

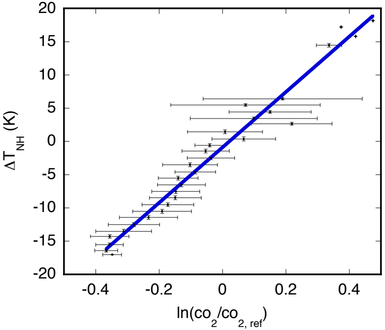
Energy Budget of Atmosphere (IPCC 2007)



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



Develop relationship atmospheric ΔT—CO$_2$



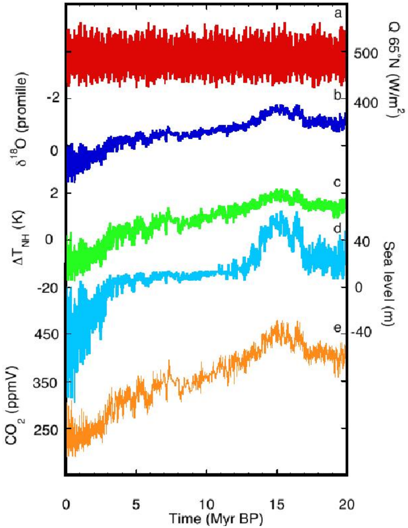
$$\Delta T_{NH40-80} = C \cdot \ln\frac{\mathrm{CO_2}}{\mathrm{CO_{2,ref}}} \text{ with } C = \frac{\alpha\beta\gamma S}{1-f}$$

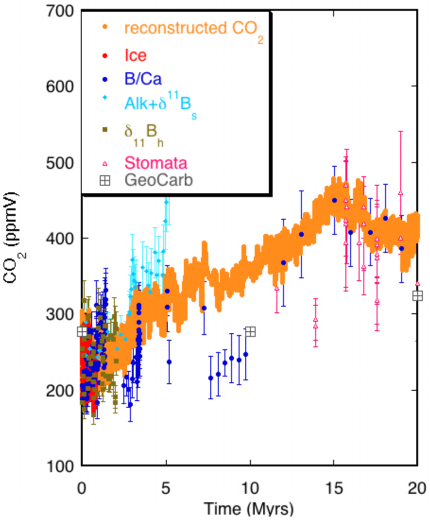
α: ratio $\Delta T_{NH40-80}/\Delta T_{global}$
β: radiative forcing of CO$_2$
γ: enhancement factor for non-CO$_2$ GHG
S: (Charney) climate sensitivity (fast feedbacks: Planck, water vapour, lapse rate, clouds, sea ice albedo)

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

Van de Wal et al., 2011, CPD

Model-based CO_2 reconstructed from benthic $\delta^{18}O$





Van de Wal et al., 2011, CPD

Validation Summary

- Calculate sea level, ΔT within one modelling framework leads to self-consistent results.
- Evaluate proxy-based CO_2 with modelling ΔT shows inconsistencies in some of the proxies (stomata, alkenones, multi-species δ^{11}B)
- Regression of ΔT 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

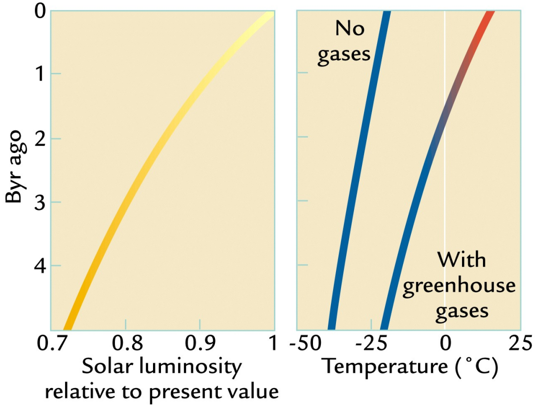
1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, $\delta^{13}C_{\text{org}}$
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO_2 outgassing
   - Weathering
   - The Phanerozoic — last 545 Myr
4. Summary

Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
    - δ^{11}B
    - B/Ca
    - Alkenones, $\delta^{13}C_{\rm org}$
    - 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

The Faint young sun Paradox I

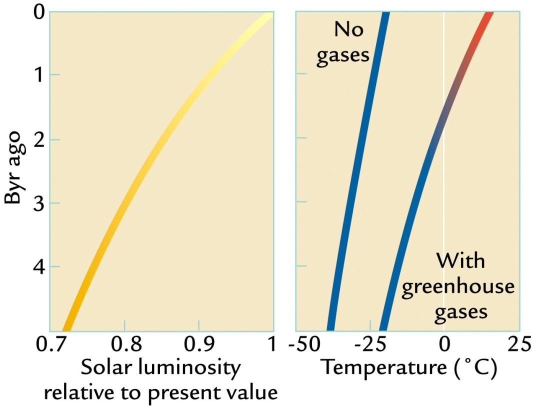
Solar luminosity increased over earth’s history: Early sun was about 30% weaker than today.



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

The Faint young sun Paradox I

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

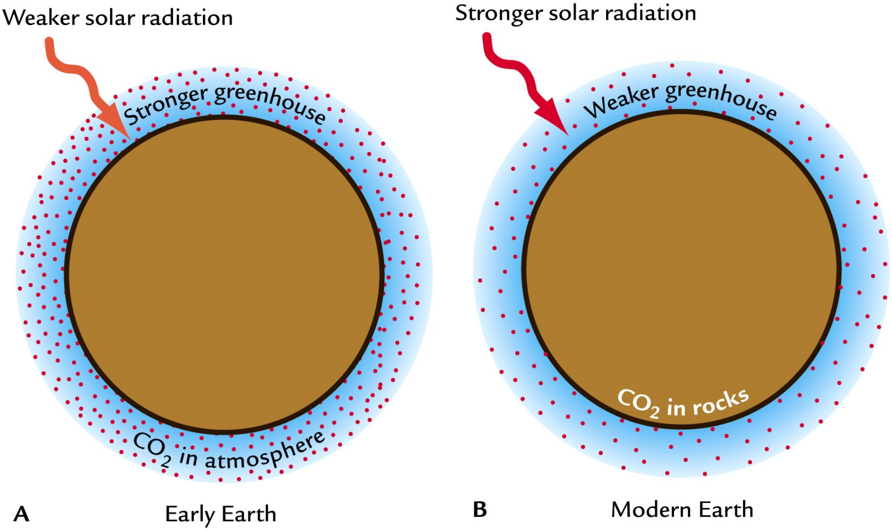
The Faint young sun Paradox II

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 posess a thermostat

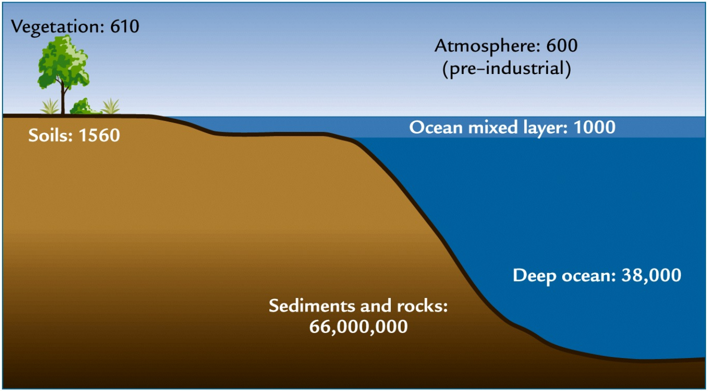
Greenhouse Effect

The main candidate: A stronger greenhouse effect in early earth



Carbon Pools

This requires more CO_2 in the early atmosphere. Where did it come from? The largest reservoir nowadays is in rocks

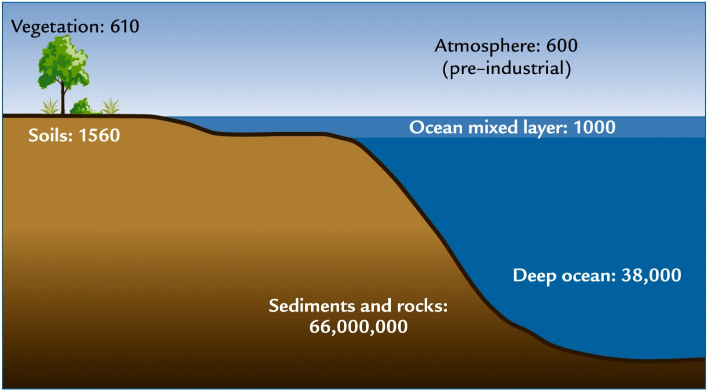


A Major carbon reservoirs (gigatons; 1 gigaton = 10^{15} grams)

How can CO_2 exchange between atmosphere and rocks?

Carbon Pools

This requires more CO_2 in the early atmosphere. Where did it come from? The largest reservoir nowadays is in rocks



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

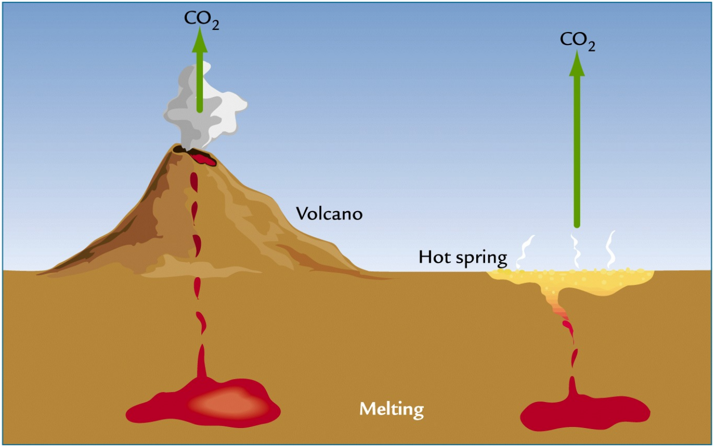
How can CO_2 exchange between atmosphere and rocks?

Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{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

Rock to Atmosphere Flux: Volcanic Emissions

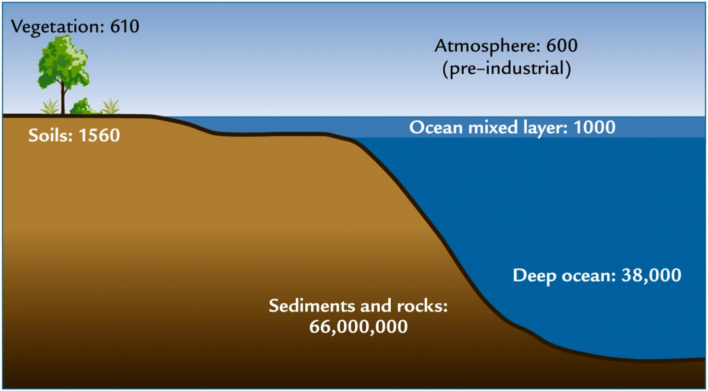
Volcanoes presently emit ca. 0.15 Pg C a^{-1}, mostly in the form of CO_2 (also some emission of CH_4). This activity might have been stronger.



Rock to Atmosphere Flux: Volcanic Emissions

Residence time of C in A/O/B with respect to volcanic outgassing:

$$\tau = \frac{41700 PgC}{0.15 PgC\ yr^{-1}} \approx 278000 yr.$$



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

Rock to Atmosphere Flux: Volcanic Emissions

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

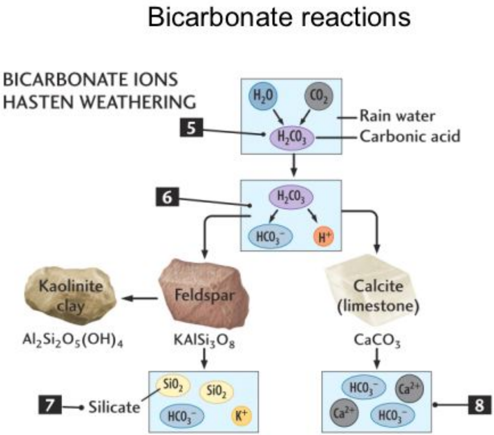
1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, $\delta^{13}C_{\mathrm{org}}$
   - Stomata
   - Validation of different approaches
   - Greenhouse Effect
3. Processes
   - The Faint young sun Paradox
   - CO_2 outgassing
   - **Weathering**
   - The Phanerozoic — last 545 Myr
4. Summary

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.

Atmosphere to Rock Flux: Weathering

weathering reactions with carbonic acid in rainwater



Limestone

Carbonate Weathering

Limestone ($CaCO_3$) is easily broken down in the dissolution reaction

$$H_2O + CO_2 \Rightarrow H_2CO_3 \qquad (1)$$

rain + atmosphere ⇒ carbonic acid

$$CaCO_3 + H_2CO_3 \Rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

limestone + carbonic acid ⇒ continental weathering

Silicate Minerals

Typical silicate minerals: Olivine, feldspar and quartz

Silicate Weathering

Typical silicate weathering reaction: Na-feldspar is converted to secondary mineral kaolinite

$$H_2O + CO_2 \Rightarrow H_2CO_3 \tag{3}$$

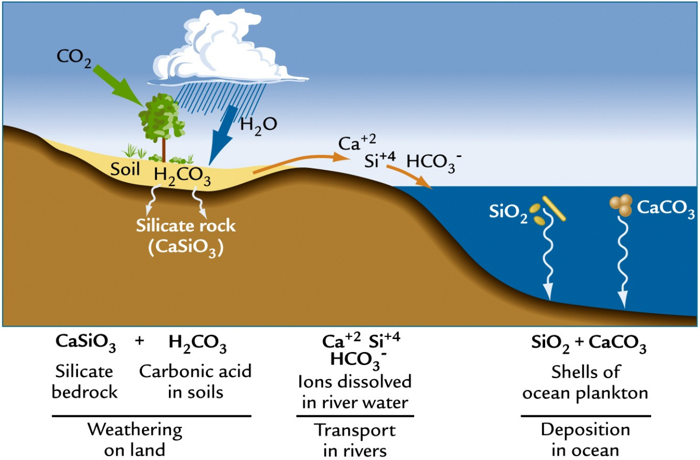
rain + atmosphere ⇒ carbonic acid

$$\begin{gathered} 2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \\ \Rightarrow 2Na^{2+} + 2HCO_3^- + 4H2SiO_4 + Al_2Si_2O_5(OH)_4 \end{gathered}$$

All C in silicate weathering comes from the atmosphere!

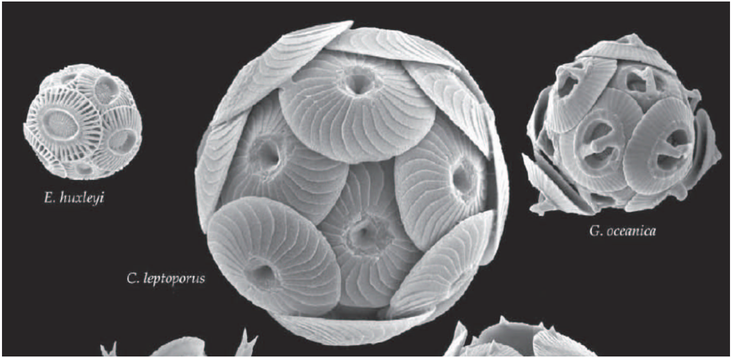
After Weathering

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



Carbonate Precipitation

carbonate Precipitation: done by several groups, e.g. coccolithophorids



Budget of $CaCO_3$ pump

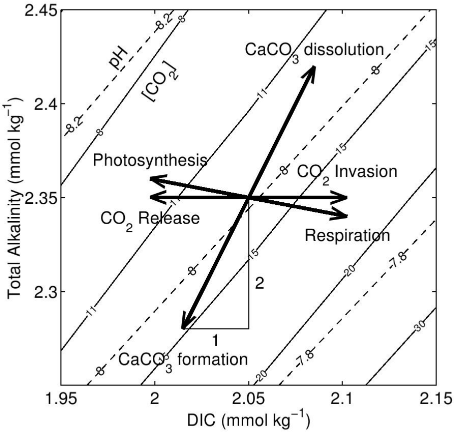
Organic production of $CaCO_3$ in the ocean:
Net reaction formula:

$$\mathrm{Ca}^{2+} + 2\mathrm{HCO}_3^- \Leftrightarrow \mathrm{CaCO}_3 + \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \qquad (4)$$

- 1 mol $CaCO_3$ reduced DIC by 1 mol
- 1 mol $CaCO_3$ reduced alkalinity by 2 mol

It is not that each mol $CaCO_3$ produces 1 mol CO_2 as might be suggested from this equation and the illustrations. Most of the CO_2 is immediately transfomed into HCO_3^-.
However, the asynchronous changes in alkalinity and DIC change the carbonate system.

Carbonate Cycle

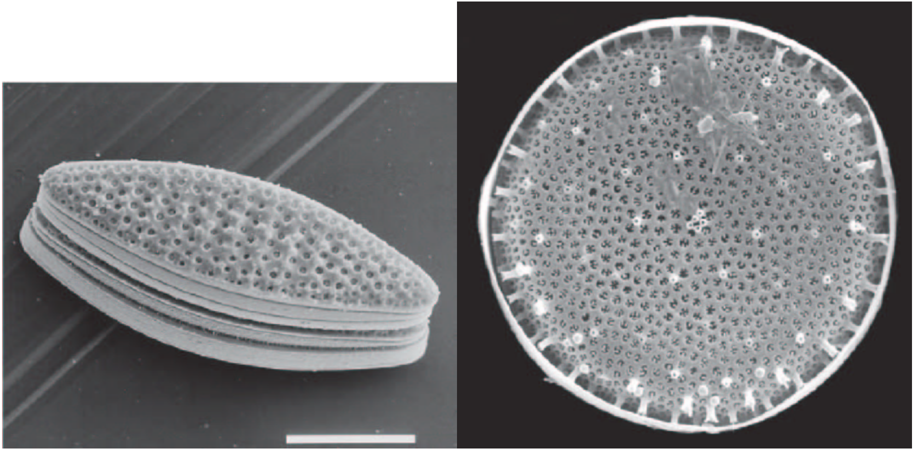


Zeebe & Wolf-Gladrow 2001

- 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]

Silicate Precipitation

Silicate precipitation: today mostly done by diatoms



Weathering

The net effect of weathering can be summarized into the basic equation:

igneous rocks + acid volatiles ⇒ 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 weahtering might exists via chemical reaction of the oceanic sediment.

Weathering

The net effect of weathering can be summarized into the basic equation:

igneous rocks + acid volatiles ⇒ 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 weahtering might exists via chemical reaction of the oceanic sediment.

Weathering

The net effect of weathering can be summarized into the basic equation:

igneous rocks + acid volatiles ⇒ 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 weahtering might exists via chemical reaction of the oceanic sediment.

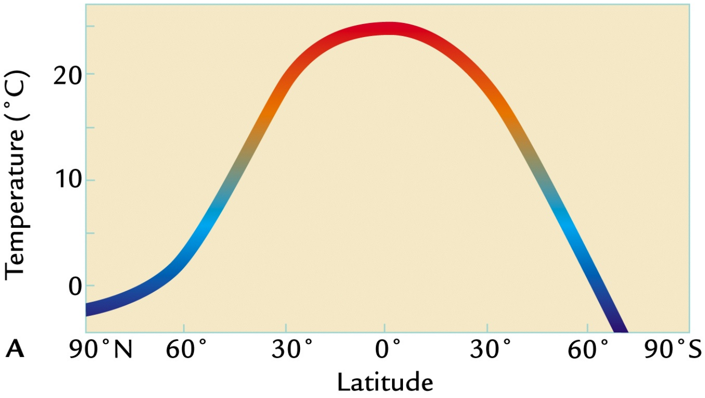
Weathering

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

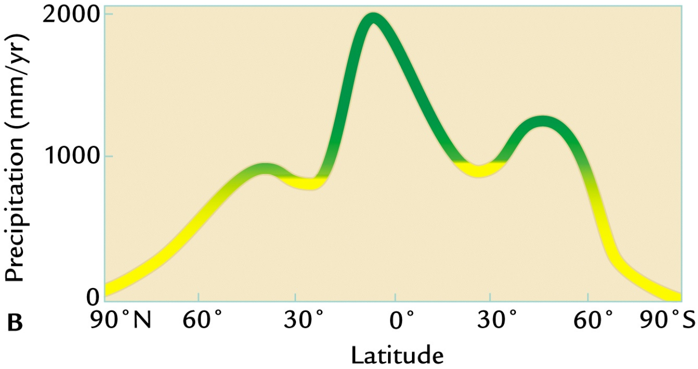
Weathering Feedback

Temperature: higher weathering in warmer regions



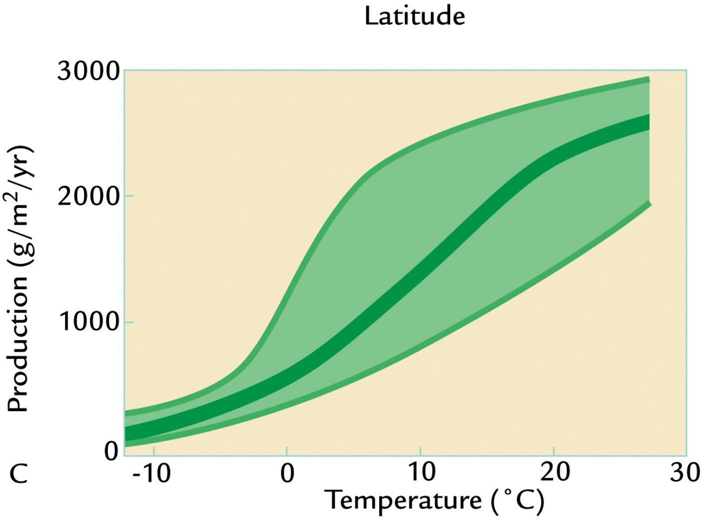
Weathering Feedback

Precipitation: highest weathering in tropics



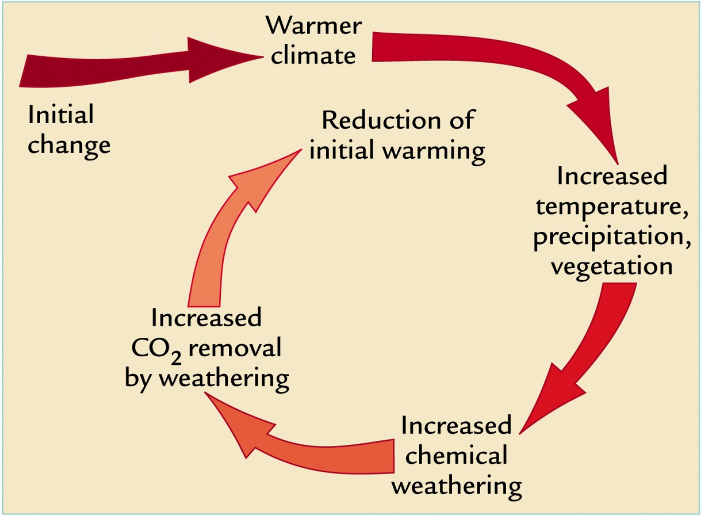
Weathering Feedback

Plant growth: increases with temperature



Weathering Feedback

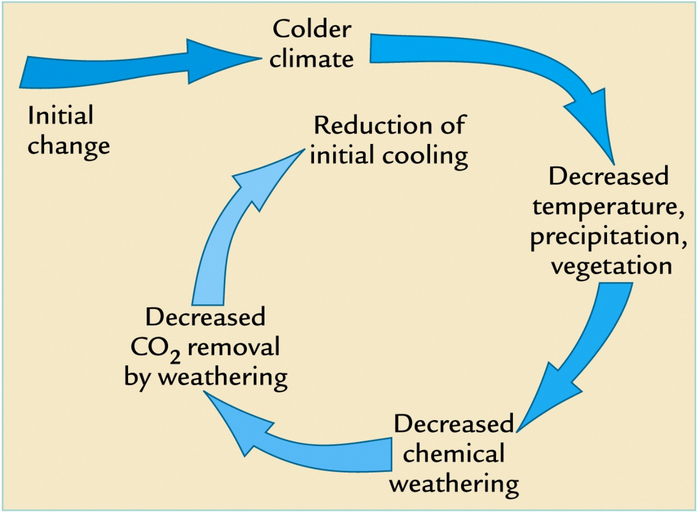
Warmer and wetter climate leads to increased weathering



A

Weathering Feedback

Sediment yield is a measure for intensity of weathering



B

Summary Weathering

Over long timescales, greenhouse strength is driven by the balance between

- source of CO_2 from volcanism
- sink of CO_2 from silicate weathering

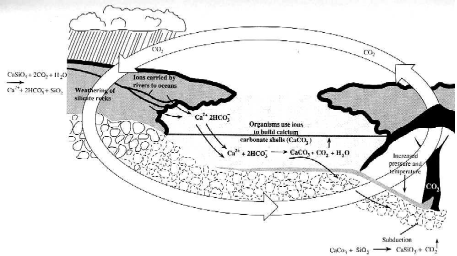


Figure 2.8 The interaction between the carbonate and silicate cycles at the surface of the Earth. Long term control of atmospheric CO_2 is achieved by dissolution of CO_2 in surface waters and its participation in the weathering of rocks. Eventually carbon is buried as part of carbonate rocks in the oceanic crust. CO_2 is released to the atmosphere when these rocks undergo metamorphism at high temperature and pressure in the Earth's crust. Modified from Kasting et al. Copyright © 1988 by Scientific American, Inc.

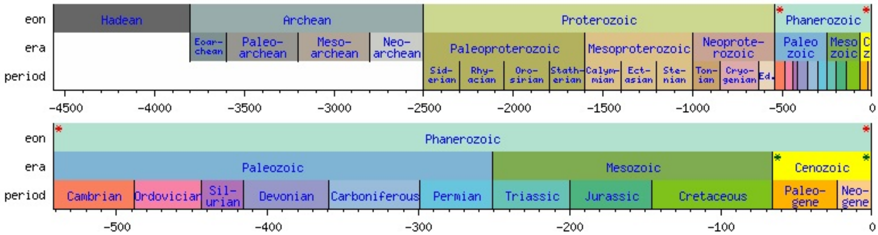
Important to notice:

- Changes in climate driven e.g. by CO_2 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. CO_2 reconstructions
   - δ^{11}B
   - B/Ca
   - Alkenones, δ^{13}C $_{\mathrm{org}}$
   - 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

The Phanerozoic I



For earth's early history only weak constraints exist on how stable climate really was:

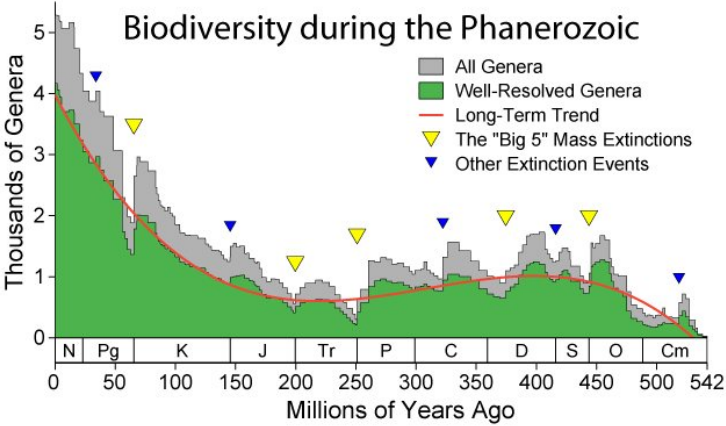
- an ocean was present: 0 °C$< T <$ 100 °C
- life could evolve: $T <\approx$ 40 °C? (degradation of most proteins; however thermophiles exist)

Much more information on climate over the last 545 million years, the Phanerozoic

The Phanerozoic II

This is a time of rapid biological change: Evolution of land plants

Many new species appeared, but also some mass extinctions



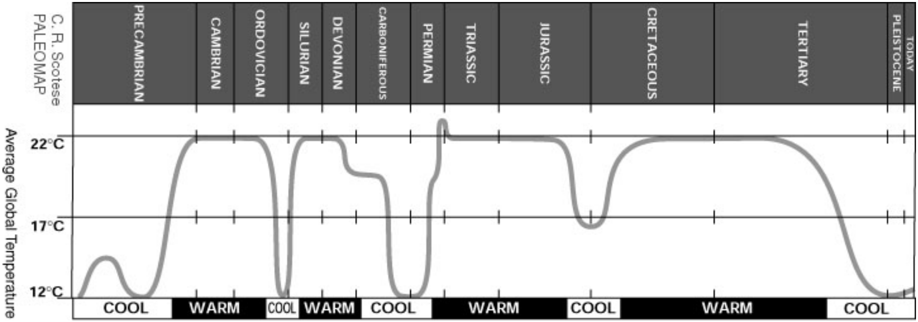
The Phanerozoic III

Ice sheets present on land: 430 or 325–240 or 35 Myr BP till now.

The Phanerozoic IV

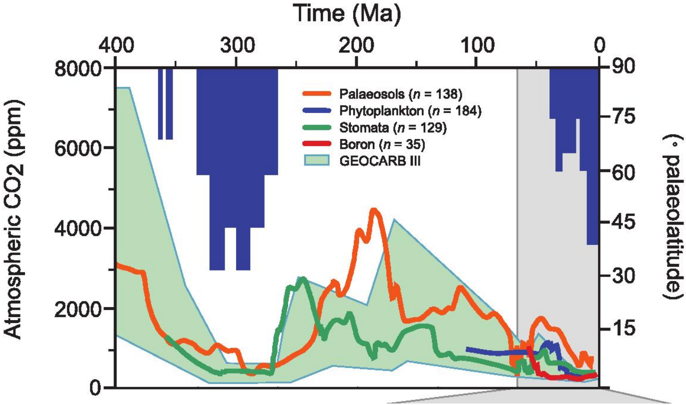
Warm-loving species (broadleaf plants, crocodiles, etc) present at high latitudes: 430–325 or 240–35 Myr BP (interrupted by somewhat cooler time)

The Phanerozoic V



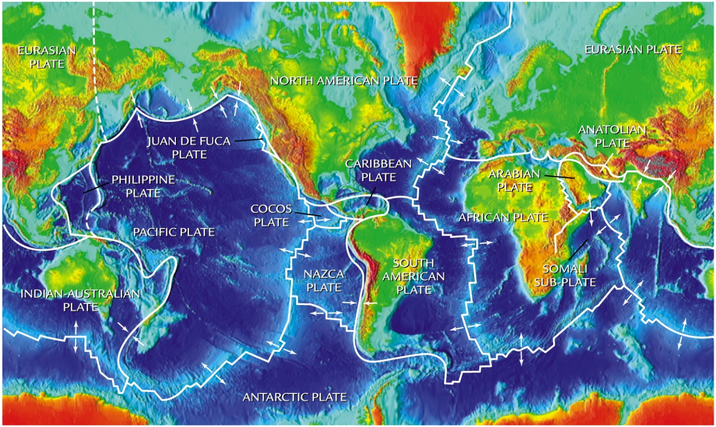
Phanerozoic CO_2

CO_2 model reconstructions generally agree with proxy data and show some relation to sequence of warm/cold climates



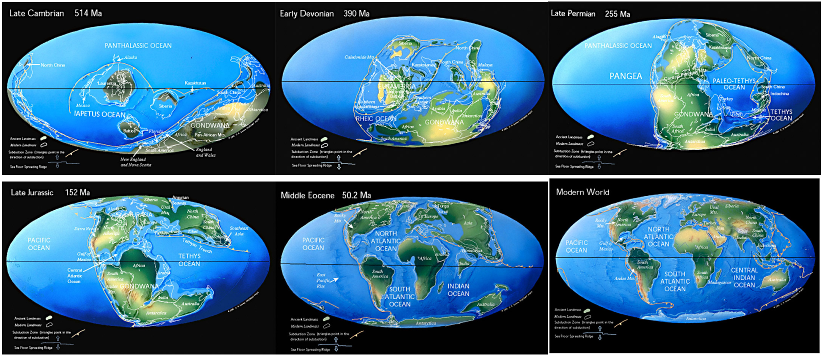
What are the mechanisms?

Plate Tectonics



Most explanations focus on role of plate tectonics

Plate Tectonics



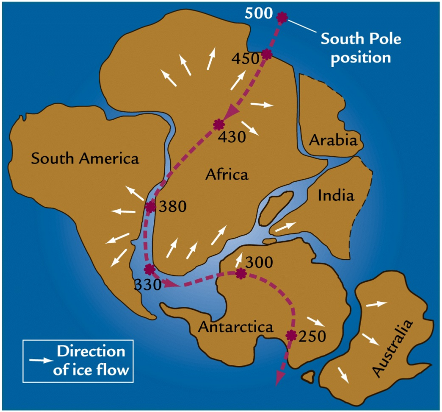
Tectonics and CO_2

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 supercontinent Gondwana

Polar Landmass Hypothesis

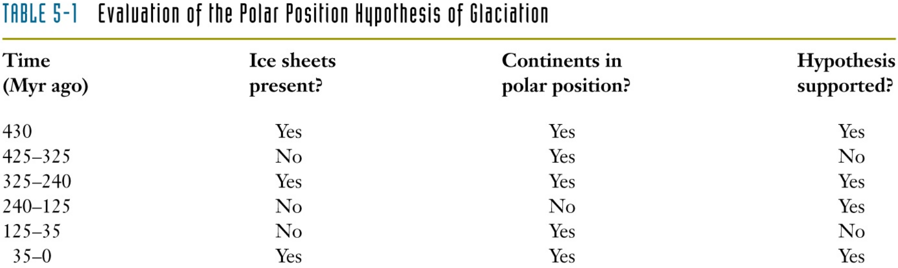


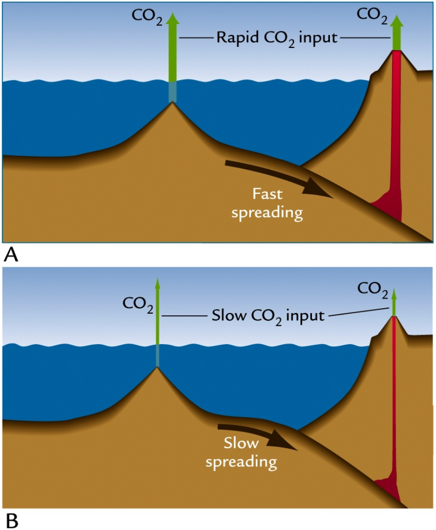
TABLE 5-1 Evaluation of the Polar Position Hypothesis of Glaciation

Time (Myr ago)	Ice sheets present?	Continents in polar position?	Hypothesis supported?
430	Yes	Yes	Yes
425–325	No	Yes	No
325–240	Yes	Yes	Yes
240–125	No	No	Yes
125–35	No	Yes	No
35–0	Yes	Yes	Yes

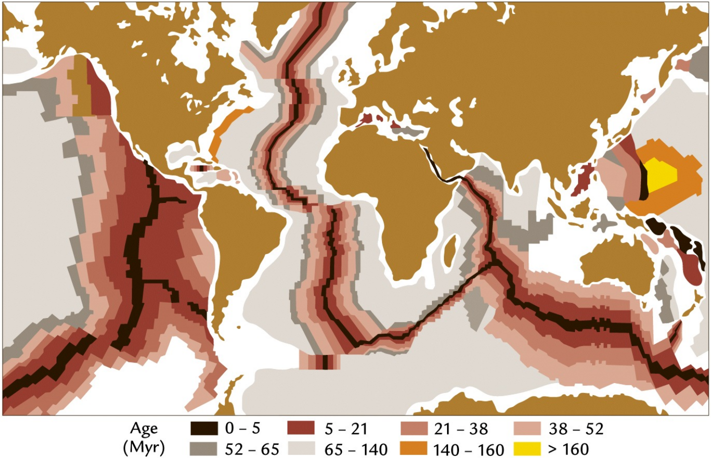
Hypothesis only for some times supported by data

Spreading Rate Hypothesis

More active plate tectonics leads to higher outgassing of CO_2, driving warmer climate



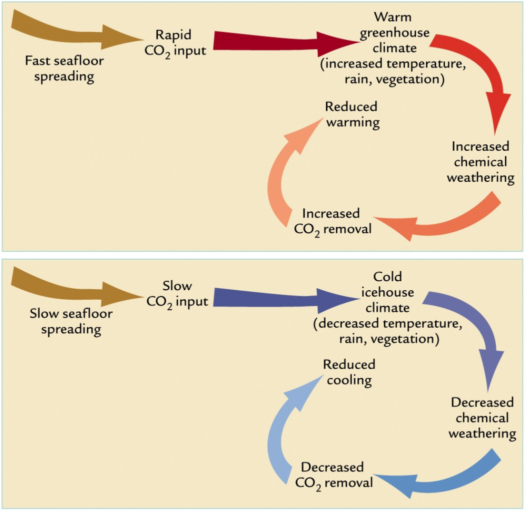
Spreading Rate Hypothesis



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

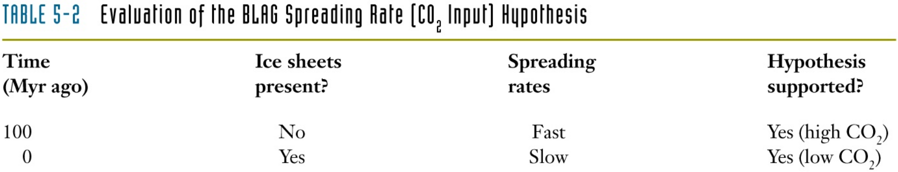


TABLE 5-2 Evaluation of the BLAG Spreading Rate [CO_2 Input] Hypothesis

Time (Myr ago)	**Ice sheets present?**	**Spreading rates**	**Hypothesis supported?**
100	No	Fast	Yes (high CO_2)
0	Yes	Slow	Yes (low CO_2)

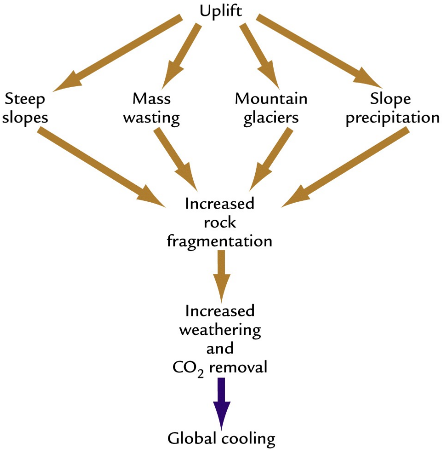
Hypothesis supported by data

Uplift/Weathering Hypothesis

Collision of continental plates leads to formation of large mountain ranges

Uplift/Weathering Hypothesis

Higher mountains lead to stronger weathering, CO_2 removal and colder climate



Uplift/Weathering Hypothesis

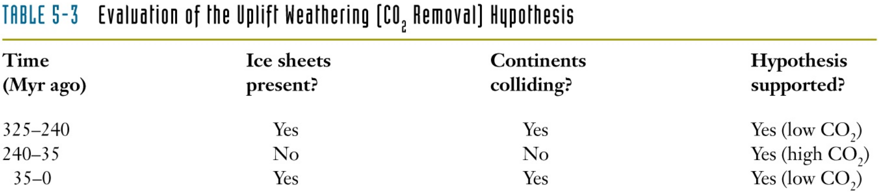


TABLE 5-3 Evaluation of the Uplift Weathering [CO_2 Removal] Hypothesis

Time (Myr ago)	Ice sheets present?	Continents colliding?	Hypothesis supported?
325–240	Yes	Yes	Yes (low CO_2)
240–35	No	No	Yes (high CO_2)
35–0	Yes	Yes	Yes (low CO_2)

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 introduce 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

Stable Cenozoic Weathering???

Vol 465|13 May 2010|doi:10.1038/nature09044 nature

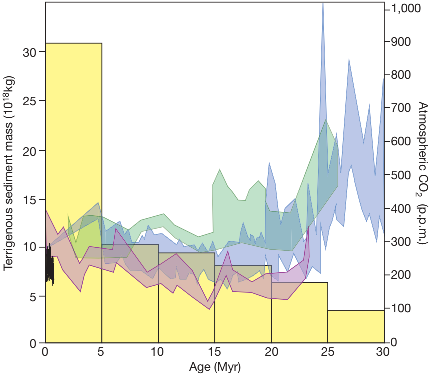
LETTERS

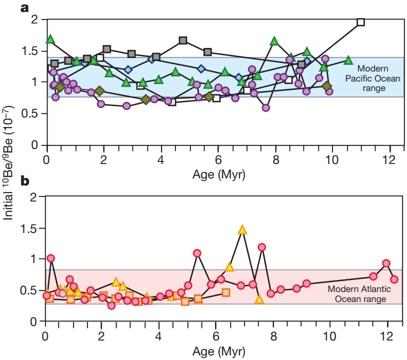
Long-term stability of global erosion rates and weathering during late-Cenozoic cooling

Jane K. Willenbring[1] & Friedhelm von Blanckenburg[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

No Faint Young Sun Paradox???

nature Vol 464 | 1 April 2010 | **doi:10.1038/nature08955**

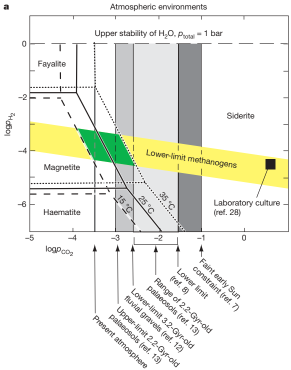
LETTERS

No climate paradox under the faint early Sun

Minik T. Rosing[1,2,4], Dennis K. Bird[1,4], Norman H. Sleep[5] & Christian J. Bjerrum[1,3]

Rosing 2010 N

No Faint Young Sun Paradox???



Existience of Fe(II-III) oxides (magenite) in banded iron formations is inconsitent with high CO_2 necessary under fain 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
    - δ^{11}B
    - B/Ca
    - Alkenones, $\delta^{13}C_{\mathrm{org}}$
    - 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

Summary

- Pre-ice core CO_2 is estimated from different proxies (δ^{11}B, B/Ca, stomata, $\delta^{13}\text{C}_{\text{ORG}}$) 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.

References I

Hönisch, B. and Hemming, N. G.: Ground-truthing the boron isotope-paleo-pH proxy in planktonic foraminifera shells: partial dissolution and shell size effects, Paleoceanography, 19, PA4010, doi: 10.1029/2004PA001 026, 2004.

Hönisch, B., Hemming, N. G., Archer, D., Siddall, M., and McManus, J. F.: Atmospheric Carbon Dioxide Concentration Across the Mid-Pleistocene Transition, Science, 324, 1551–1554, doi:10.1126/science.1171477, 2009.

Köhler, P., Bintanja, R., Fischer, H., Joos, F., Knutti, R., Lohmann, G., and Masson-Delmotte, V.: What caused Earth's temperature variations during the last 800,000 years? Data-based evidences on radiative forcing and constraints on climate sensitivity, Quaternary Science Reviews, 29, 129–145, doi:10.1016/j.quascirev.2009.09.026, 2010.

Kürschner, W. M., Kvaček, Z., and Dilcher, D. L.: The impact of Miocene atmospheric carbon dioxide fluctuations on climate and the evolution of terrestrial ecosystems, Proceedings of the National Academy of Sciences, 105, 449–453, doi:10.1073/pnas.0708588105, 2008.

Leemans, R. and Cramer, W. P.: The IIASA climate database for land areas on a grid with 0.5^o resolution, vol. RR-91-18 of *Research Reports*, International Institute for Applied Systmes Analysis, Laxenburg, Austria, 1991.

Levitus, S. and Boyer, T.: World Ocean Atlas Volume 4: Temperature, NOAA Atlas NESDIS 4, U.S. Department of Commerce, Washington, D.C., 1994.

Pagani, M., Zachos, J. C., Freeman, K. H., Tipple, B., and Bohaty, S.: Marked Decline in Atmospheric Carbon Dioxide Concentrations During the Paleogene, Science, 309, 600–603, doi:10.1126/science.1110063, 2005.

Pagani, M., Liu, Z., LaRiviere, J., and Ravelo, A. C.: High Earth-system climate sensitivity determined from Pliocene carbon dioxide concentrations, Nature Geoscience, 3, 27–30, doi:10.1038/ngeo724, 2010.

Pearson, P. N. and Palmer, M. R.: Atmospheric carbon dioxide concentrations over the past 60 million years, Nature, 406, 695–699, 2000.

Rosing, M. T., Bird, D. K., Sleep, N. H., and Bjerrum, C. J.: No climate paradox under the faint early Sun, Nature, 464, 744–747, doi:10.1038/nature08955, 2010.

Ruddiman, W. F.: Earth's Climate, past and future, Freeman, 2001.

Rundgren, M. and Beerling, D.: Fossil leaves: effecitve bioindicators of ancient CO_2 levels?, Geochemistry, Geophysics, Geosystems, 4, 1058, doi: 10.1029/2002GC000 463, 2003.

Rundgren, M., Björck, S., and Hammarlund, D.: Last interglacial atmospheric CO_2 changes from stomatal index data and their relation to climate variations, Global and Planetary Change, 49, 47–62, 2005.

Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K., and Pancost, R. D.: Alkenone and boron-based Pliocene pCO2 records, Earth and Planetary Science Letters, 292, 201 – 211, doi:10.1016/j.epsl.2010.01.037, 2010.

Tripati, A. K., Roberts, C. D., and Eagle, R. A.: Coupling of CO2 and Ice Sheet Stability Over Major Climate Transitions of the Last 20 Million Years, Science, 326, 1394–1397, doi:10.1126/science.1178296, 2009.

van de Wal, R., de Boer, B., Lourens, L., Köhler, P., and Bintanja, R.: Continuous and self-consistent CO_2 and climate records over the past 20 Myrs, Climate of the Past Discussions, 7, 437-461, doi:10.5194/cpd-7-437-2011, 2011.

Willenbring, J. K. and von Blanckenburg, F.: Long-term stability of global erosion rates and weathering during late-Cenozoic cooling, Nature, 465, 211–214, doi:10.1038/nature09044, 2010.

Yu, J., Foster, G. L., Elderfield, H., Broecker, W. S., and Clark, E.: An evaluation of benthic foraminiferal B/Ca and δ^{11}B for deep ocean carbonate ion and pH reconstructions, Earth and Planetary Science Letters, 293, 114 – 120, doi:10.1016/j.epsl.2010.02.029, 2010.