CO_2 reconstructions and carbon cycle in the past (20 Myr)

ESSReS-L9

Earth System Science: a combined data-modelling paleoperspective

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Outline

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

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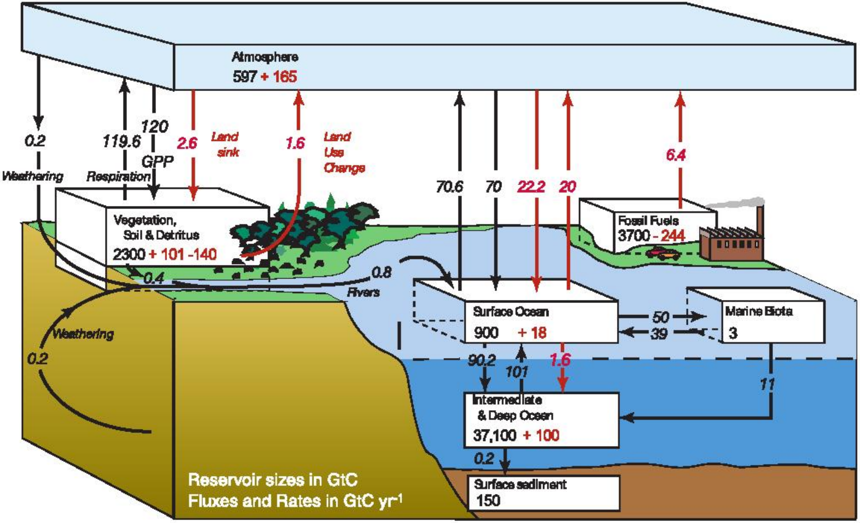
C Pools and C fluxes



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.

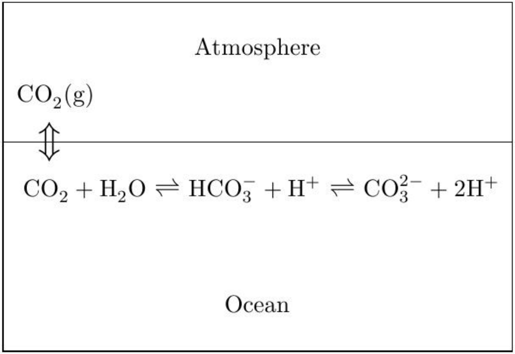


Figure 1.1.1: Schematic illustration of the carbonate system in the ocean. CO_2 is exchanged between atmosphere and ocean via equilibration of $CO_2(g)$ and dissolved CO_2. Dissolved CO_2 is part of the carbonate system in seawater that includes bicarbonate, HCO_3^-, and carbonate ion, CO_3^{2-}.

Zeebe & Wolf-Gladrow 2001

Chemical System in Equilibrium

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

[H_2CO_3] is negligible and the equation reduced to

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

Dissolved Inorganic Carbon — DIC

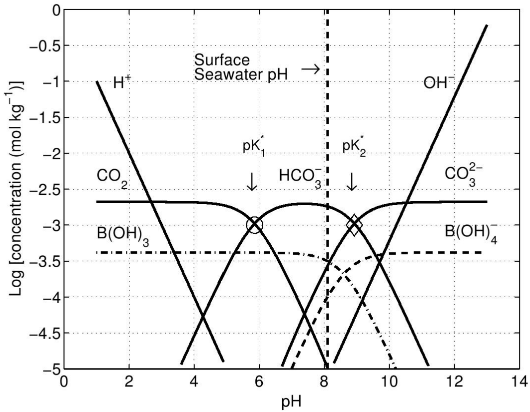
$$DIC \equiv \Sigma CO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

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:

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

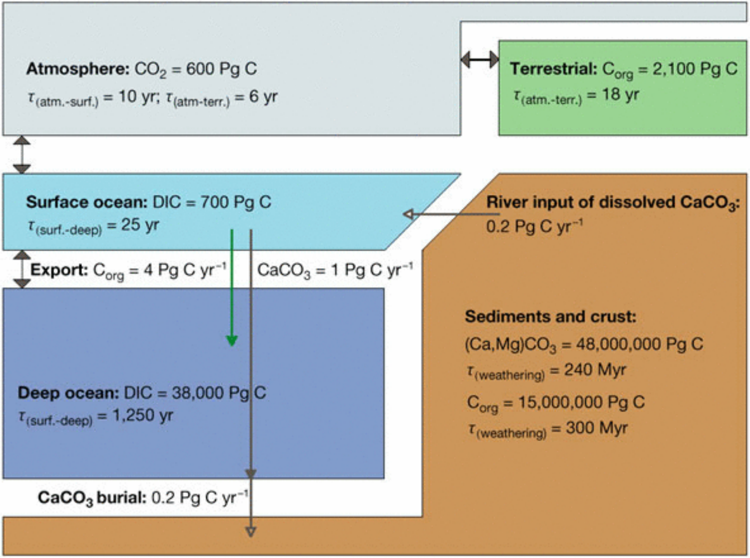
Carbonate System

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

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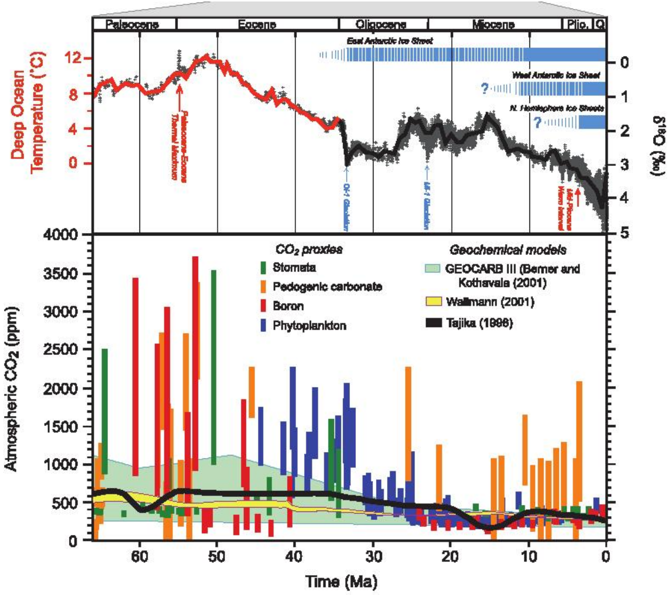
CO_2 Reconstructions, 65,000,000 yr (IPCC 2007)



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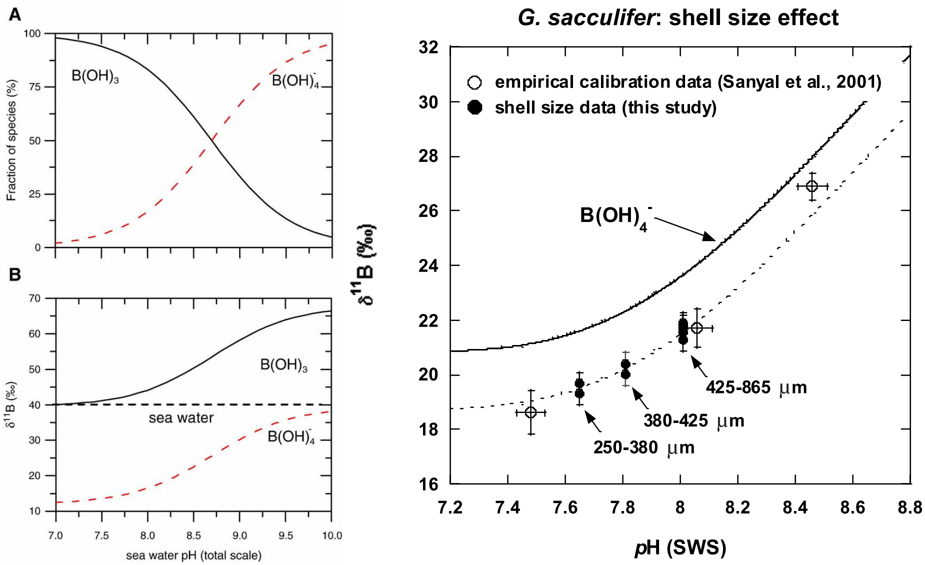
$\delta^{11}B$, pH—$\delta^{11}B$, pH—B



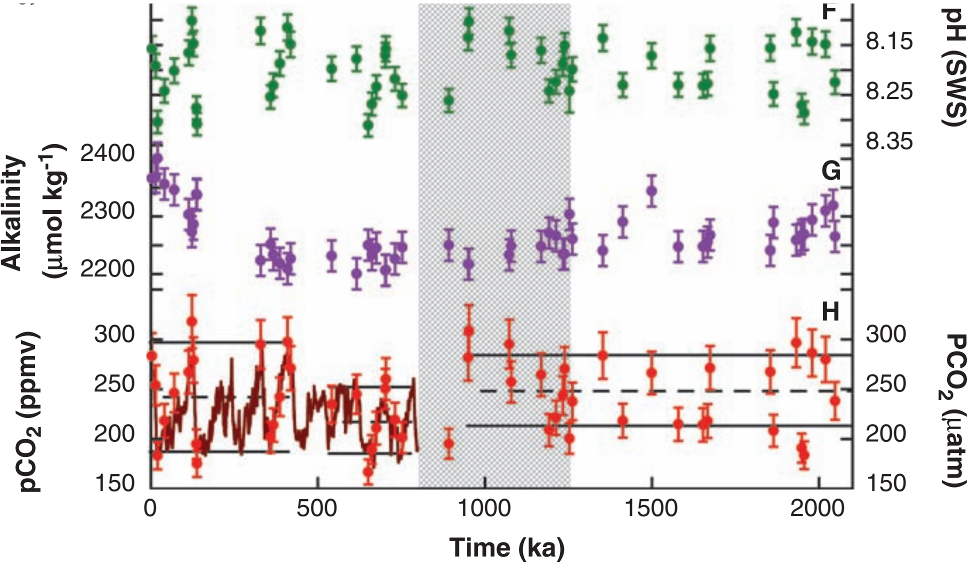
Yu et al., 2010 EPSL; Hönisch 2004, P

δ^{11}B, boron isotopes

General approach:

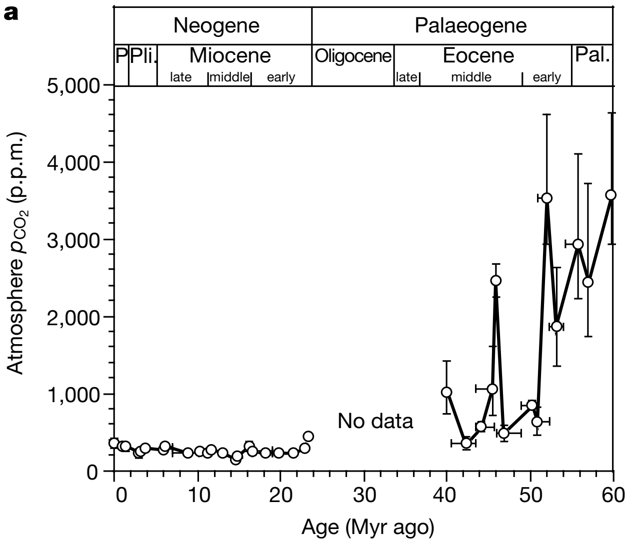
- Calculate surface water pH out of δ^{11}B.
- Determine independently another parameter of the carbonate system (CO_2, HCO_3^-, CO_3^{2-}, pH, DIC, alkalinity), mostly alkalinity is estimated.
- Surface water pCO_2 can be calcuated out of pH and 2nd parameter.
- Under the assumption that surface water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

$\delta^{11}B$ example I, single species, last 2 Myr



Hönisch et al 2009, S

$\delta^{11}B$ example II, multi-species, last 60 Myr



Pearson and Palmer 2000 N

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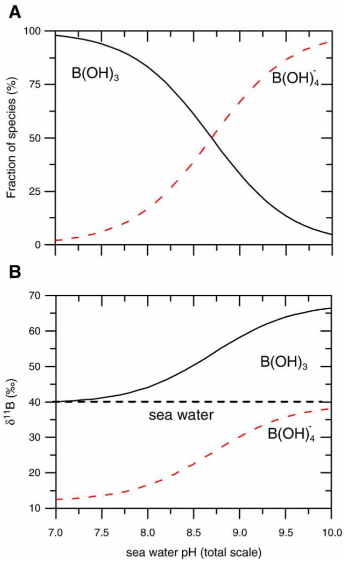
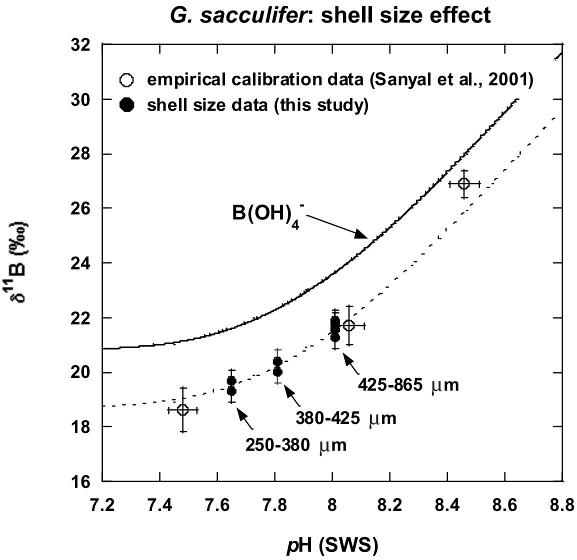
$\delta^{11}B$, pH—$\delta^{11}B$, pH—B





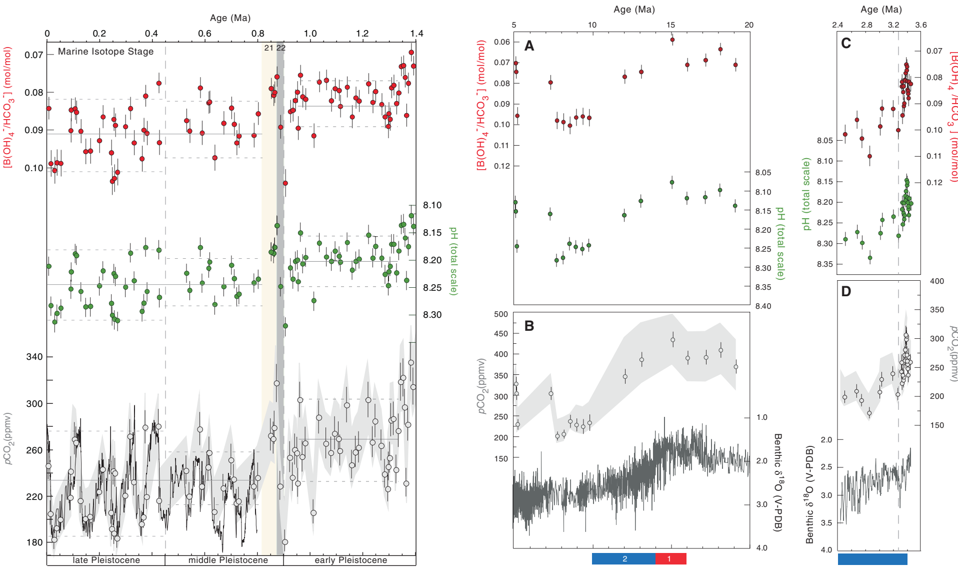
Yu et al., 2010 EPSL; Hönisch 2004, P

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

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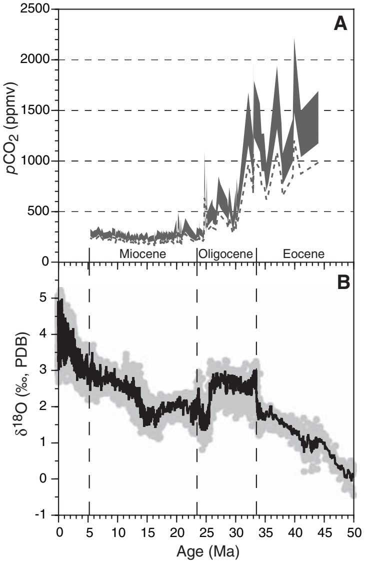
Alkenones, or $\delta^{13}C_{org}$

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.

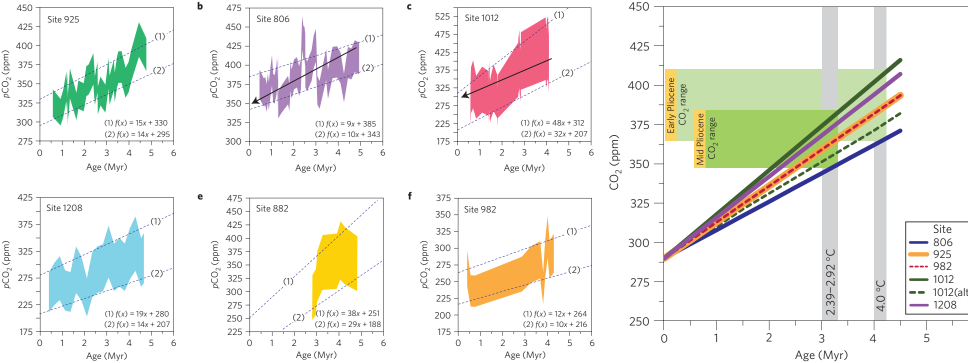
- **Disadvantage:** Based on analogue, not on chemistry, atm-surf-equilibrium might have changed over time

Alkenones, example I, last 60 Myr



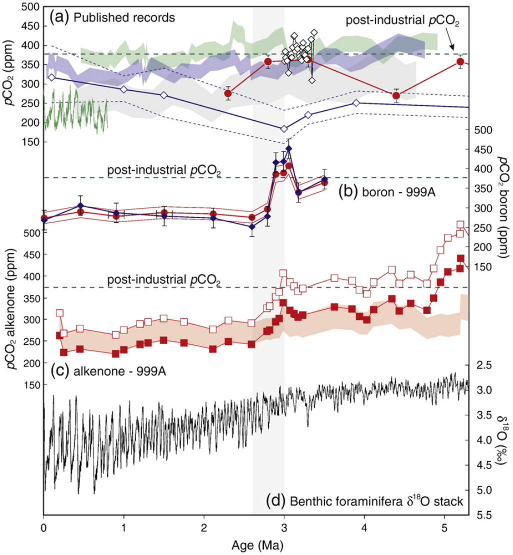
Pagani et al., 2005 S

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

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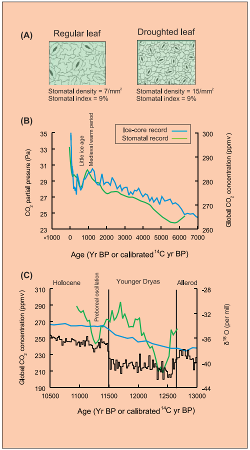
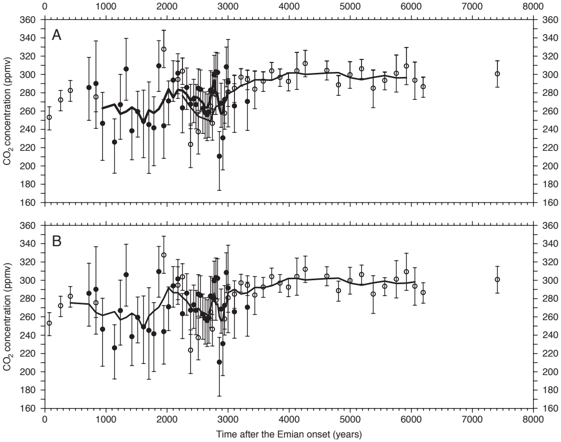
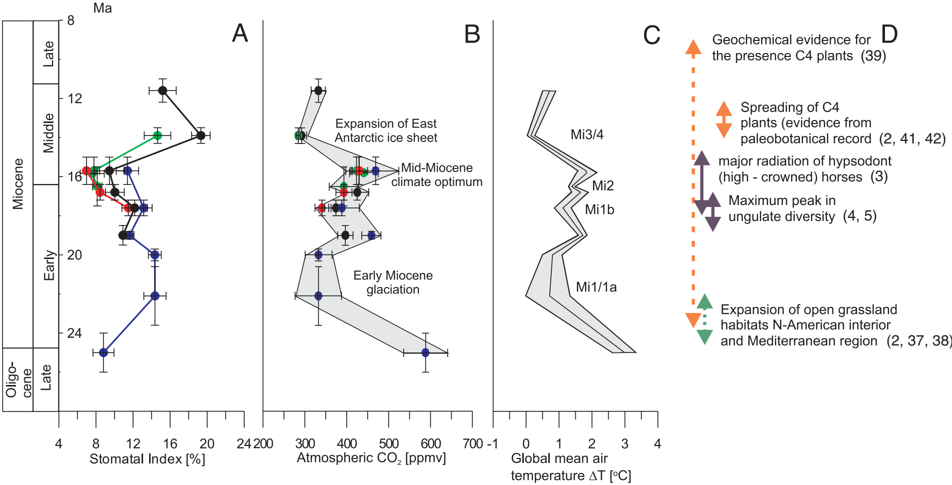
Stomata





Rundgren 2003 GGG, Rundgren 2005 GPC

Stomata



Kuerschner 2008 PNAS

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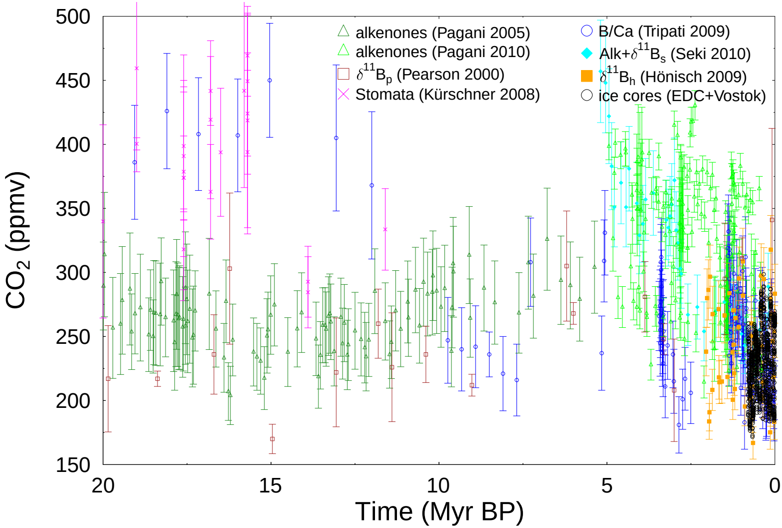
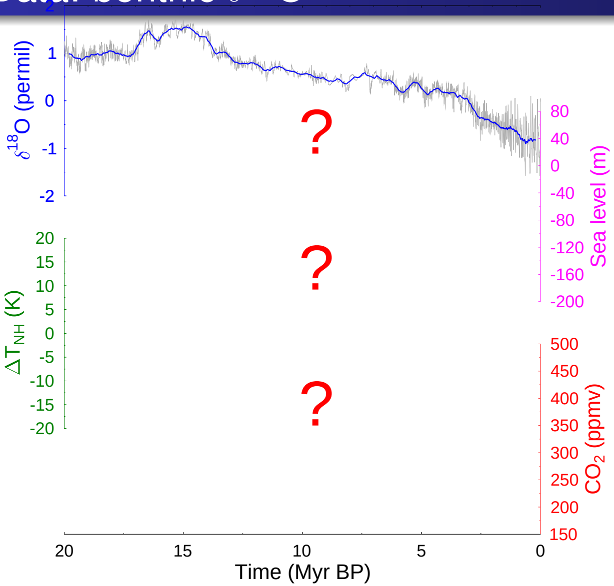
CO_2: proxy diversity



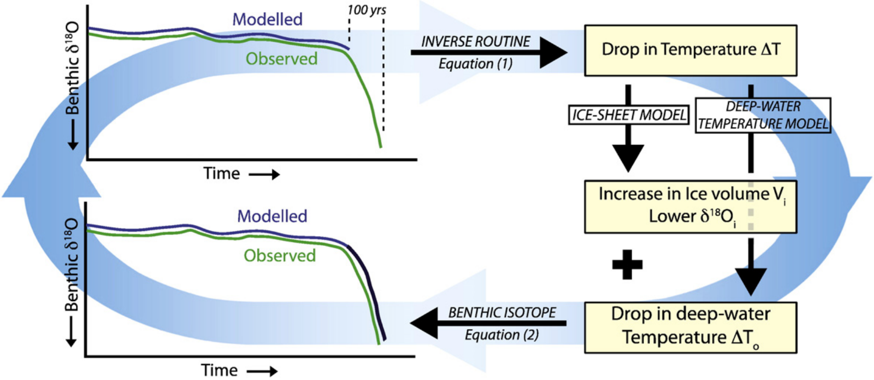
after van de Wal et al., 2011 CPD

Climate Data: benthic $\delta^{18}O$



(Zachos et al., 2008, N)

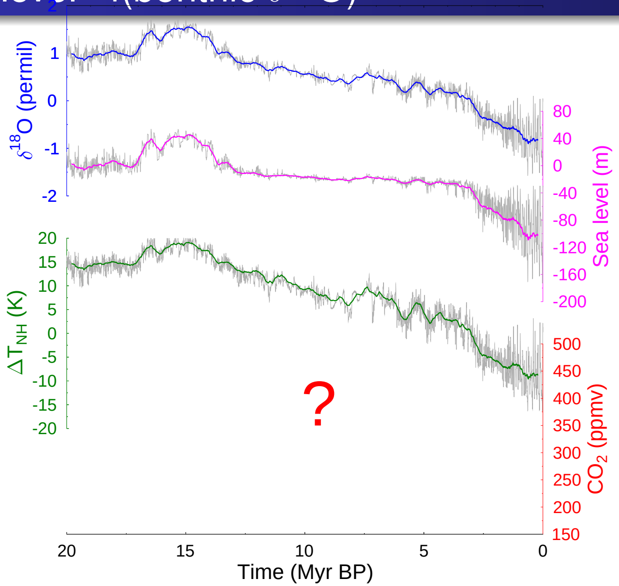
Ice Sheets, ΔT and benthic δ^{18}O



Deconvolute stacked benthic δ^{18}O into climate variables ($\Delta T_{\text{deep o}}$, $\Delta T_{\text{atm (40–80°N)}}$, size of ice sheets, sea level, snow cover)

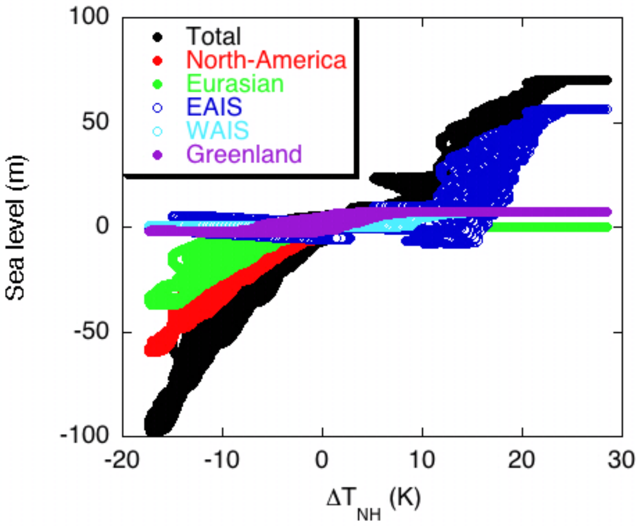
(Bintanja et al., 2005; de Boer et al., 2011)

ΔT, Sea level =f(benthic $\delta^{18}O$)



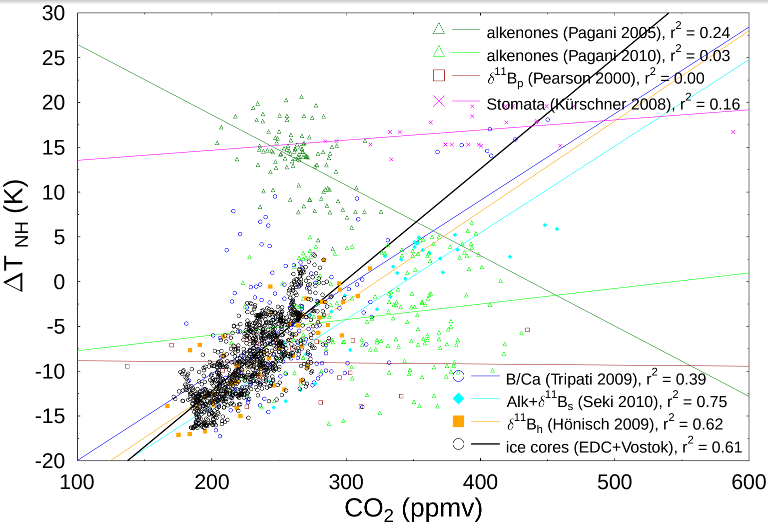
(after Bintanja et al., 2005; van de Wal et al., 2011; de Boer et al., 2011)

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



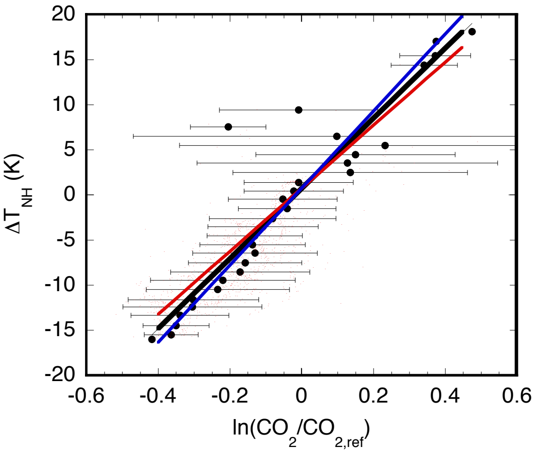
Van de Wal et al., 2011, CPD

Relationship ΔT_{NH}—CO_2



(after van de Wal et al., 2011 CPD)

ΔT_{NH}—CO_2 1: Empirical Relationship



resampled and binned data in intervals of $\Delta(\Delta T_{NH}) = 1$ K

$C = 39 \pm 4K$ regression slope from modelled ΔT_{NH} and CO_2 data

(van de Wal et al., 2011, CPD)

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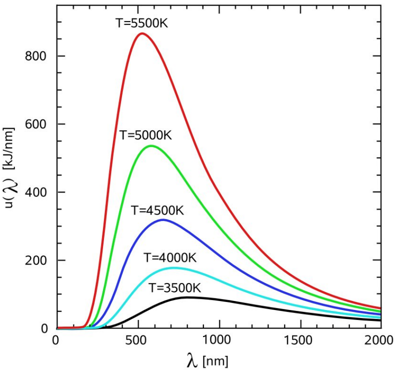
Planck's Law

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.

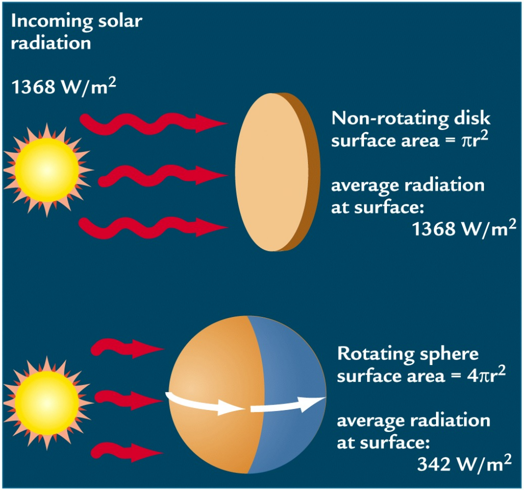


- Birth of Quantum Mechanics: Light (photons) have discrete energies
- Plancks Constant $h \sim 6.6 \cdot 10^{-34}$Js
- $E = h \cdot \nu$. ν: frequency
- Planck's Law brought together 2 approximations (Wien; Rayleigh-Jeans)
- Wien's displacement law: $\lambda_{\max} \cdot T = 2.9 \cdot 10^{-3}$ m K.
- 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: $\sigma = 5.67 10^{-8} W/(m^2 \cdot K^4)$
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

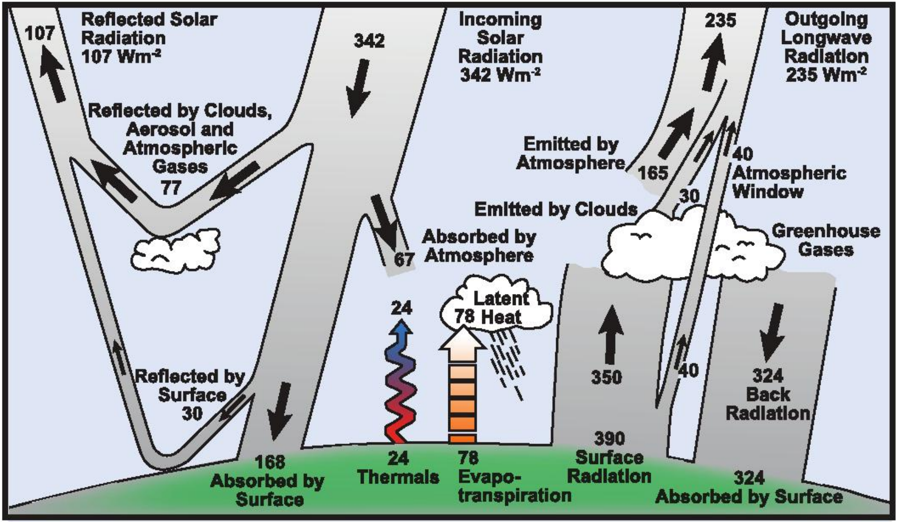
$$S_M(1-\alpha) 4 \pi r^2 = R 4 \pi r^2$$

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

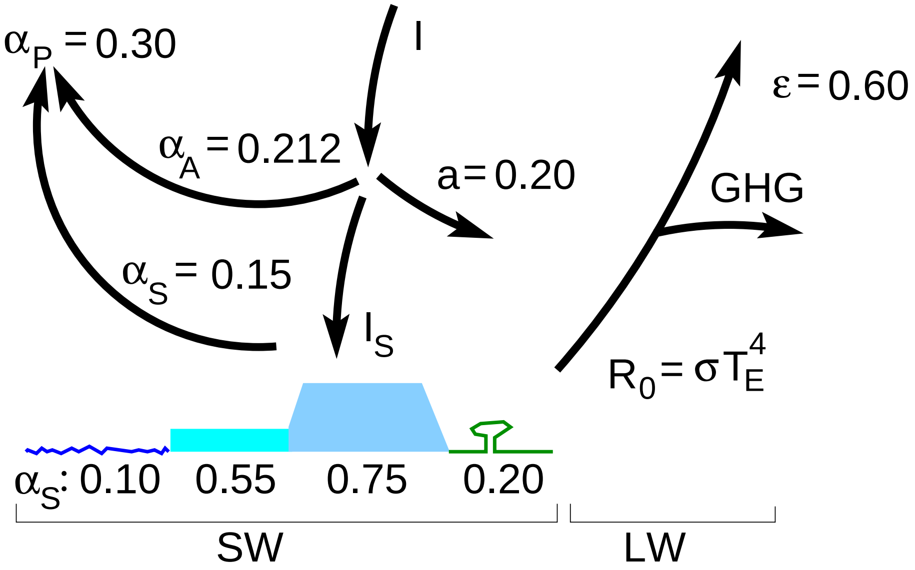
$$T_{e,0} = 255 K (-18^\circ C)$$

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)



ΔT_{NH}—CO_2 2: Theoretical Relationship

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

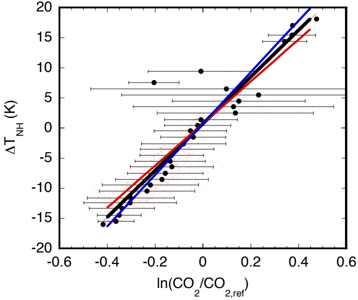
LGM parameters:

$\alpha = \Delta T_{NH}/\Delta T_{global} = 15\ \mathrm{K}/6\ \mathrm{K} = 2.5$
$\beta = 5.35$: radiative forcing of CO_2
$\gamma = 1.3$: enhancement factor for non-CO_2 GHG (CH_4, N_2O)
$S_C = 0.72$: Charney climate sensitivity (fast feedbacks: Planck, water vapour, lapse rate, clouds, sea ice, albedo)
$f = 0.72$: feedbacks of slow processes (land ice, dust, vegetation)

$C = 43K$ theoretical calculation based LGM data and constant climate sensitivity

For comparision:
pure S_{Charney} $(f = 0; \gamma = 1; \alpha = 1) \Rightarrow C_C = 3.9$ K and $\Delta T_{global} = 2.7$ K
(van de Wal et al., 2011, CPD)

Develop relationship atmospheric ΔT_{NH}—CO_2



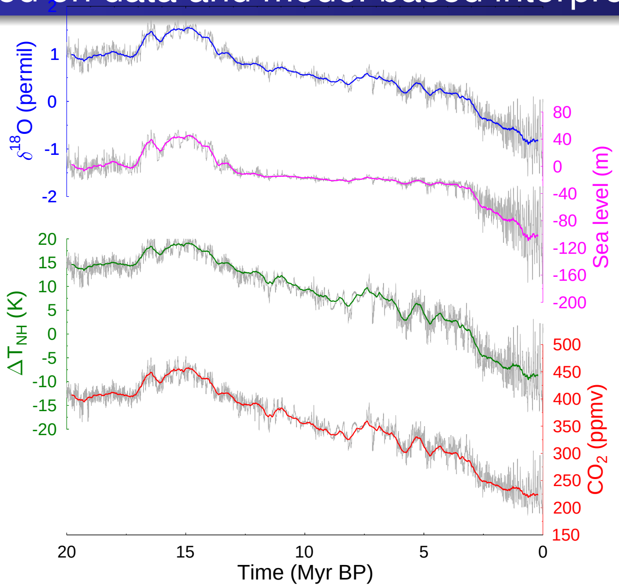
$$\Delta T_{NH} = C \cdot \ln \frac{CO_2}{CO_{2,ref}} \text{ with } C = \frac{\alpha\beta\gamma S}{1-f}$$

Two independent approaches to calculate the slope:

1. $C = 39 \pm 4K$ regression slope from modelled ΔT_{NH} and CO_2 data
2. $C = 43K$ theoretical calculation based LGM data and constant S

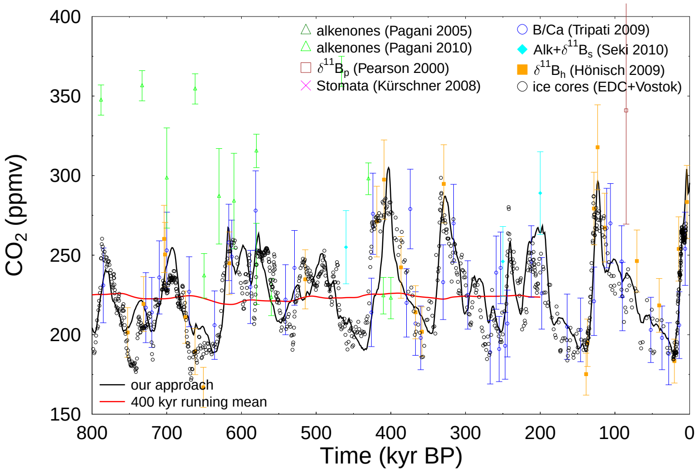
(van de Wal et al., 2011, CPD)

CO_2 based on data and model-based interpretation



after van de Wal et al., 2011 CPD

CO_2 reconstructions, the last 20 Myr



Glacial/interglacial amplitudes captured, details wrong

after van de Wal et al., 2011 CPD

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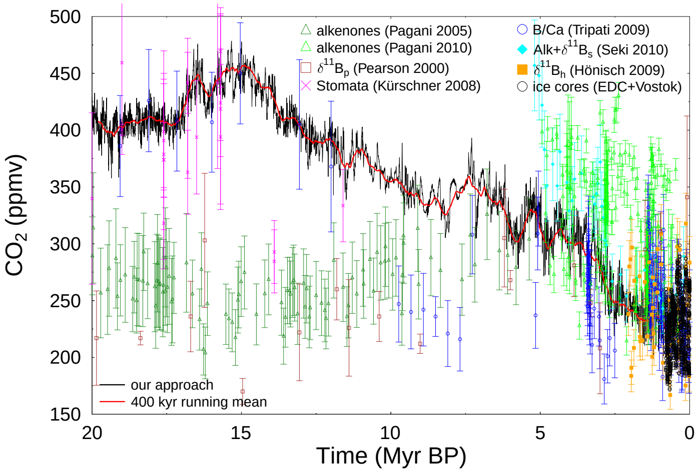

Assumption: relation CO_2-ΔT unchanged with time!!!

after 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

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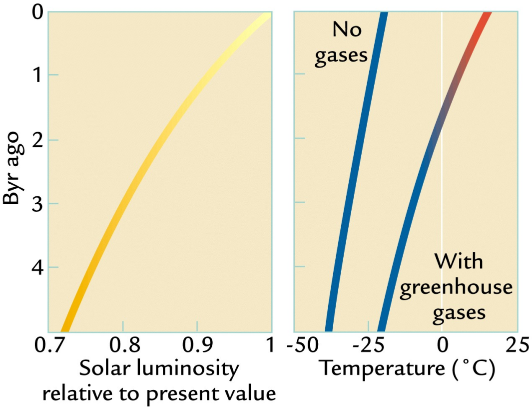
The Faint young sun Paradox I

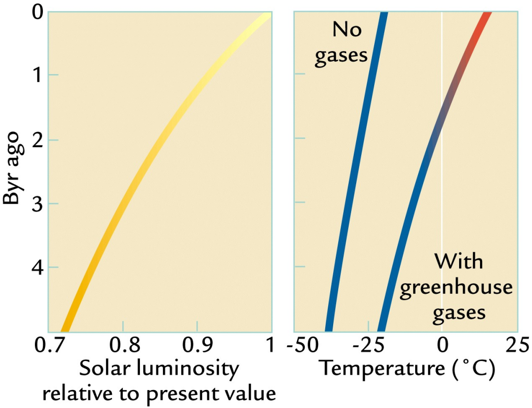
Solar luminosity increased over earth's history: Early sun was about 30% weaker than today.



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

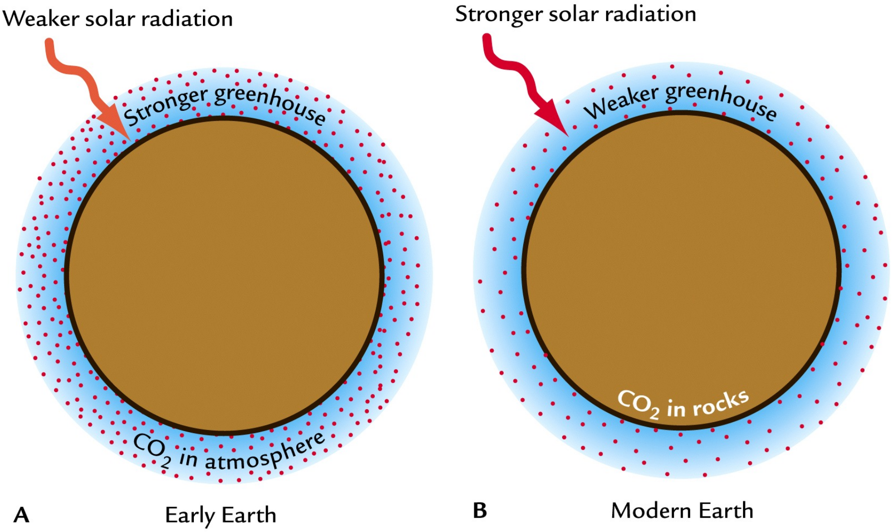
The Faint young sun Paradox II

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

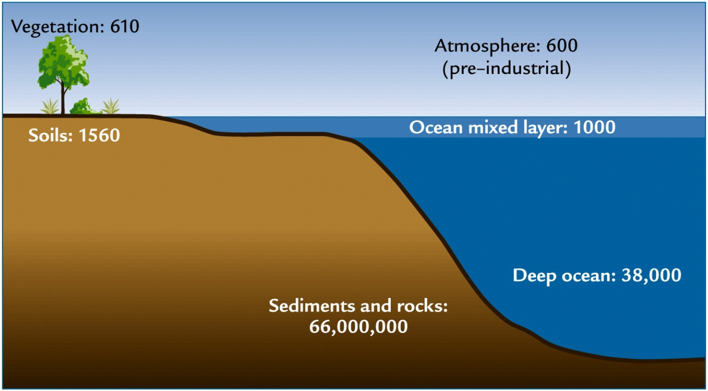
Greenhouse Effect

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

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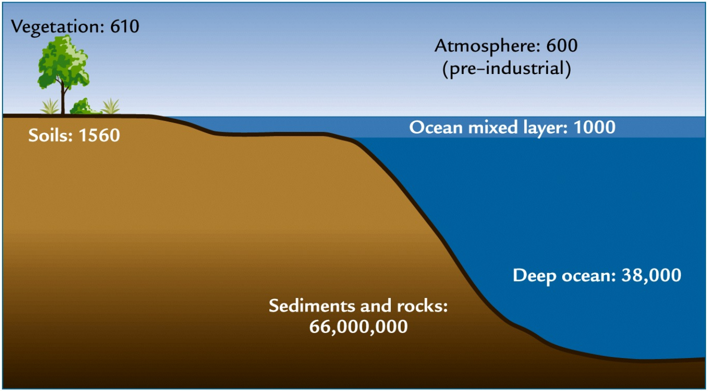

A Major carbon reservoirs (gigatons; 1 gigaton = 10^{15} grams)

How can CO_2 exchange between atmosphere and rocks?

Outline

1. Basics on the Carbon Cycle
2. CO_2 reconstructions
   - $\delta^{11}B$
   - B/Ca
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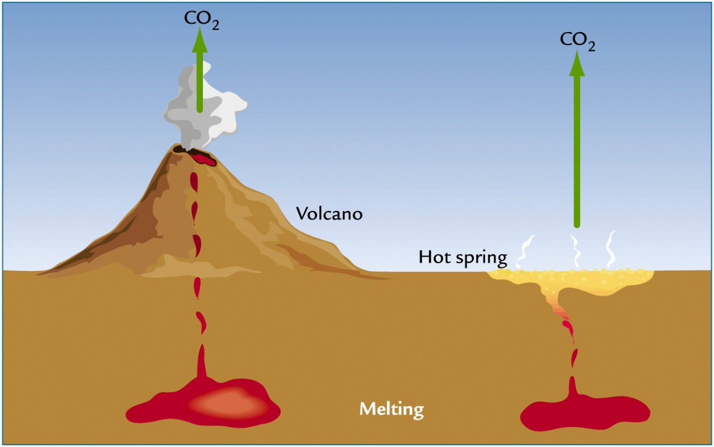
   - CO_2 outgassing
   - Weathering
4. Summary

Rock to Atmosphere Flux: Volcanic Emissions

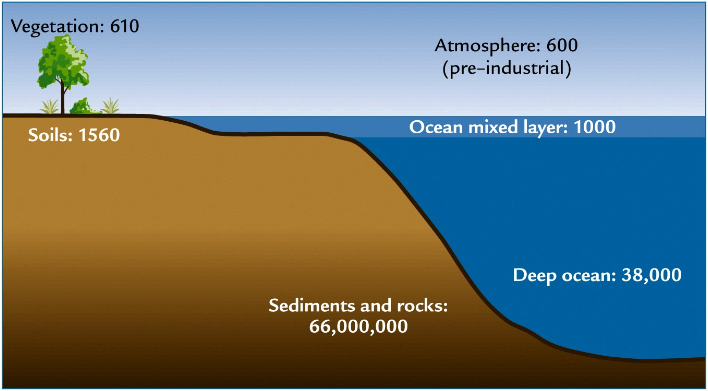
Volcanoes presently emit ca. 0.15 Pg C a^{-1}, mostly in the form of CO_2 (also some emission of CH_4). This activity might have been stronger.



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

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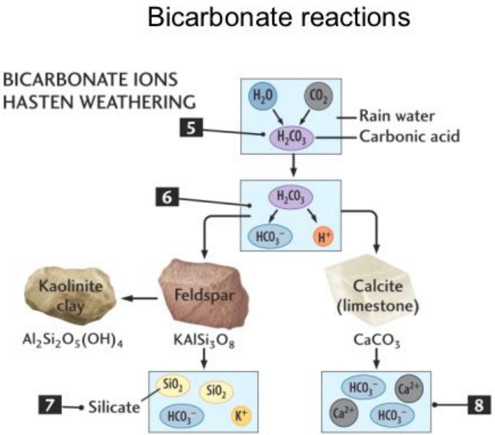
Atmosphere to Rock Flux: Weathering

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

$$H_2O + CO_2 \Rightarrow H_2CO_3 \qquad (3)$$

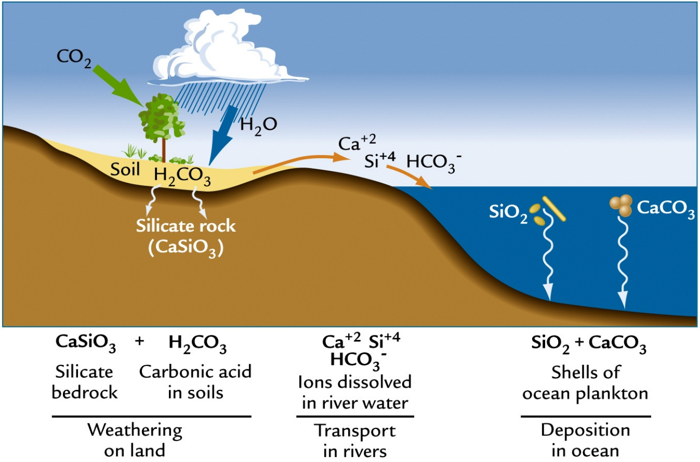
rain + atmosphere ⇒ carbonic acid

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

All C in silicate weathering comes from the atmosphere!

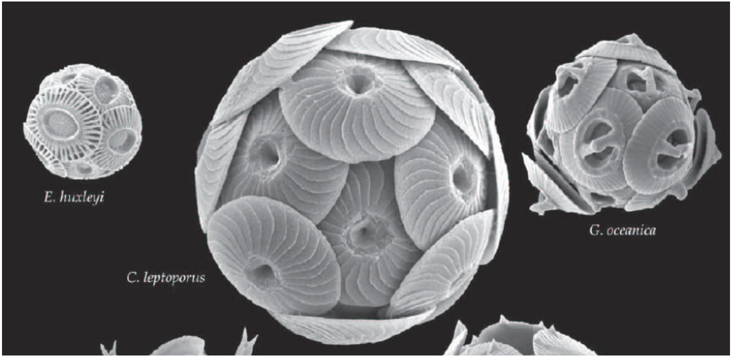
After Weathering

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



Carbonate Precipitation

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



Budget of $CaCO_3$ pump

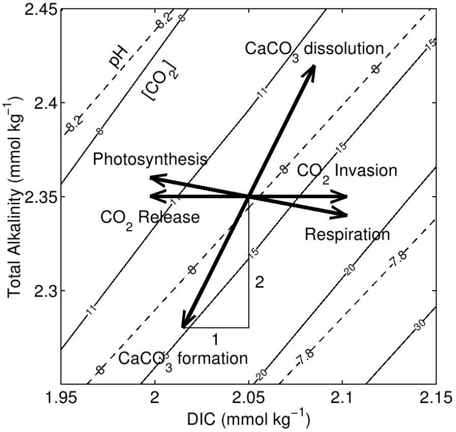
Organic production of $CaCO_3$ in the ocean:
Net reaction formula:

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O \quad (4)$$

- 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.

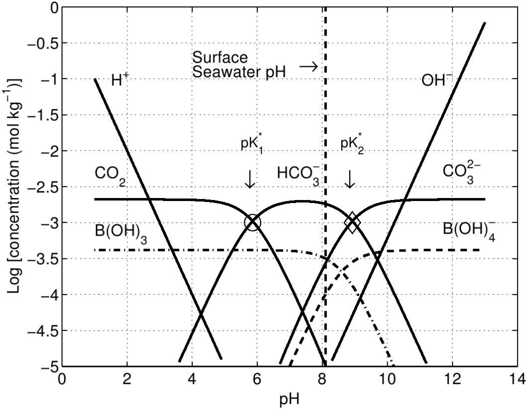
Carbonate Cycle



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]

Bjerrum Plot

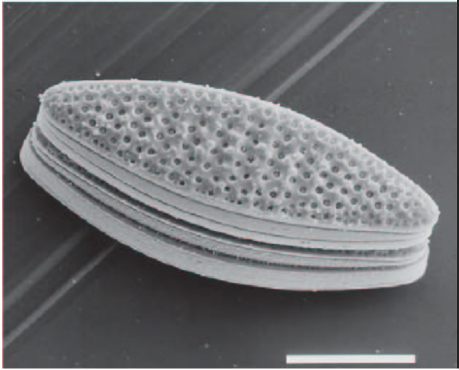


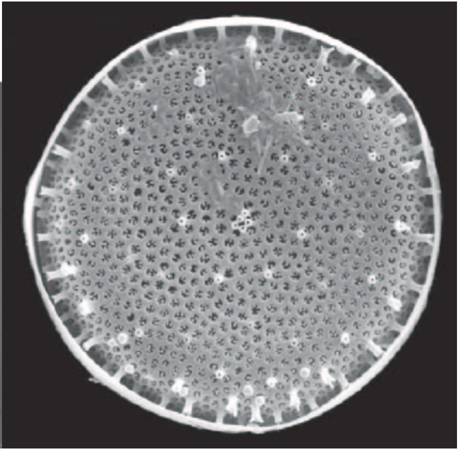
A reduced pH shifts the carbonate system towards higher CO_2 values

Zeebe & Wolf-Gladrow 2001

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 weathering might exists via chemical reaction of the oceanic sediment.

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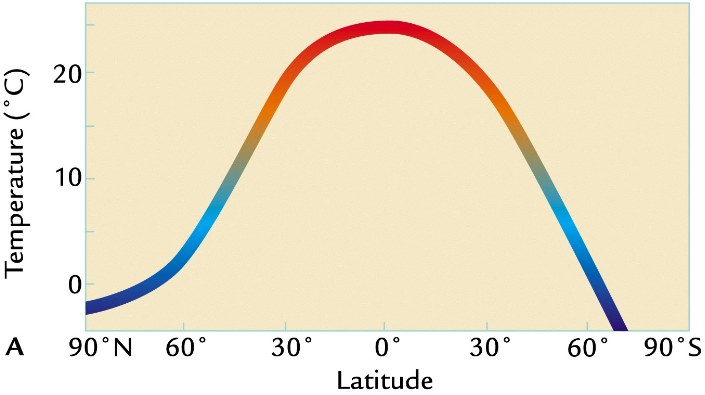
Weathering

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

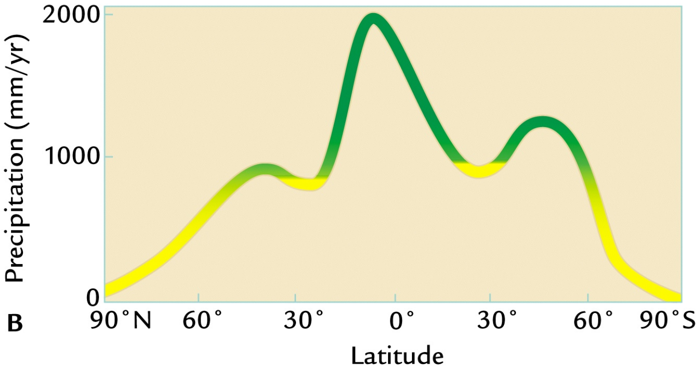
Weathering Feedback

Temperature: higher weathering in warmer regions



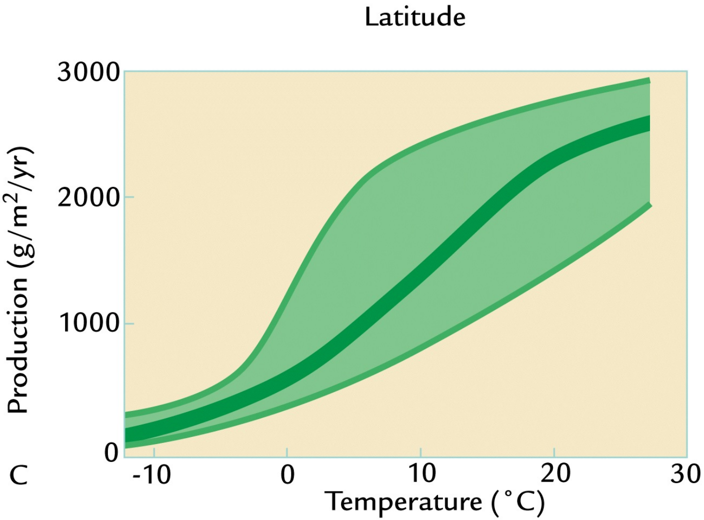
Weathering Feedback

Precipitation: highest weathering in tropics



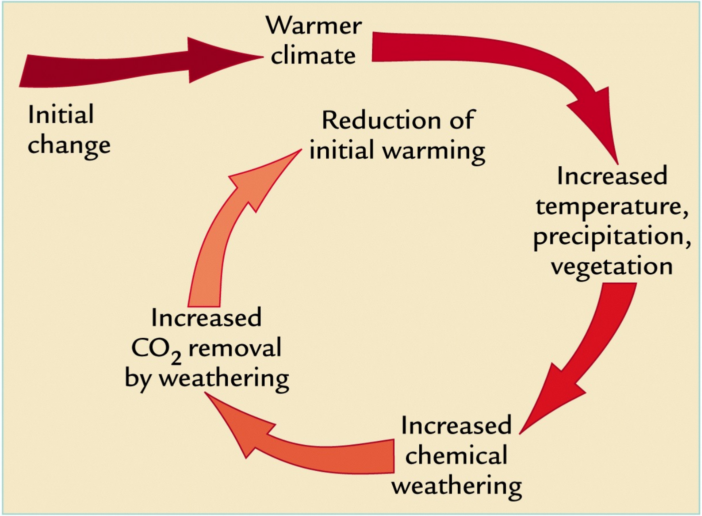
Weathering Feedback

Plant growth: increases with temperature



Weathering Feedback

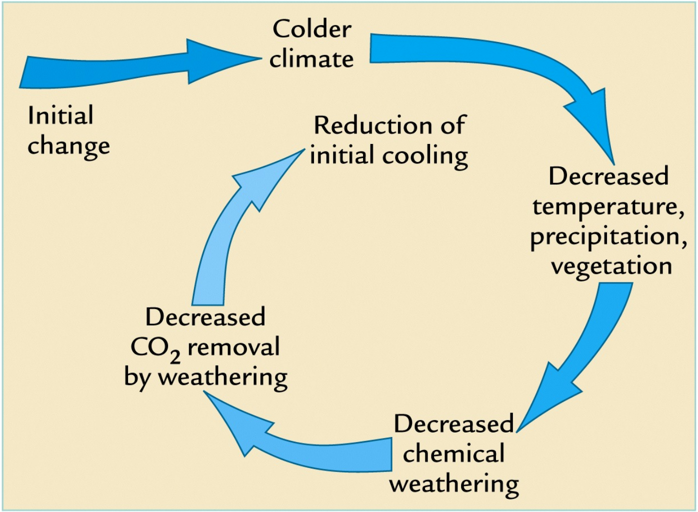
Warmer and wetter climate leads to increased weathering



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

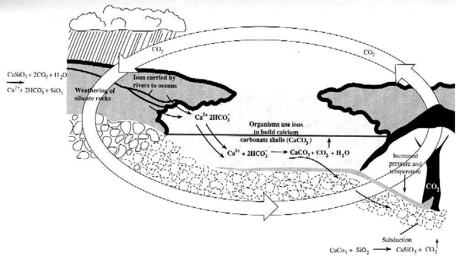


Figure 2.8 The interaction between the carbonate and silicate cycles at the surface of the Earth. Long term control of atmospheric CO_2 is achieved by dissolution of CO_2 in surface waters and its participation in the weathering of rocks. Eventually carbon is buried as part of carbonate rocks in the 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!

Stable Cenozoic Weathering???

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

nature

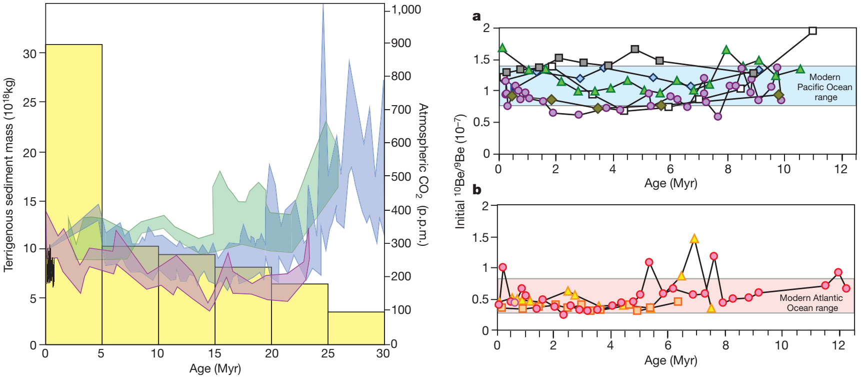
LETTERS

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 sedimenation 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**

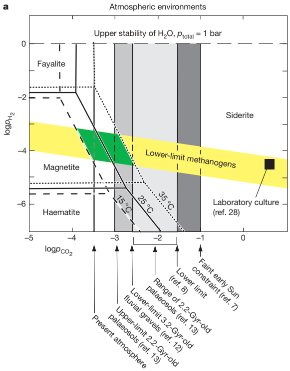
LETTERS

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

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Summary

- Pre-ice core CO_2 is estimated from different proxies (δ^{11}B, B/Ca, stomata, $\delta^{13}C_{ORG}$) 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.
- New data weakens weathering hypothesis and Faint Young Sun Paradox.

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