Climate on Geologic Time Scales & The CO$_2$-Climate Connection
Where We’ve Been & Where We Will Go

- Reviewed what processes control CO$_2$ greenhouse effect over geologic time (i.e., geochem. C cycle).
- And what negative feedbacks (e.g., T-weathering, CO$_2$-weathering) might keep climate system from reaching &/or remaining in extreme states (e.g., Venus).
- But data (geologic evidence) to support the theory (strong control of climate by CO$_2$) is lacking*.
- Now turn to geologic evidence for CO$_2$-climate link during last 500 Myr.

* Prior to ~550 Ma the lack of animals with hard skeletons and vascular plants to date has resulted in little or no fossil evidence of atmospheric CO$_2$ levels.
→ **Facts:**
  - Trace atmospheric gas that efficiently traps outgoing IR

→ **Hypotheses and theories:**
  - Solution to FYSP
  - Through influence on CO₂: weathering, tectonics and organic carbon burial/oxidation control climate on geologic timescales
  - Negative feedbacks:
    1. Temp. – Weathering
    2. CO₂ - Weathering

→ **Tests:**
  - Comparisons between "proxies" for CO₂ and T

→ **State of the science:**
  - Substantial support for close link… with notable exceptions….
Atmospheric CO$_2$ During the Phanerozoic (540-0 Ma)

Low (CO$_2$+S) = Glaciation?

Crowley (2000)
Geologic Evidence for a CO$_2$-Climate Connection: Case Studies

Permo-Carboniferous Glaciations

Adapted from Kump et al (1999)
Geologic Evidence for a CO$_2$-Climate Connection: Case Studies

Mesozoic Warmth

Adapted from Kump et al (1999)
Geologic Evidence for a CO$_2$-Climate Connection: Case Studies

Cenozoic Cooling

Adapted from Kump et al (1999)
Permo-Carboniferous Glaciations (~300-275 Ma)

Stanley (2000)
Phanerozoic CO₂ Evolution

Permo-Carboniferous Glaciations Followed a period of marked CO₂ decline

- The CO₂ decline likely resulted from the spread of rooted vascular plants in the Devonian, 400-360 Ma.
- Dissolution of bedrock (weathering) from: secreted acids, metabolic CO₂ from Cₐₑₓ decomposition, & anchoring of clay-rich soil to rock (which retains water).

Stanley (2000)
Phanerozoic CO$_2$ Evolution

Vertical bars: paleosol $\delta^{13}$C
Line: geochemical (BLAG-type) model

Berner (1997), Science, Vol. 276, pp. 544-547
$C_{\text{org}}$ burial rate estimated from $\delta^{13}C$ in $\text{CaCO}_3$

Atmospheric $O_2$ estimated from $C_{\text{org}}$ burial rate

Stanley (2000)
Low CO$_2$ during Permo-Carboniferous Glaciations Resulted from Massive Burial of C$_{org}$
High $C_{org}$ Burial Results in High $^{13}C/^{12}C$ in Seawater & CaCO$_3$

On longer time scales, higher burial rates of C, relative to weathering rates, results in elevated $^{13}C/^{12}C$ in atmos./ocean

Stanley (2000)
Mesozoic Warmth

Jurassic 220-140 Ma

- Ferns & alligators in Siberia
- Dinosaur bones in AK (N of Arctic Circle)

Cretaceous 140-65 Ma

Stanley (2000)
20°-60° Warmer at Poles!

2°-6° Warmer at Equator

Decreased Equator-to-Pole Temperature Gradient

Kump et al. (1999)
Photosynthetic fractionation of carbon isotopes depends on $[\text{CO}_2]_{\text{aq}}$

The Rubisco enzymatic photosynthesis pathway can be limited by available free CO$_2$ within a cell. It seems that many photosynthetic algae uptake carbon by the diffusion of CO$_2$ across the cell wall. When CO$_2$ is abundant, this process results in a carbon isotope difference of ~30‰; it only uses a part of the available cellular CO$_2$ and shows maximal isotopic fractionation. In the limit of extremely scarce aqueous CO$_2$, the C fixation rate is diffusion limited, and the isotopic composition of the carbon entering the cell is the same as the aqueous dissolved CO$_2$ (i.e., ~ -7‰). So as aqueous CO$_2$ becomes more limiting, the isotopic composition of organic matter is shifted to more positive values.
Carbon Isotopic Fractionation Indicates $p\text{CO}_2$

Fig. 1

$\delta_d$ (Dissolved CO$_2$)

$\delta_P$ (Photosynthate)

$\varepsilon_P = 13.9\%$

$N.\ dutilrei$

$+\varepsilon_{m/d}(T)$

$+\Delta_{m/f}$

$\delta^{13}\text{C}$ (‰ PDB)

$+3.8\%$

$C_{37}$ Alkadenone

$\omega_P (a/oo)$

Dissolved CO$_2$ (μmol/L)

$p\text{CO}_2$ (μatm)

$\frac{CO_2 (aq)}{K_H (T)}$

Jasper & Hayes (1992)
Paleo $p$CO2 Estimates from Carbon Isotopic Fractionation by Algae

Royer et al. (2001)
Carbon Isotopic Fractionation Indicates $p\text{CO}_2$

$\delta_d$ (Dissolved CO$_2$) $\delta_p$ (Photosynthetic)

$\varepsilon_p = 13.9\%$
Fossil leaf cuticles provide evidence for elevated CO$_2$ during Mesozoic.

SI(%) = SD/(SD+ED) * 100

SD = stomatal density
ED = epidermal cell density

(i.e., the proportion of epidermal cells that are stomata)

Calibrating the Leaf Stomatal "Paleo-barometer"

Extrapolation to high pCO₂ not established by calibration data...


Response of stomata to $[\text{CO}_2]$ is species-dependent

Limiting SI-derived paleo-$\text{CO}_2$ estimates to times and places when fossilized leaves from extant species exist...
Nevertheless, calibrations of the SI appear accurate for at least the last 9 kyr

Royer et al. (2001)
Geologic Evidence for a CO$_2$-Climate Connection: Case Studies

- Permo-Carboniferous Glaciations
- Mesozoic Warmth
- Cenozoic Cooling

Adapted from Kump et al (1999)
Phanerozoic CO$_2$ and Climate

![Graph showing CO$_2$ levels over time.]

Mesozoic

Berner (1992)
Cenozoic CO₂ Decrease

Popp et al. (1989)
organic $\varepsilon_p$ CO$_2$ estimates

Fig. 3. (A) $p$CO$_2$ estimates calculated from $\varepsilon_p$ = $\varepsilon_f$ - $b$/[CO$_2$$_{aq}$] (39), where $b$ = $((118.52[PO_4^{3-}]) + 84.07)/(25 - \varepsilon_{p37.2})$, calculated from the geometric mean regression of all available data (19, 20, 23, 58, 59). [CO$_2$$_{aq}$] values were calculated using mean $\varepsilon_{p37.2}$ values and a range of [PO$_4^{3-}$] values for each site.

Pagani et al. (2005) Science 309:600
Boron Isotope paleo-pH method

(a) Distribution of aqueous boron species vs. pH calculated from K values of Hershey et al., (1986).
(b) $\delta^{11}B$ of the two dominant aqueous species of boron vs. pH calculated from the fractionation factor of Kakehara et al. (1977). Also plotted is seawater (diamond) at pH=8.2.
Cenozoic $p_{\text{CO}_2}$ from B isotopes:
Boron Isotopes in Seawater Also Indicate Large Cenozoic CO₂ Decline

- B in seawater: B(OH)₃, B(OH)₄⁻
- Relative abundance controlled by pH
- B incorporated into calcite: B(OH)₄⁻
- Strong isotopic fractionation between ^10B & ^11B:
  ^10B = tetrahedral coordination, -19.8‰ relative to ^11B

δ¹¹B = \left[ \frac{(^{11}B/^{10}B)_{sampl}}{(^{11}B/^{10}B)_{std}} - 1 \right] \times 1000‰

in Zachos et al. (2001)
Cenozoic Cooling 80-0 Ma

Why?
Declining seafloor spreading rates are consistent with decreasing CO$_2$ in early Cenozoic (more continental area to weather as sea-level fall, less subducted CaCO$_3$ recycling).
But sea-level and sea-floor spreading rates in the past are uncertain...

**MEETINGS**

**Seafloor Spreading, Sea Level, and Ocean Chemistry Changes**

High Cretaceous ocean crust production rates have been causally linked to high global sea level and global CO₂ due to increased outgassing. However, recent studies have questioned the empirical basis for high Cretaceous global seafloor spreading rates, high Cretaceous sea level (230–320 m above present), and the relationship between geochemical fluxes and spreading rates.

Although this topic has been discussed at several recent international meetings, there has been little opportunity for the protagonists in the debate of constant versus variable global seafloor spreading rates to interact. However, a group of tectonophysicists, stratigraphers, and geochemists recently met at Rutgers, The State University of New Jersey (Piscataway, N.J.) to discuss global seafloor spreading changes and their possible relationships to sea level and geochemical variations.

The conference refined the boundaries of what is known and showed that, like the fixity of hot spots, hypotheses linking seafloor spreading, sea level, and ocean chemistry changes over the past 100 Myr may not be true.

Sessions were held on seafloor spreading, long-term (10⁷ years) sea level, and ocean chemistry changes. Steve Cande (Scripps Institution of Oceanography) took participants on a global tour of seafloor spreading rate changes through time and highlighted the influence of timescales. The duration of the Cretaceous long polarity quiet zone has progressively been lengthened from 84–106 Ma in earlier timescales to 84–125 Ma recent timescales, thus reducing estimates of Cretaceous global seafloor spreading rates.

Ken Miller summarized Phanerozoic sea level changes and included a new backstripped sea level synthesis of the past 100 Myr based on data from the New Jersey margin (K. Miller et al., The Phanerozoic record of global sea level change, submitted to Science, 2005). His estimate shows a Cretaceous peak of 50–70 m above present, although comparisons with other data sets suggest that the Cretaceous sea level increase was 100±50 m and not the 230–320 m previously assumed.

David Rowley (University of Chicago) not only questioned high global Cretaceous seafloor spreading rates, but also argued that the record of oceanic crustal production is compatible with a model of a constant global rate over the past 180 Myr [Rowley, 2002].

Dennis Kent (Rutgers University) moderated a lively discussion of seafloor spreading rates, emphasizing problems in reconstructing ocean crust older than 52 Myr (i.e., 50% of crust older than this has been destroyed).

There was no agreement among the participants as to whether global seafloor spreading rates have remained constant over the past 100 Myr.
Himalayan Orogeny & Uplift of Tibetan Plateau?
(Raymo et al.)
Abyssal carbonate $^{87}\text{Sr} / ^{86}\text{Sr}$ is balance between:

1. Deep-sea hydrothermal input of non-radiogenic Sr (0.7035)
2. More radiogenic input riverine flux from continental weathering (0.712)

Raymo et al. suggest that Increasing Strontium Isotopic Composition of Seawater During Cenozoic Implies Increasing Weathering Rates:

DePaolo & Ingram (1985) in Edmond (1992)
Strontium Isotope Systematics

World Average River $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.711$

Ganges-Brahmaputra $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.8$

Co-Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ & CO$_2$ through the Phanerozoic

High weathering &/or Low magmatism

- Weathering & magmatism may control CO$_2$, but does CO$_2$ control climate?

$$\varepsilon_p \sim \varepsilon_{\text{toc}} = \delta^{13}\text{C}_{\text{CaCO}_3} - \delta^{13}\text{C}_{\text{org}}$$

$$\varepsilon_p \sim p\text{CO}_2$$


Fig. 1. Data for $\varepsilon_{\text{toc}}$ (red filled circles) (3) and $^{87}\text{Sr}/^{86}\text{Sr}$ (blue open squares) (4). The time scale for $\varepsilon_{\text{toc}}$ has been revised from the original to match the scheme (32) used for the strontium data. The capital letters correspond to the following geologic periods: Ordovician, Silurian, Devonian, Carboniferous, Permian, Triassic, Jurassic, Cretaceous, and Tertiary.
CO$_2$ During the last 450 kyr from the Vostok, Antarctica Ice Core

Covariation Between CO$_2$ and T in Pleistocene

Vostok Ice Core, Central East Antarctica

What caused glacial-interglacial CO$_2$ variations?
(a still-unanswered question!)

One Possible Scenario for Lower Glacial CO$_2$: The Martin Hypothesis

• Increased:
  Equator-Pole T gradient, Wind strength, Dust flux to ocean, Iron flux to ocean
• 50% of global 1° production occurs in ocean
• Ocean 1° production is limited by iron (in major regions)
• Higher 1° production draws CO$_2$ out of atmosphere & sequesters it in the deep ocean & sediments
• Colder seawater dissolves more CO$_2$
While a large and growing body of evidence indicates that CO$_2$ and climate co-vary, there is some indication that the two may not be closely linked at all times....

(& we all know that correlation does not require causation)
Cool Tropics - High CO₂ (?)

Intervals of high CO₂

Model-Data SST Comparison

Tropical SST anomaly (Data)
- Assumes 2‰ of 3-5‰ δ¹⁸O range due to ice volume (2x present ice volume in “icehouse”; No ice in “greenhouse”).
- Leaves ~2‰, or ~9°C of SST change

Simple E Balance Model
- CO₂ (Berner, 1992)
- Solar constant increasing by 5% over Phanerozoic

\[ T_s - \Delta T_g = T_{eff} \]

\[ \sigma T_{eff}^4 = S/4*(1-A) \]


Records of change. (A) Comparison of CO$_2$ concentrations from the GEOCARB III model (6) with a compilation (9) of proxy-CO$_2$ evidence (vertical bars). Dashed lines: estimates of uncertainty in the geochemical model values (6). Solid line: conjectured extension to the late Neoproterozoic (about 590 to 600 Ma). RCO$_2$, ratio of CO$_2$ levels with respect to the present (300 parts per million). Other carbon cycle models (21, 22) for the past 150 million years are in general agreement with the results from this model. (B) Radiative forcing for CO$_2$ calculated from (23) and corrected for changing luminosity (24) after adjusting for an assumed 30% planetary albedo. Deep-sea oxygen isotope data over the past 100 Ma (13, 14) have been scaled to global temperature variations according to (7). (C) Oxygen isotope-based low-latitude paleotemperatures from (5). (D) Glaciological data for continental-scale ice sheets modified from (7, 8) and based on many sources. The duration of the late Neoproterozoic glaciation is a subject of considerable debate.

Other Evidence for Weak CO₂-Climate Connection during Phanerozoic

\[ \varepsilon_p \sim p_{CO_2} \]

\[ \varepsilon_p \sim \varepsilon_{toc} = \delta^{13}C_{CaCO3} - \delta^{13}C_{org} \]

Fig. 4. Fluctuations of \( p_{CO_2} \) for the last 500 My, normalized by the estimated \( p_{CO_2} \) obtained from the most recent value of \( \varepsilon_p \). The solid line is obtained from Eq. 12 by using \( \delta_0 = 36\% \). The lower and upper limits of the gray area surrounding the \( p_{CO_2} \) curve result from \( \delta_0 = 38 \) and 35\%, respectively. The gray bars at the top correspond to periods when Earth’s climate was relatively cool; the white spaces between them correspond to warm modes (18).
But different CO$_2$ proxies lead to different results….

\[ \varepsilon_{\text{toc}} = \delta^{13}C_{\text{CaCO}_3} - \delta^{13}C_{\text{org}} \]

Soil carbonate $\delta^{13}C$ & geochemical model

Fig. 4. Fluctuations of $p$CO$_2$ for the last 500 My, normalized by the estimate of $p$CO$_2$ obtained from the most recent value of $\zeta$. The solid line is obtained from Eq. 12 by using $\varepsilon_0 = 36\%$. The lower and upper limits of the gray area surrounding the $p$CO$_2$ curve result from $\varepsilon_0 = 38$ and 35\%, respectively. The gray bars at the top correspond to periods when Earth’s climate was relatively cool; the white spaces between them correspond to warm modes (18).

Rothman (2002)
Further Evidence for Low CO$_2$ During Miocene Warm Period

Pre-Industrial CO$_2$ levels!

Did a Gas Hydrate Release of Methane (2600 Gt) caused Late Paleocene Thermal Maximum?

Benthic foraminifera from Atlantic & Pacific

\[ \text{CO}_2 \] not the only greenhouse gas we need to consider when evaluating warm episodes.

Zachos et al. (2001)
Substantial evidence exists for a link between CO$_2$ & climate on a variety of timescales….

With some notable exceptions!

Additional paleoclimate reconstructions & numerical model simulations are necessary. But the biggest (non-controlled) experiment ever attempted is now underway…
Chicxulub Crater
Gulf of Mexico

- 200 km crater
- 10-km impactor
- 65 Myr BP
- Extinction of 75% of all species!
Chicxulub Crater
Gulf of Mexico

- 200 km crater
- 10-km impactor
- 65 Myr BP
- Extinction of 75% of all species!
Evidence for Meteorite Impact at K-T Boundary

Iridium spike

Tertiary
Cretaceous

65.0 Ma

Temperature
microspherules

Pressure
shocked quartz
Phanerozoic History of Extinctions

**FIGURE 10-11**

The fossil record of extinction rate, shown as the percentage of existing genera that went extinct in a particular interval (*stage*) of geologic time. (After Sepkoski, J.J. Jr., *Geotimes*, March, 1994, 15–17.)
But:

Stigler and Wagner (1987) Science 238:940 say that the 26 million year period is an artifact of how the time scale is organized.
26 Myr Period of Extinctions? 

Astronomical Hypotheses

FIGURE 10-11
The fossil record of extinction rate, shown as the percentage of existing genera that went extinct in a particular interval (stage) of geologic time. (After Sepkoski, J.J. Jr., Geotimes, March 1994, 15–17.)

FIGURE 10-12
Three astronomical hypotheses explaining the 26-million-year periodicity in the fossil record of extinction. Figures not drawn to scale. (After Raup, D.M., 1986. See Further Reading.)

Kump et al. (1999)
Cosmic Ray Forcing of Climate?


\[ \frac{F_{CR}}{F_{CR,\text{today}}} : 25\% - 135\% \]

\[ F_{CR,\text{today}}: +10 \text{ to } -5 \text{ k} \]
Cosmic Ray Influence on Climate?


**Fig. 1.** Variation of low-altitude cloud cover, cosmic rays, and total solar irradiance between 1984 and 1994. The cosmic ray intensity is from Huancayo observatory, Hawaii. [Adapted from (4)]

**Fig. 3.** 11 year average of northern hemispheric marine and land temperatures (dash-dotted line) compared with (a) unfiltered solar cycle length; (b) 11 year average of cosmic ray flux (from ion chambers 1937–1994, normalized to 1965), thick solid line; the thin solid line is cosmic ray flux from Climax, Colorado neutron monitor (arbitrarily scale); (c) 11 year average of relative sunspot number; (d) decade variation in reconstructed solar irradiance (zero level corresponds to 1367 W/m², adapted from Lean et al. [6]). Note the 11 year average has removed the solar cycle in (b) and (c).
Correlation does not require Causation