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.
CO₂-Climate Connection

→ 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….

Sarmiento and Gruber, 2005; Houghton et al., 1990.

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Atmospheric CO$_2$
During the Phanerozoic (540-0 Ma)

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

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Permo-Carboniferrous Glaciations (~300-275 Ma)

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Stanley (2000) Figure 11.11.
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 $C_{org}$ decomposition, & anchoring of clay-rich soil to rock (which retains water).

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$_3$

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20°-60° Warmer at Poles!

2°-6° Warmer at Equator

Decreased Equator-to-Pole Temperature Gradient

Kump et al. (1999) Figure 8-15.

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Photosynthetic fractionation of carbon isotopes depends on \([\text{CO}_2]_{\text{aq}}\)

The Rubisco enzymatic photosynthesis pathway can be limited by available free \(\text{CO}_2\) within a cell. It seems that many photosynthetic algae take up carbon by the diffusion of \(\text{CO}_2\) across the cell wall. When \(\text{CO}_2\) is abundant, this process results in a carbon isotope difference of \(\sim 30\%\); it only uses a part of the available cellular \(\text{CO}_2\) and shows maximal isotopic fractionation. In the limit of extremely scarce aqueous \(\text{CO}_2\), the C fixation rate is diffusion limited, and the isotopic composition of the carbon entering the cell is the same as the aqueous dissolved \(\text{CO}_2\) (i.e., \(\sim -7\%\)). So as aqueous \(\text{CO}_2\) becomes more limiting, the isotopic composition of organic matter is shifted to heavier values.
Carbon Isotopic Fractionation Indicates $pCO_2$

Fig. 1

$\delta_d$ (Dissolved CO$_2$)

$\delta_P$ (Photosynthate)

$\varepsilon_p = 13.9\%$

Jasper & Hayes (1992)
Paleo $p$CO$_2$ Estimates from Carbon Isotopic Fractionation by Algae

Royer et al. (2001) Figure 1.

Image removed due to copyright restrictions.
Carbon Isotopic Fractionation Indicates $p\text{CO}_2$
Fossil leaf cuticles provide evidence for elevated CO$_2$ during Mesozoic.

Image removed due to copyright restrictions.

\[
\text{SI(\%)} = \frac{\text{SD}}{\text{SD} + \text{ED}} \times 100 \%
\]

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 pCO$_2$ not established by calibration data...


Citation: Retallack (2001), Nature 411: 287-290.
Response of stomata to [CO$_2$] is species-dependent

Limiting SI-derived paleo-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)
organic $\varepsilon_p \text{CO}_2$ estimates

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Citation: Figure 3. Paganiet al. (2005) Science 309:600.
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:
  - δ¹¹B = [(¹¹B/¹⁰B)_{sample} / (¹¹B/¹⁰B)_{std}] - 1 x 1000‰

in Zachos et al. (2001)

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• Urey (1947) calculated that the oxygen isotope fractionation between calcium carbonate and water should be temperature-dependent.

\[ \delta^{18}O = 1000 \left[ \frac{R_{\text{sample}}}{R_{\text{s tan dard}}} - 1 \right] \]

• Epstein (1953) grew molluscs in the laboratory and empirically determined the O18-T relationship:

![Isotopic temperature scale and original data points of Epstein et al. (1953). Temperature is in degrees Celsius. The \( \delta \) values are the \( \delta \)-corrected values, which are equal to \( \delta_c - \delta_w \). After Epstein et al. (1953).](image)
Declining seafloor spreading rates are consistent with decreasing CO₂ in early Cenozoic (more continental area to weather as sea-level fall, less subducted CaCO₃ recycling)
But sea-level and sea-floor spreading rates in the past are uncertain...

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 sea-floor 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 sea-floor 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 sea-floor 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 sea-floor spreading, sea level, and ocean chemistry changes over the past 100 Myr may not be true.

Sessions were held on sea-floor spreading, long-term (10⁷ years) sea level, and ocean chemistry changes. Steve Cande (Scripps Institution of Oceanography) took participants on a global tour of sea-floor 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 84–108 Ma in earlier timescales to 84–125 Ma recent timescales, thus reducing estimates of Cretaceous global sea-floor spreading rates.

David Rowley (University of Chicago) not only questioned high global Cretaceous sea-floor 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 sea-floor 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 sea-floor spreading rates have remained constant over the past 100 Myr.

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

SW \(^{87}\text{Sr}/^{86}\text{Sr}\) 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)

DePaolo & Ingram (1985) in Edmond (1992)

Abyssal carbonate \(^{87}\text{Sr}/^{86}\text{Sr}\) 
\(^{87}\text{Rb}--^{87}\text{Sr}, t_{1/2} \sim 48 \text{ Gyr}\)
Strontium Isotope Systematics

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

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

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

High weathering &/or Low magmatism

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

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

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

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Citation: Figure 1. Rothman (2002) *PNAS*, Vol 99(7):4167.
Did a Gas Hydrate Release of Methane (2600 Gt) caused Late Paleocene Thermal Maximum?

Zachos et al. (2001)

- CO₂ not the only greenhouse gas we need to consider when evaluating warm episodes.

Benthic foraminifera from Atlantic & Pacific
Substantial evidence exists for a link between \( \text{CO}_2 \) & 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!

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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.
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Image courtesy of NASA.

Cosmic Ray Influence on Climate?


Correlation does not require Causation