

Paleo-perspective on Ocean pH, Carbonate Ion and the Carbon Cycle

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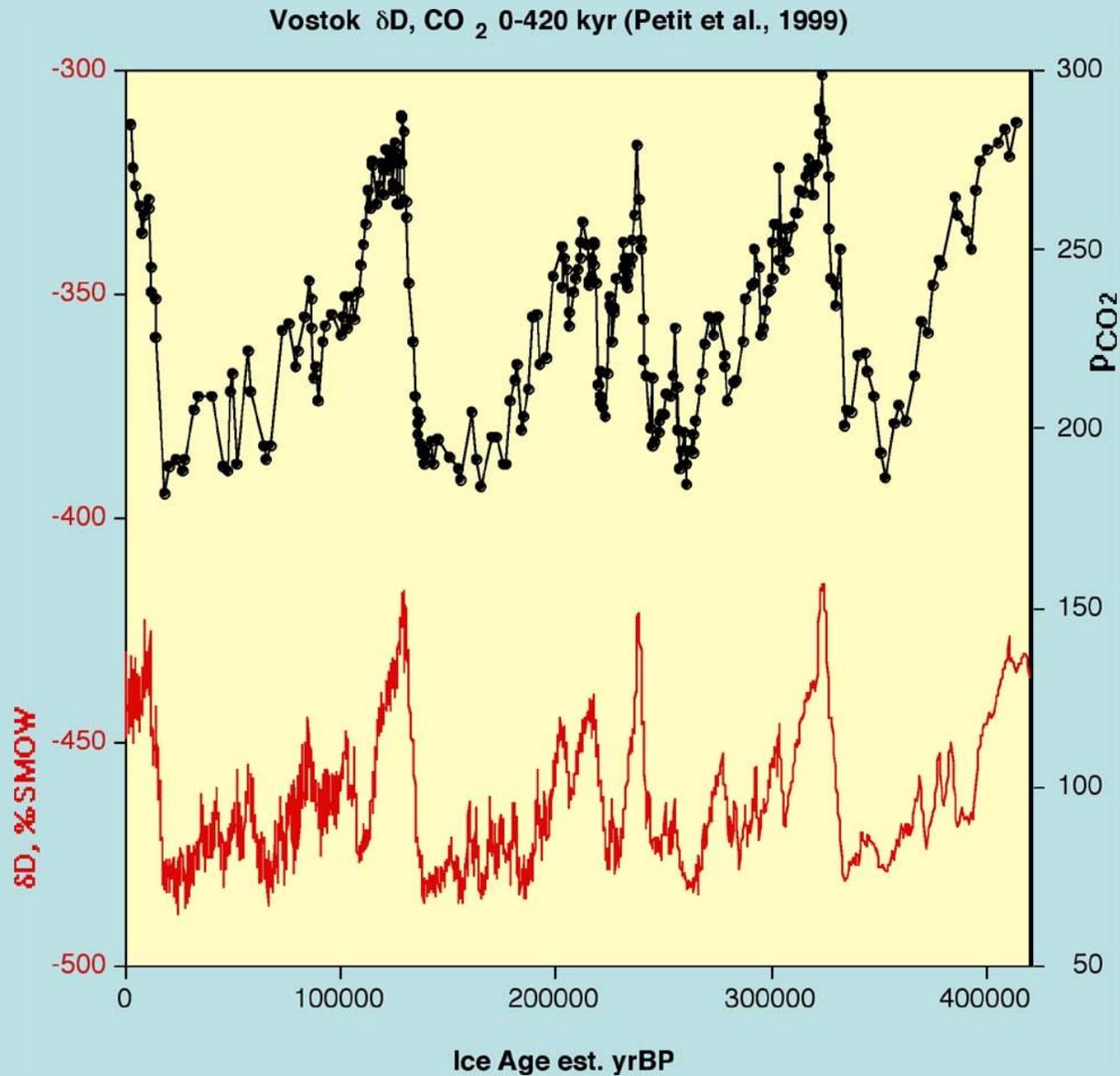
Outline

- Measurements and models of CO₂ during glacial/interglacial cycles and the Phanerozoic: comments
- 90 ppmV Glacial/Interglacial CO₂ cycles: basic considerations
- Oceanic pH and carbonate ion monitors as constraints on ocean carbon cycle mechanisms for atmospheric CO₂ changes
- Back into the distant past: mechanisms, models, and estimates of Cenozoic and Phanerozoic CO₂

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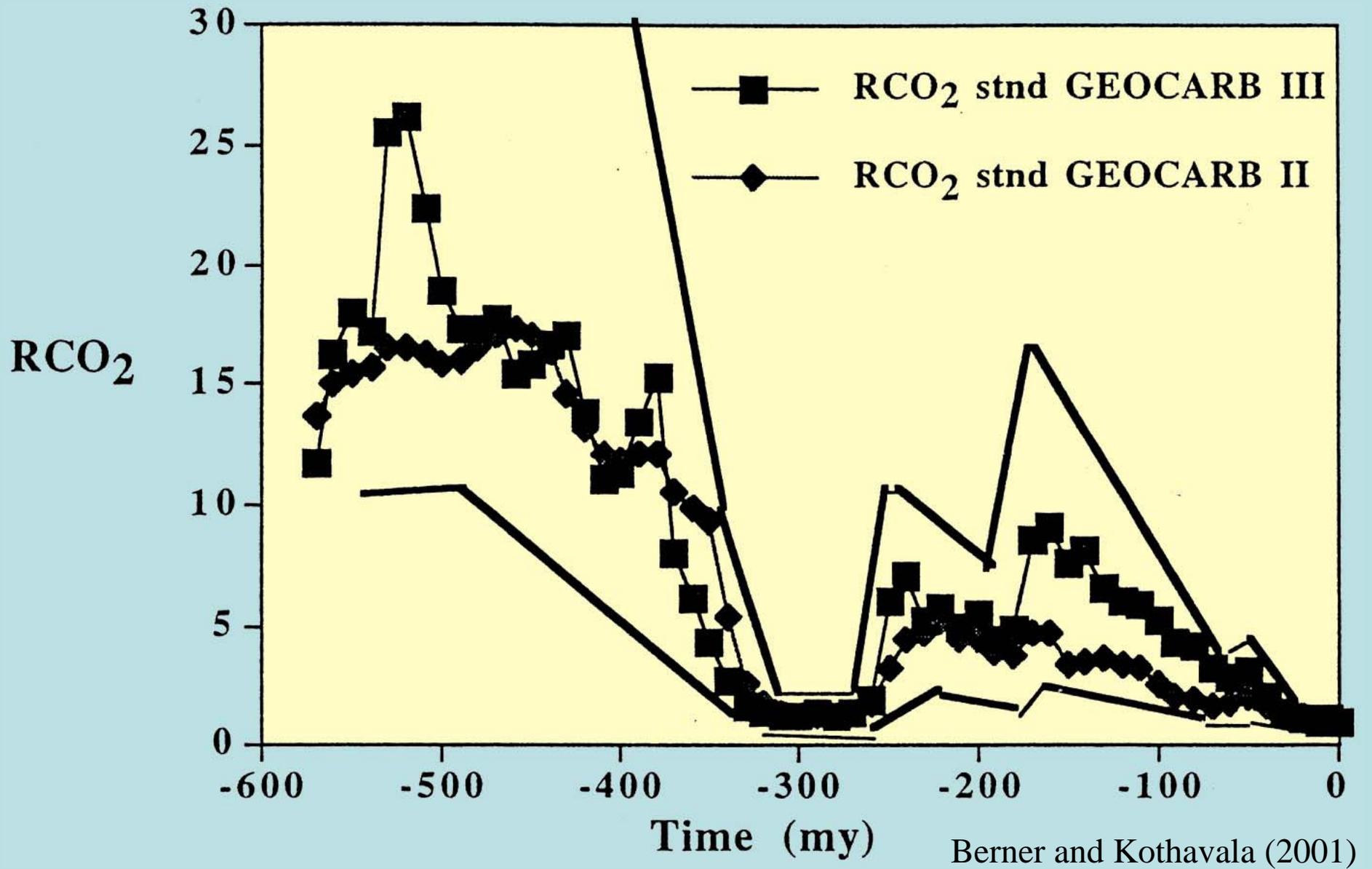
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We know exactly how CO₂ has varied in the atmosphere for the past 400,000 years...



...but we can't explain it.

We don't know how CO₂ has varied in the atmosphere over the past 700 million years...



...but we can explain it.

Outline

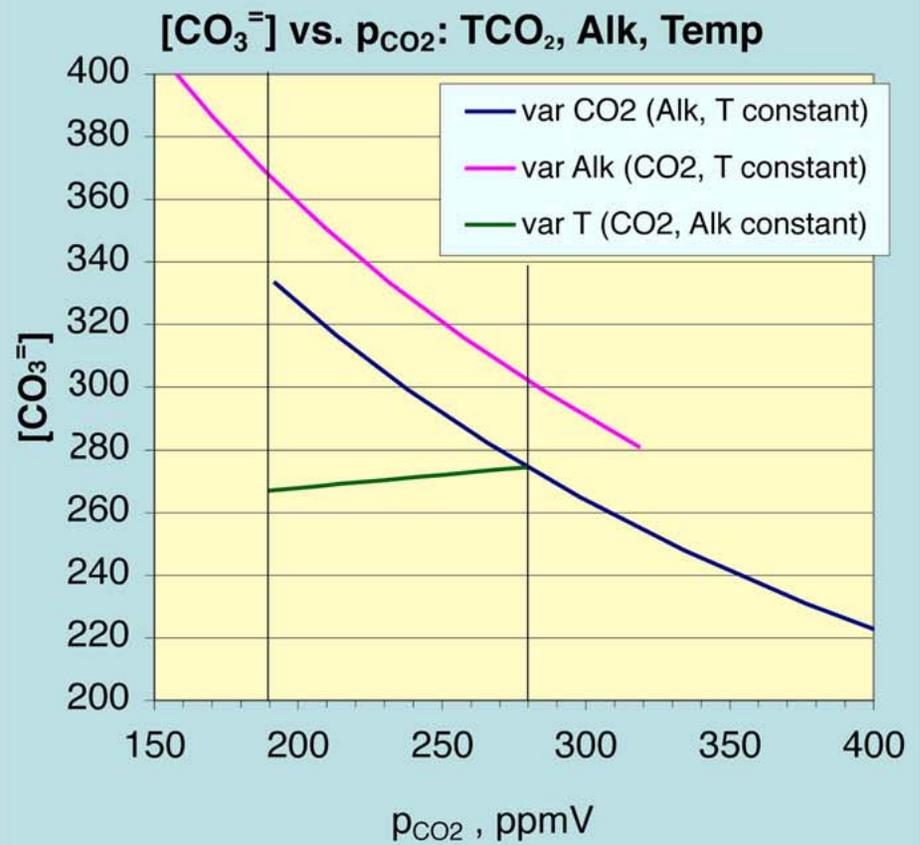
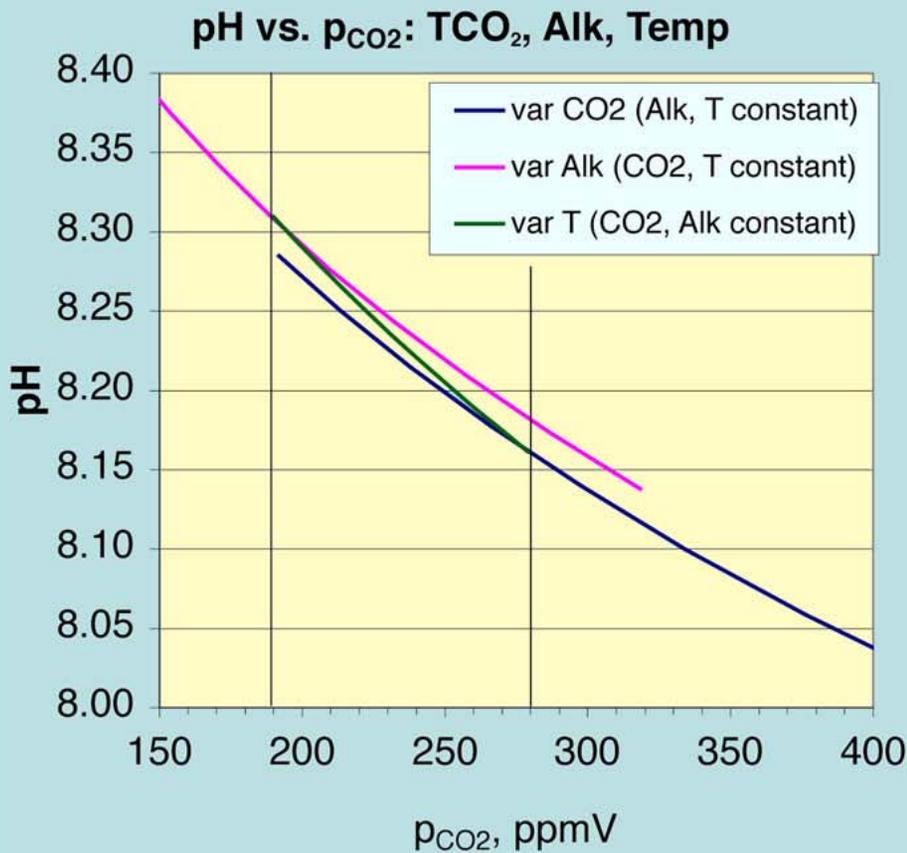
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- 90 ppmV Glacial/Interglacial CO₂ cycles:
basic considerations
 - Total dissolved CO₂, alkalinity, temperature, gas exchange: effect on pH and carbonate ion concentration.
 - Well quantified effects
 - Not-so-well quantified effects
 - “Radioactive” glacial CO₂ theories: the youngest and strongest

There are only four ways to change atmospheric CO₂:

- Change the total dissolved carbon dioxide content of ocean surface water
- Change the alkalinity of ocean surface water
- Change the temperature of ocean surface water (salinity also, to a lesser magnitude).
- Alter gas exchange between the surface ocean and the atmosphere.

- Total dissolved CO_2 , alkalinity, temperature, gas exchange: effect on pH and carbonate ion concentration.



Outline

- 90 ppmV Glacial/Interglacial CO₂ cycles:
basic considerations

- **Well quantified effects**

1. Effect of lower sea surface temperature: -5°C low latitude, -2.5°C high latitude cooling LGM --> **-30 ppmV**

note: “abiotic Ocean GCM/box model crisis” averted by Ito and Follows (2003, J. Mar. Res. 61:465) who point out that this problem was due to lack of ventilated thermocline in box models.

2. Effect of higher glacial sea surface salinity:
 $+3\%$ salinity--> **+7 ppmV**

3. Effect of CO₂ from continental biospheric shrinkage during glaciation: LGM --> **+45 ppmV** (+15 ppmV 10,000 years after CaCO₃ compensation)

4. Sum of well-known effects: **-8 ppmV** (compensated) to **+19 ppmV** (uncompensated).

Outline

- 90 ppmV Glacial/Interglacial CO₂ cycles:
basic considerations

- **Not-so-well quantified effects**

Bottom line: few of these mechanisms could account for as much as half of G/IG CO₂ change without violating something we know, most considerably less. Is there a single major factor or two (that we haven't thought of yet), or a "swarm" of minor effects (and if the latter, how could we ever know which ones)?

1. Phosphorus mass balance and its effect on strength of biological pump.
2. High latitude pre-formed phosphate (and its iron companion).
3. Coral reef growth
4. Ocean-wide nutrient deepening
5. Organic/inorganic "rain ratio" and its effect on sedimentary CaCO₃ dissolution.
6. Nitrogen cycle: higher LGM NO₃⁻ reservoir (due to higher N fixation and/or lower denitrification): the Redfield Ratio be damned
7. LGM Southern Ocean Gas Exchange limitations.

Outline

- 90 ppmV Glacial/Interglacial CO₂ cycles:
basic considerations

- **“Radioactive” glacial CO₂ theories: the youngest and strongest**

It seems as if theories for glacial/interglacial CO₂ change are radioactive with a half life of about 2 years.

1. Southern Ocean Gas Exchange limitation due to change in mode of deep water formation from (relatively) equilibrated shelf water mode to unequilibrated deep water convection (Toggweiler, in preparation).
2. The Si-N hypothesis (Matsumoto et al., 2002, GBC 16:10.1029/2001GB001442, Brzezinski et al., 2003, GRL 29, 1564). A constrained and chained potpourri of causative mechanisms:
 - a. Southern Ocean Fe fertilization (hence some pre-formed P effect)
 - b. Higher Fe causes lower Si:N in Southern Ocean phytoplankton – hence more Si escapes into the thermocline of the low-latitude ocean.
 - c. Higher thermocline Si leads to higher low-latitude diatom productivity relative to coccolithophorids: hence a rain-ratio effect.
 - d. Higher diatom productivity leads to deeper nutrient regeneration (because diatoms sink faster than other phytoplankton), hence nutrient deepening effect.
 - e. Total: about –60 ppmV.

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Outline

- Oceanic pH and carbonate ion monitors as constraints on ocean carbon cycle mechanisms for atmospheric CO₂ changes
 - A. Coral reef calcification: is it controlled by carbonate ion saturation and is survival of corals in Bermuda (LGM T ~ 13°C) a proof of the role of [CO₃[−]] on coral calcification?
 - B. Effect of carbonate ion on foraminiferal calcification as a measure of surface water [CO₃[−]]
 - C. Is benthic foraminiferal Mg/Ca a tracer of T or [CO₃[−]]?
 - D. Boron Isotope paleo-pH indicator: status
 - E. Oops! : the kinetics of calcium carbonate dissolution, a need for a re-evaluation.

- Oceanic pH and carbonate ion monitors as constraints on ocean carbon cycle mechanisms for atmospheric CO₂ changes
- **Coral reef calcification: is it controlled by carbonate ion saturation and is survival of corals in Bermuda (LGM T ~ 13°C) a proof of the role of [CO₃⁼] on coral calcification?**

Saturation state and the evolution and biogeography of symbiotic calcification

by

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Bulletin de l'Institut océanographique, Monaco, n° spécial 14, 4 (1996)

Key words: Actinaria, saturation state, calcification, symbiosis.

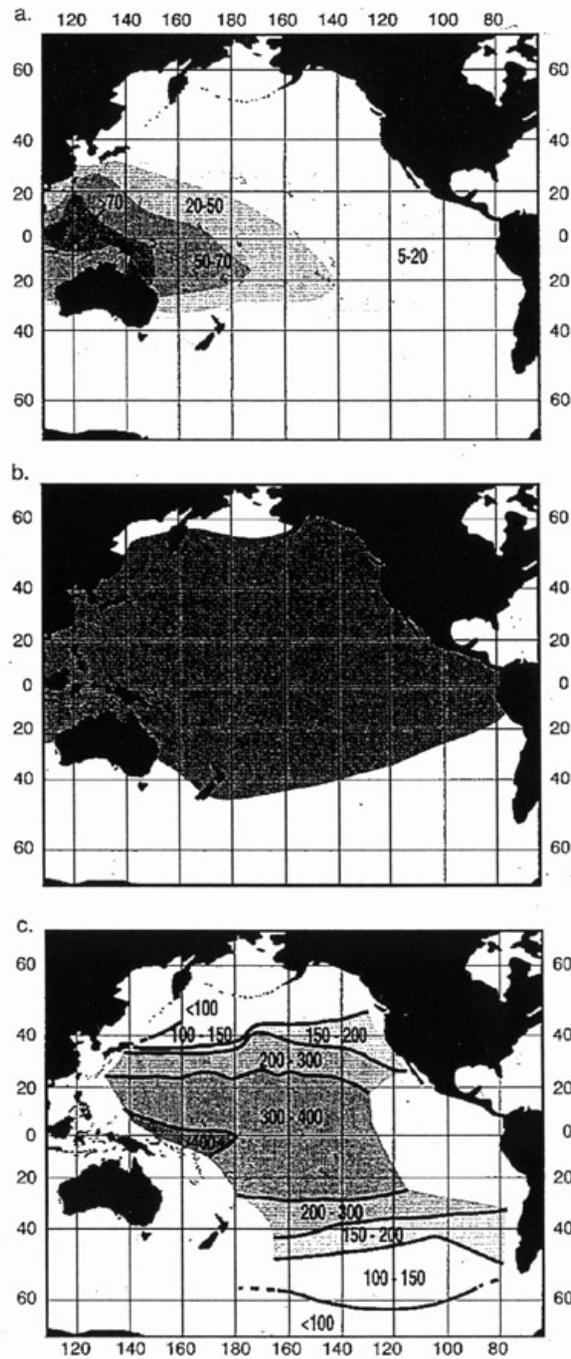
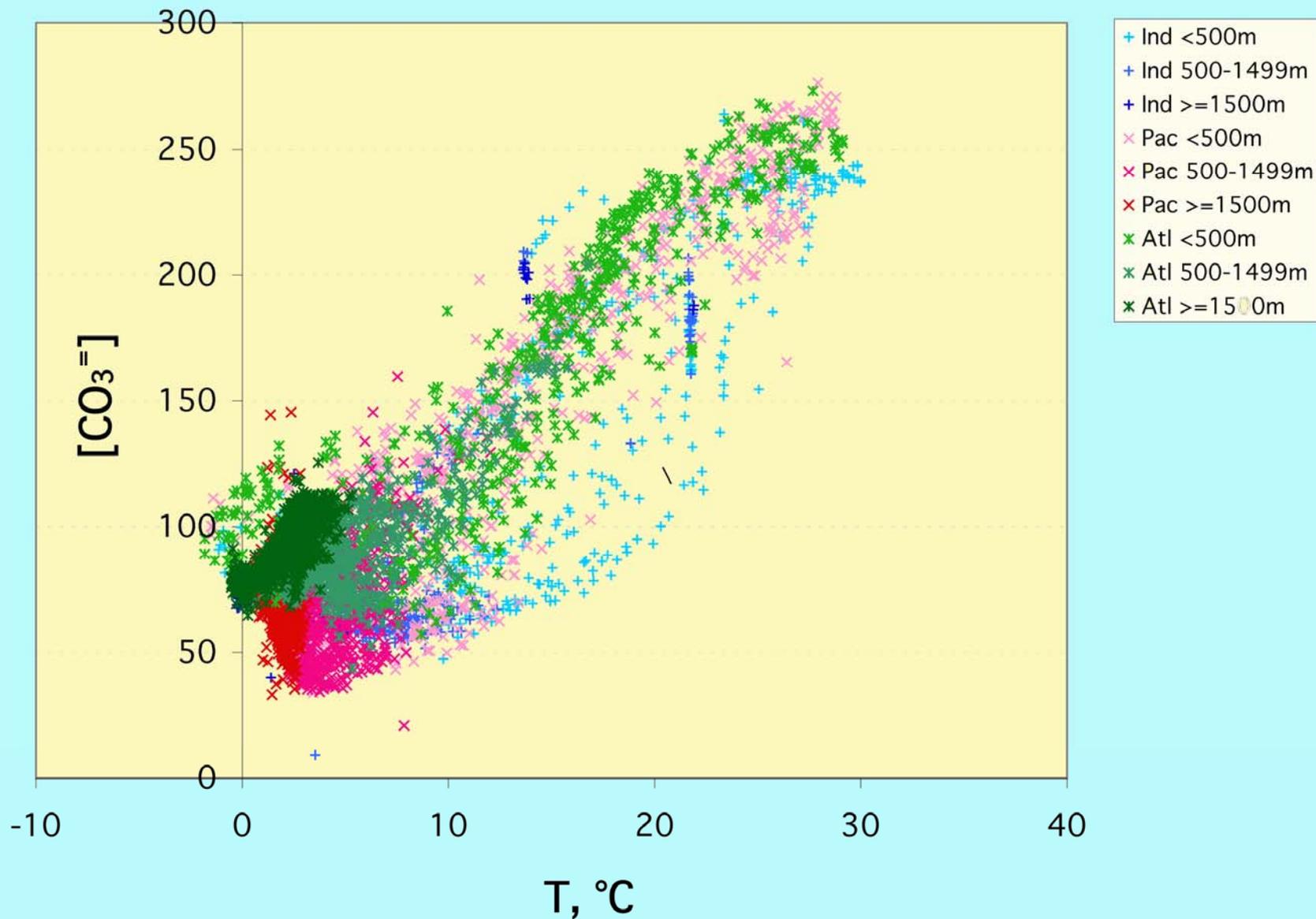


Figure 1 – Pacific Basin distributions of biological and chemical features.
 (a) Biogeographic distribution of the number of genera of reef-forming (zooxanthellate) corals (VERON, 1986); (b) Biogeographic distribution of symbiotic (zooxanthellate) sea anemones; (c) Average percent aragonite saturation in surface water (LYAKHIN, 1968).

GEOSECS Global $[\text{CO}_3^{=}]$ - T data



$[\text{CO}_3^{=}]$ and T are correlated on a global scale...

For some time, the survival of reef-building corals on Bermuda at the last glacial maximum was a bit of a puzzle:

- modern minimum winter temperatures are $\sim 18^{\circ}\text{C}$, which is thought to be near the minimum survivable temperature for reef corals
- LGM temperature estimates are about 13°C (both CLIMAP and alkenones agree)

On the other hand, if the carbonate ion concentration is more important than temperature, then the 40-60 $\mu\text{mol/kg}$ rise in $[\text{CO}_3^{2-}]$ during the LGM (associated with lower p_{CO_2}) may explain the survival of reef corals on Bermuda.

- Oceanic pH and carbonate ion monitors as constraints on ocean carbon cycle mechanisms for atmospheric CO₂ changes
- **Effect of carbonate ion on foraminiferal calcification as a measure of surface water CO₃⁼**

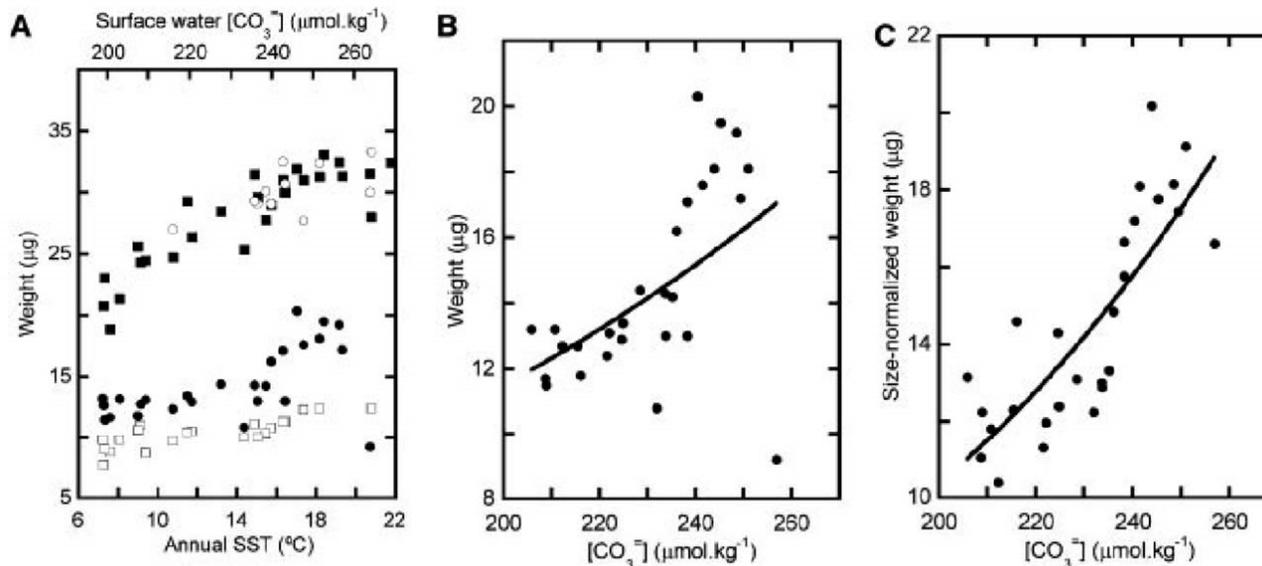


Fig. 1. (A) Shell weights of four species of planktonic foraminifera from the North Atlantic between 60° and 30°N latitude plotted against modern sea surface temperature (SST) at the core sites (28). Also shown are corresponding values of surface water [CO₃²⁻] (based on the linear relation between temperature and [CO₃²⁻]) corrected to preindustrial values (20). Solid circles, *Globorotalia bulloides* (300 to 355 µm); open circles, *Globorotalia truncatulinoides* (300 to 355 µm); solid squares, *Globorotalia inflata* (300 to 355 µm); open squares, *Neogloboquadrina pachyderma* (dextral) (250 to 300 µm). (B) Shell weight and (C) size-normalized shell weight for *G. bulloides* plotted against preindustrial [CO₃²⁻] (20). Heavy lines in (B) and (C) represent best-fit exponential curves to the data.

Barker and Elderfield (2002) Science 297:833

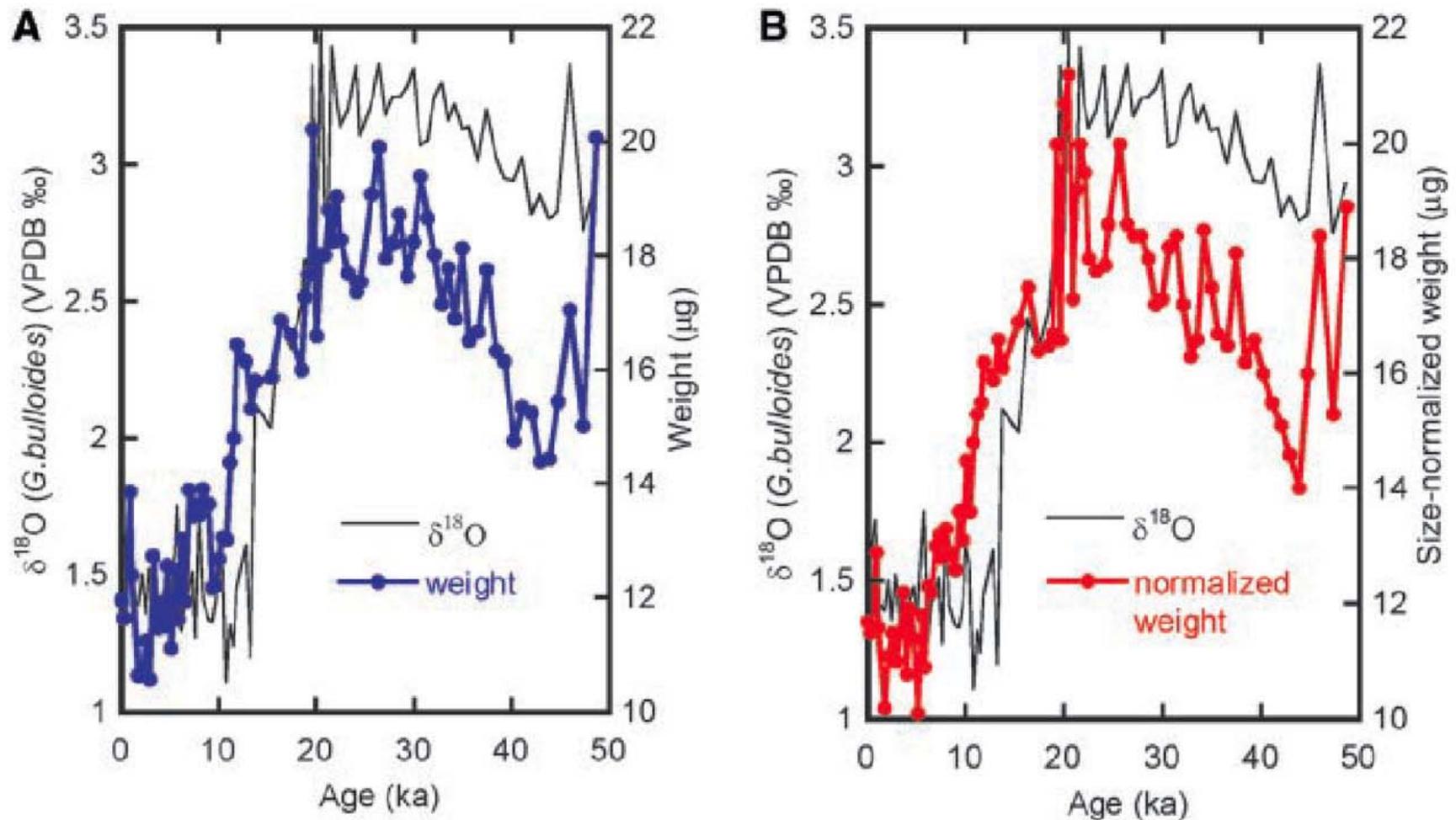
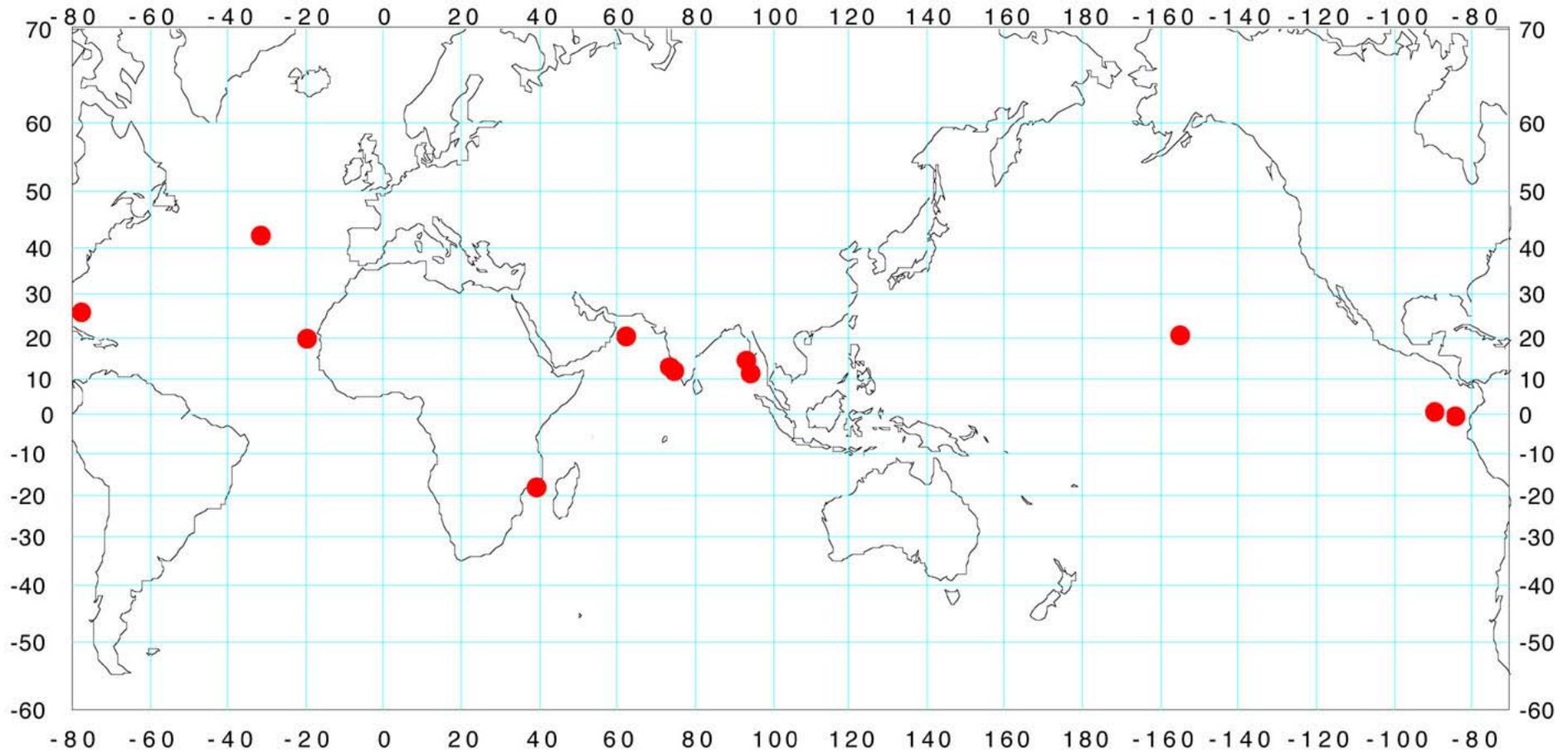


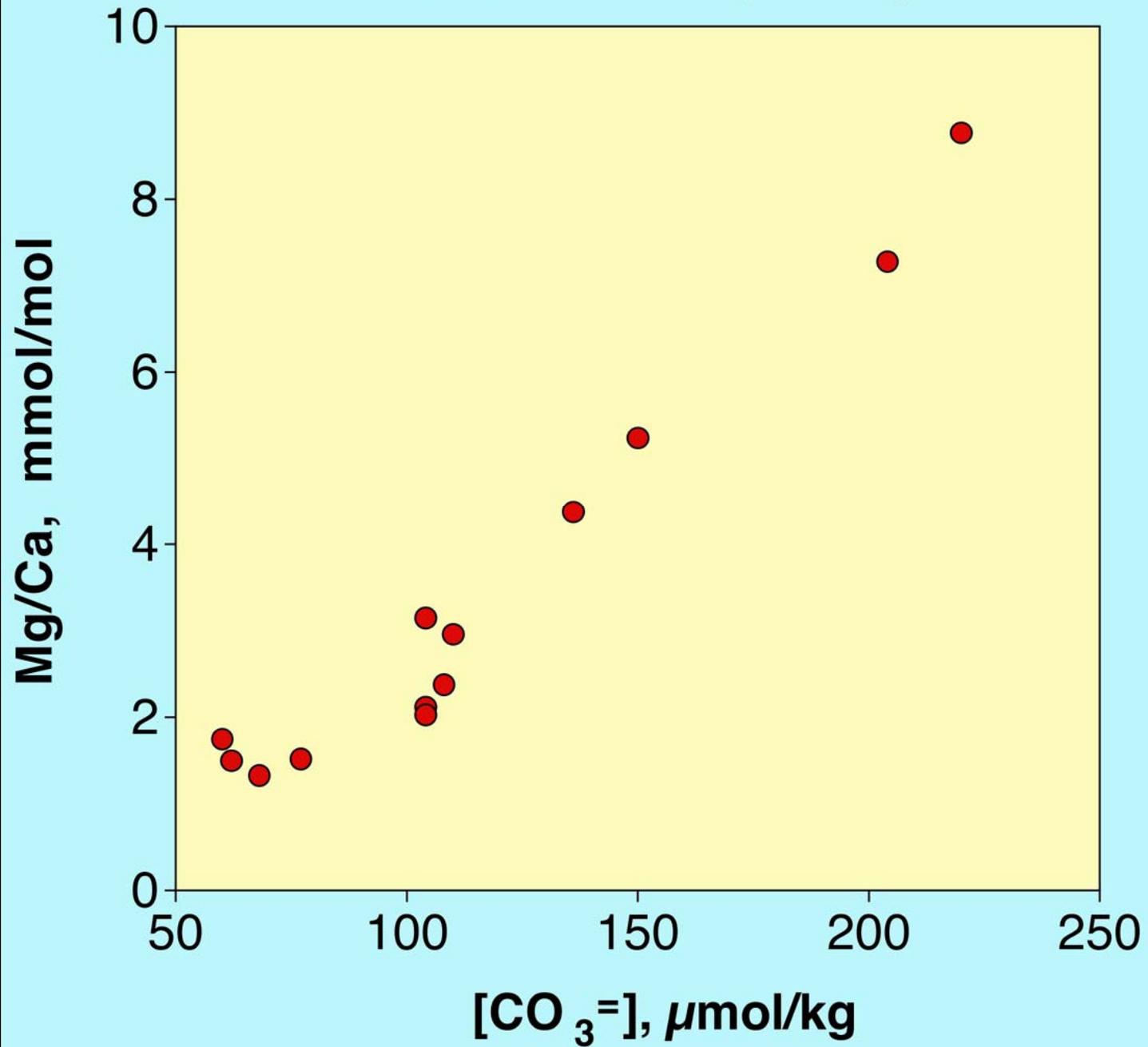
Fig. 2. (A) Measured shell weight and (B) size-normalized shell for *G. bulloides* plotted with $\delta^{18}\text{O}$ [data from (32)] for the same species in NEAP 8K [age model from (33)].

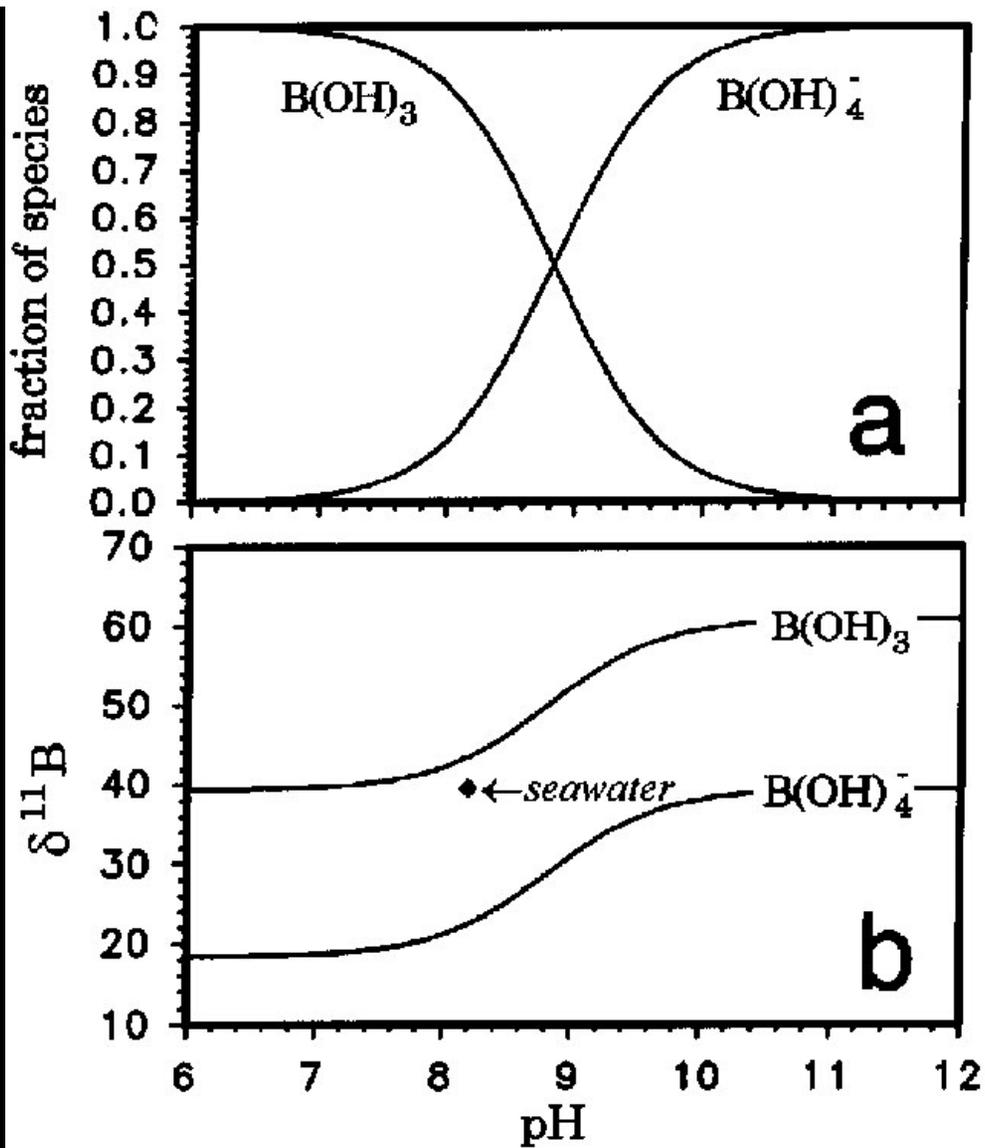
Barker and Elderfield (2002) Science 297:833

Mg/Ca in Benthic Foraminifera (Cibicoides): Core Sites



Cibicidoides Core Top Samples





(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 Kakhana *et al.* (1977). Also plotted is sea water (diamond) at pH=8.2.

SANYAL ET AL.: CHANGES IN pH IN THE EASTERN EQUATORIAL PACIFIC

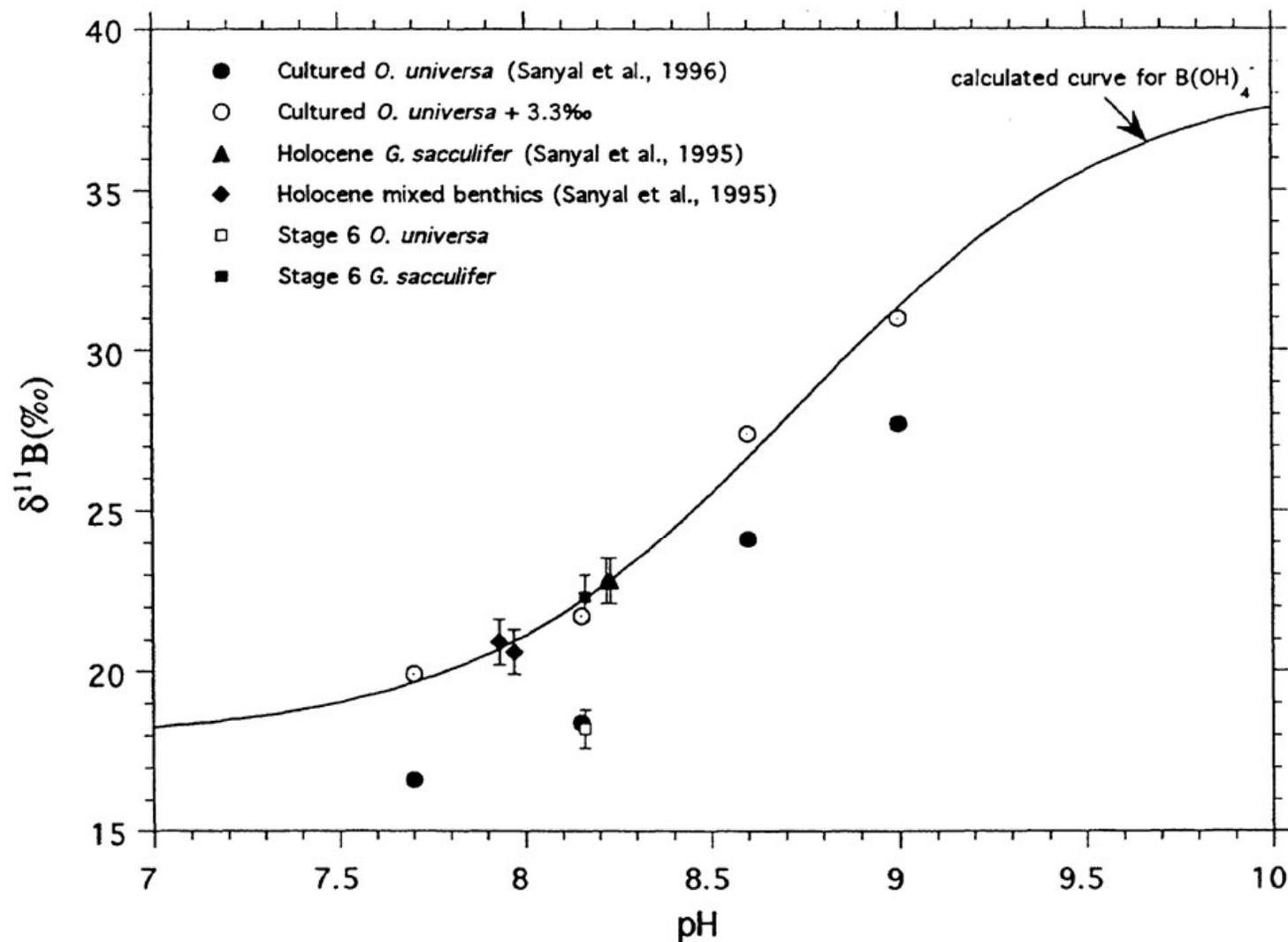


Figure 2. Plot showing the offset of boron isotopic composition of cultured *O. universa* from the theoretical curve for $B(OH)_4^-$ species (Sanyal et al., 1996). Also shown for comparison are the previously estimated boron isotopic composition of Holocene mixed benthics and *G. sacculifer* [Sanyal et al., 1995]. Stage 6 *O. universa* and *G. sacculifer* from core V19-28 in eastern equatorial Pacific have been plotted to show the constancy of the species dependent offset through time.

Oops! : the kinetics of calcium carbonate dissolution, a need for a re-evaluation of models

- Since Keir (1980, *Geochim. Cosmochim. Acta* 44:241), we have believed that the dissolution kinetics of calcite follow a 4.5-power law: $R = k (1-\Omega)^{4.5}$
- Recently, Hales (2003, *Paleoceanogr.* 18, 1099) has shown that the Keir law probably resulted from an incorrect estimation for equilibrium in the Keir experiments, and that most field data is consistent with a simple linear dissolution law.
- The Keir law leads to unreasonably abrupt behavior for carbonate dissolution.
- Almost all models for CaCO_3 behavior in the past ocean have been assuming the Keir law, and need to be re-examined.

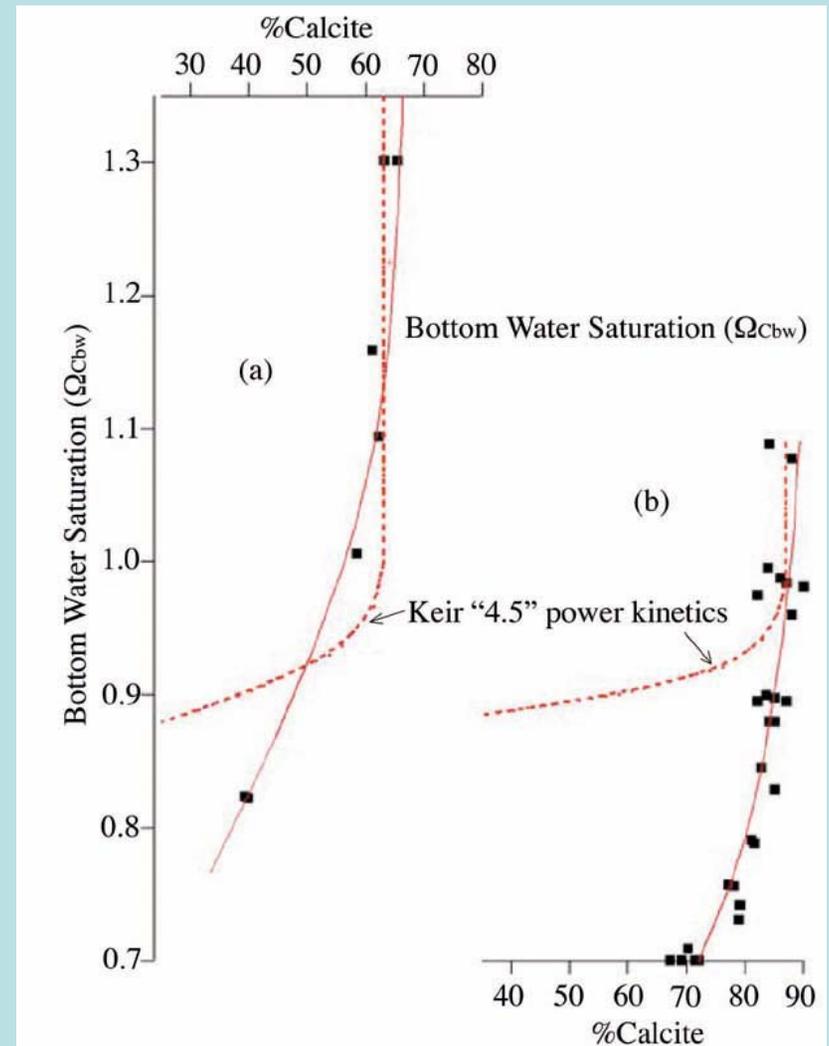


Figure 5. Modeled and observed lysocline for the (a) Ceara Rise, and (b) Ontong Java Plateau.

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Back into the distant past: mechanisms, models, and estimates of Cenozoic and Phanerozoic CO₂

- We have four ways of estimating atmospheric CO₂ before ice cores: (1) epsilon (organic-inorganic) $\delta^{13}\text{C}$; (2) boron isotope paleo-pH, (3) leaf stomatal indices, and (4) pedogenic carbonate $\delta^{13}\text{C}$
- We have one way (GEOCARB/BLAG) to explain past CO₂ variations (and one dissenting vote: Edmond and Huh, 2003).

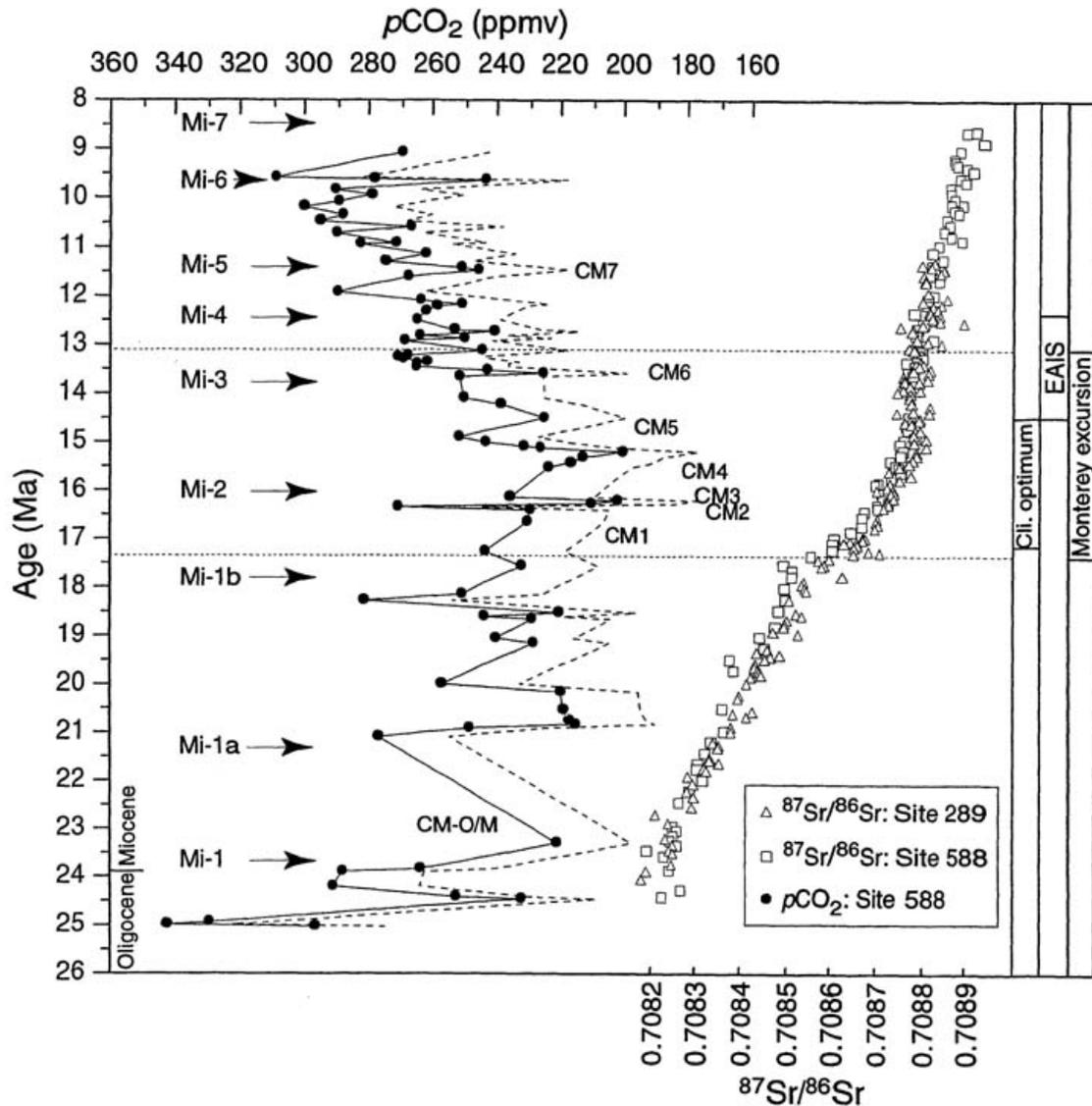


Figure 14. Maximum $p\text{CO}_2$ estimates (solid circles) using ϵ_p values from site 588, the equation for the maximum 95% confidence interval (Table 2), a $[\text{PO}_4]$ of $0.3 \mu\text{M}$, and $\epsilon_f = 27\%$. CM and Mi represent carbon maximas and inferred glacial maximas. A linear 0.5% increase and decrease in δ_w are assumed across glacial episodes Mi1, Mi1a, Mi1b, and Mi2 in addition to permanent δ_w changes during EAIS expansion (see Figure 13). Data for Sr isotope ratios are from sites 588 (open squares) and 289 (open triangles) from Hodell *et al.* [1991] and Hodell and Woodruff [1994]. Cli. optimum is climatic optimum. Note that the dashed line was calculated using the equation of the geometric mean regression (Table 2) and assuming $\epsilon_f = 25\%$. Propagation of error described in text results in a 15% uncertainty about calculated $p\text{CO}_2$ estimates.

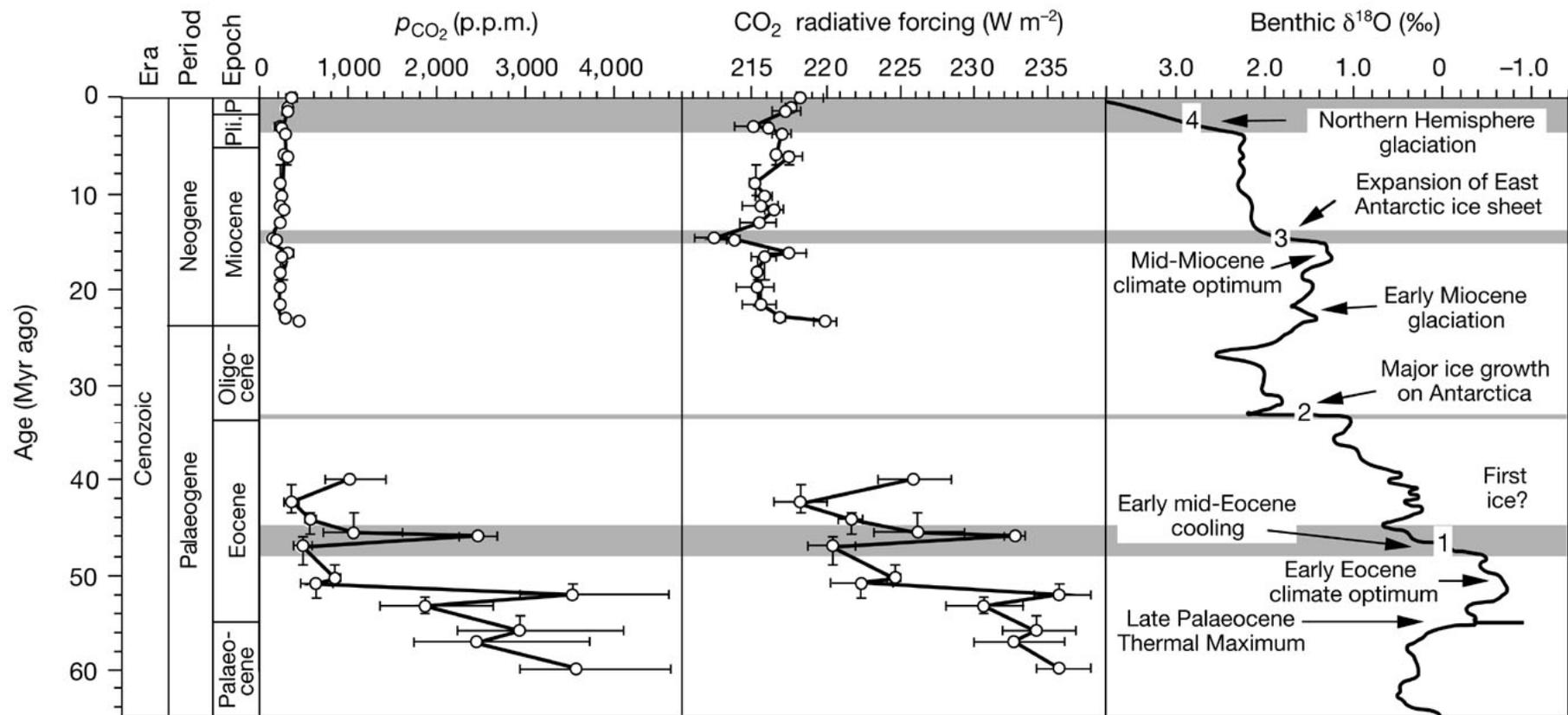


Figure 4 Carbon dioxide levels and Cenozoic climate change. The p_{CO_2} record is converted to radiative forcing (a measure of global warming) using the equation of Kiehl and Dickinson³⁴. The benthic foraminifer $\delta^{18}O$ time series is a smoothed record of many

observations summarized in refs 35–37. The trend towards more positive $\delta^{18}O$ results from a combination of deep-sea cooling and global ice volume increases. Four major steps (numbered 1 to 4) in $\delta^{18}O$ are indicated.

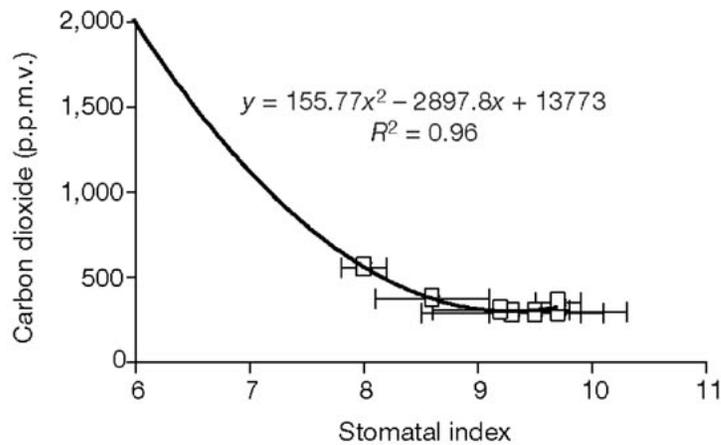
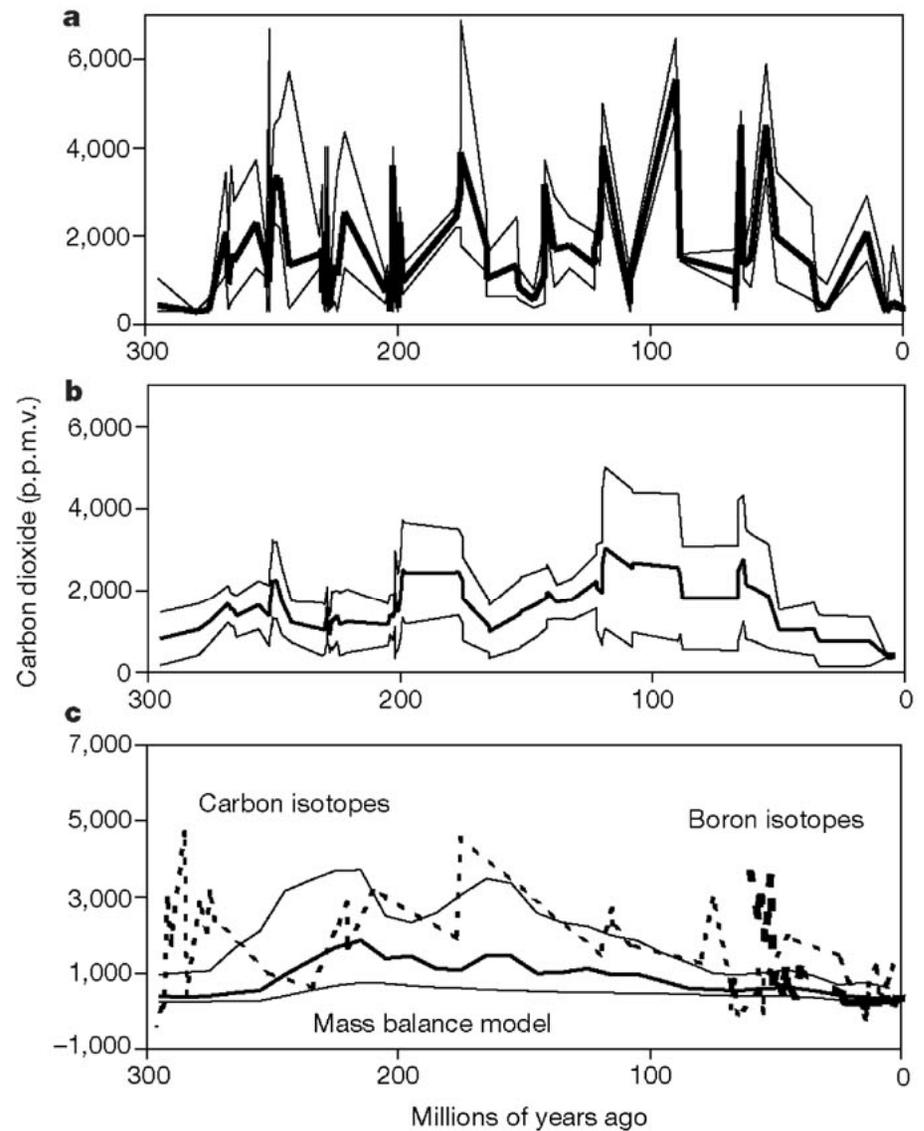
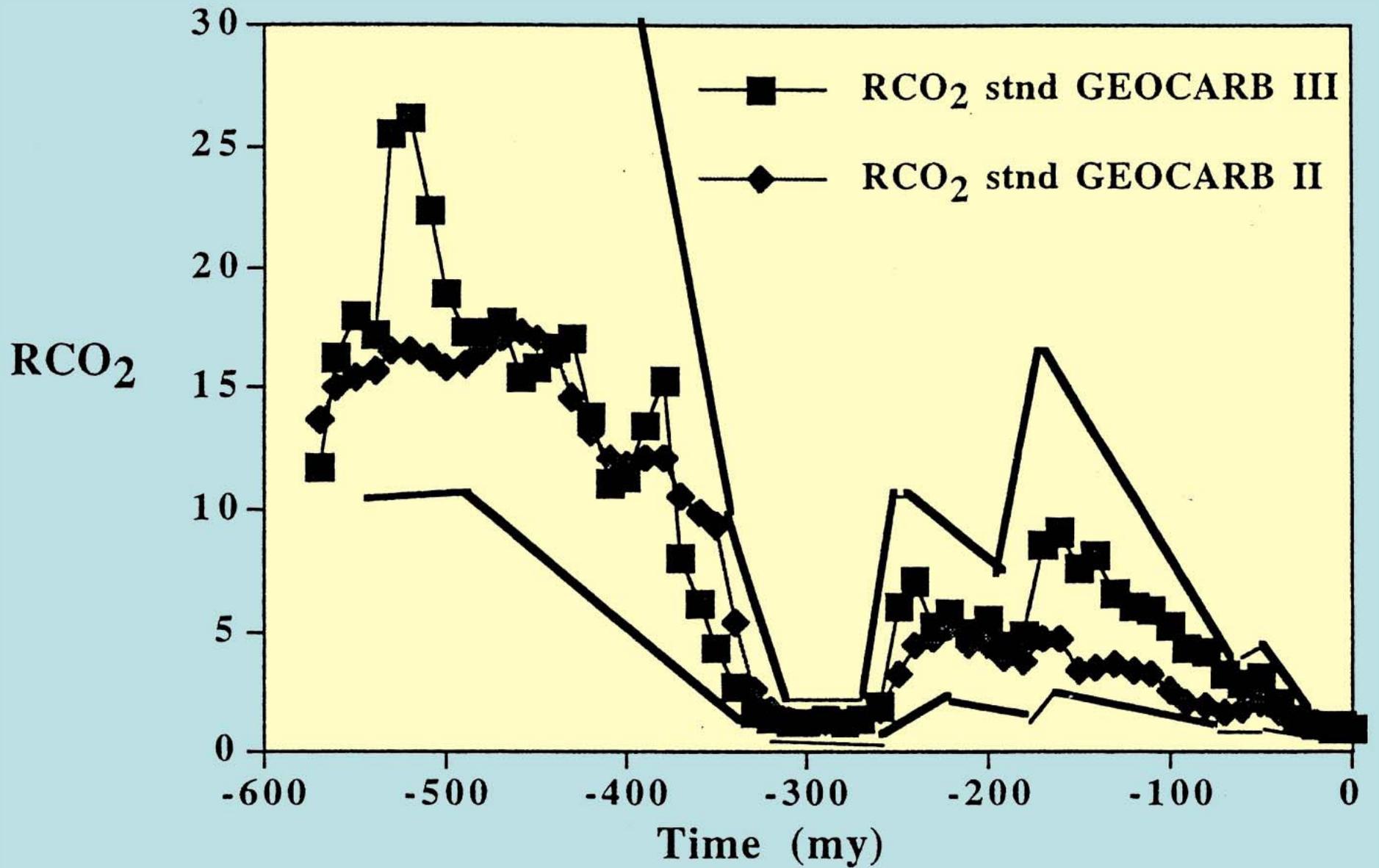


Figure 3 Palaeoatmospheric CO₂ can be inferred from fossil leaf SI by using this transfer function derived from *Ginkgo* leaves grown in greenhouse experiments⁵ and taken from herbarium sheets dating back to 1888 (see Supplementary Information).

Figure 4 Cuticular estimates (**a, b**) of atmospheric CO₂ (p.p.m.v.) can be compared with other proxies (**c**) over the past 300 million years. **a**, Unsmoothed data using transfer function (Fig. 3) on mean and standard deviation of 84 reliable SI determinations of fossil plants (Fig. 2). **b**, Five-point moving average of transformed SI determinations with flanking standard error of means. **c**, Previously published curves derived from a sedimentary mass balance model¹ (thick line), boron isotopic composition of marine foraminifera² (bold dashed line) and carbon isotopic composition of pedogenic carbonate³ (dashed line).





Non-steady state carbonate recycling and implications for the evolution of atmospheric P_{CO_2}

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Abstract

Most treatments of the Phanerozoic evolution of the carbon dioxide content of the atmosphere (P_{CO_2}) assume a steady state closed system. Release of CO_2 by mantle degassing and by biogenic precipitation of carbonates and their metamorphism in subduction zones balances the consumption by continental aluminosilicate weathering. Small perturbations in this balance bring about changes in P_{CO_2} , but given the small size of the atmospheric CO_2 reservoir relative to the rate of fixation by weathering, mechanisms that maintain this apparently precarious balance dominate current thinking. At present, the Atlantic and Indian oceans are major depocenters of $CaCO_3$, but subduction of ocean floor and the deposits on it is minimal in these basins. The locus of metamorphic regeneration of CO_2 is restricted to the trenches off Central America.

This is due to global asymmetries in the age of crust being subducted, in the distribution of oceanic carbonate productivity, and in the carbonate compensation depth, coupled with the poor preservation of old carbonate sediments. There is no causal relationship between the metamorphic release and weathering uptake of CO_2 and subsequent deposition of carbonate on timescales shorter than a complete cycle of opening and closure of a basin. We hypothesize that the low present-day P_{CO_2} is maintained by a time lag between: (1) mantle outgassing and metamorphic regeneration related to orogenic events in the geologic past, and (2) consumption driven by recent mountain building in the Tethyan zone and in the Western Americas.

If this is true, then at the present 'kinetic minimum' both the terrestrial biosphere and the weathering rates are CO_2 limited. Atmospheric P_{CO_2} levels are controlled by weathering reactions only at this limit. In epochs of tectonic stability, outgassed CO_2 can accumulate in the atmosphere to very high concentrations with no obvious limit. Thus, as in the past, the current ice age will persist for tens of millions of years, possibly until the closure of the Atlantic recycles the first deep carbonate depocenter since the destruction of the Tethys. A greater understanding of all these processes is required for the geochemical evolution of the Earth surface environment to be simulated.

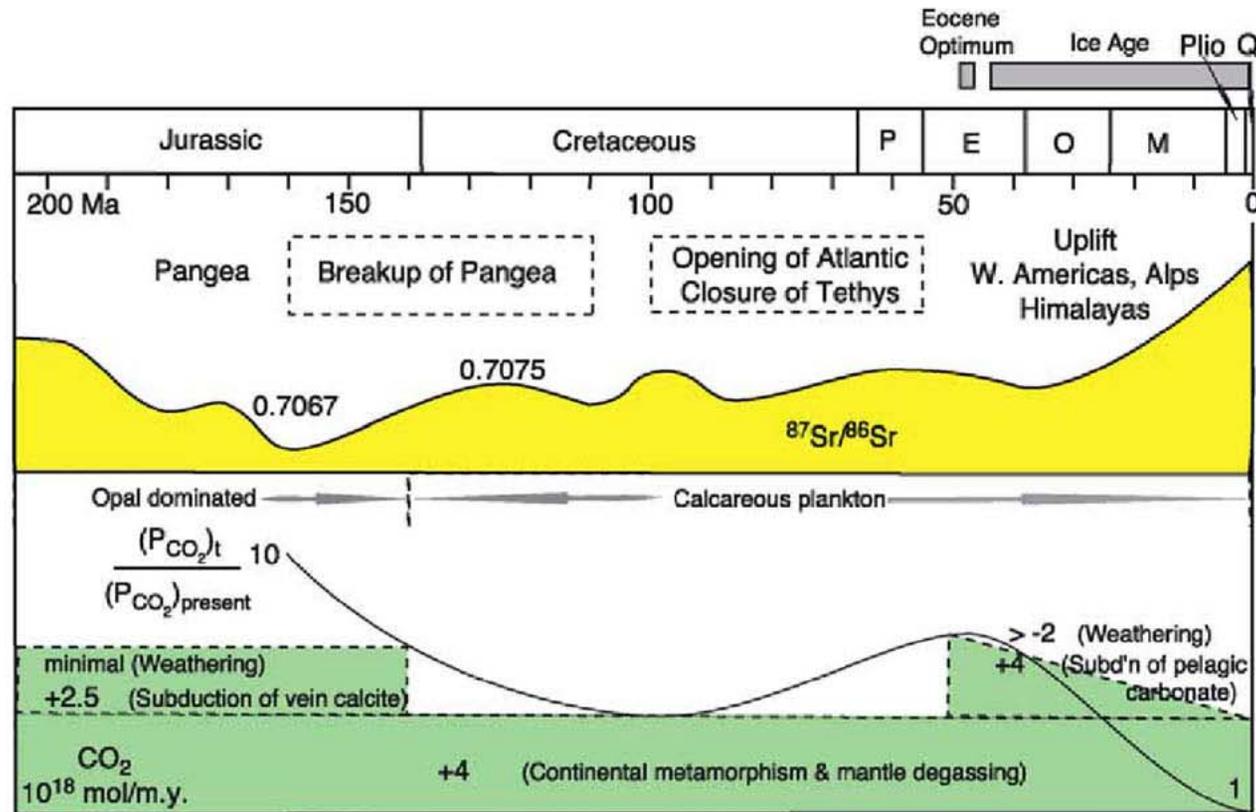


Fig. 7. Schematic illustration of the conceptual evolution of atmospheric CO₂ discussed in the text. Not drawn to scale.

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