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12.842 / 12.301 Past and Present Climate
Fall 2008

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12.842
Climate Physics and Chemistry
Fall 2008

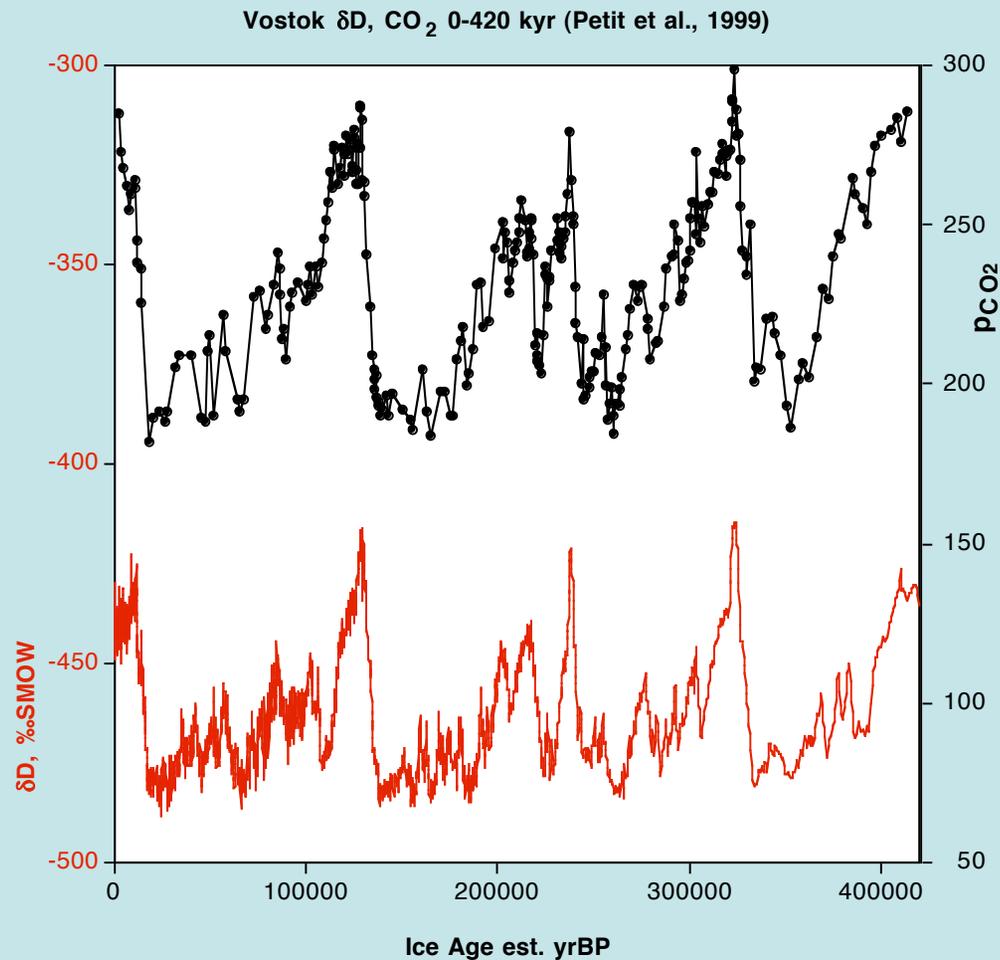
Changes in CO₂ during the past million years

Gases in Ice Cores

- Bubbles seal off at the bottom of the firn layer, ~80-120 m
- Hence gas is younger than the solid ice that contains it - the “gas age/ice age difference” depends on the accumulation rate
- Most gases are well mixed in atmosphere; so records from Antarctic and Greenland are nearly the same; features of the records can be used to correlate chronologies between hemispheres
- Gases that have been measured:
 - CO₂
 - O₂ (¹⁸O/¹⁶O ratio)
 - CH₄
 - N₂O

Recall: Ice core evidence for changes in atmospheric CO₂

- Pre-anthropogenic p_{CO₂} was about 280 ppmV
- Glacial p_{CO₂} was about 190 ppmV. Six Antarctic ice cores give same number.



Data from Petit et al (1999) *Nature*, 419:188-190

Image removed due to copyright restrictions.

$\delta^{18}\text{O}$ and CH_4
in Greenland
and Antarctica

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Ahn and Brook (2008) *Science* 322:83. Figure 1.

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Ahn and Brook (2008) *Science* 322:83. Figure 2.

Some Concepts to Explain Glacial- Interglacial CO₂ cycles

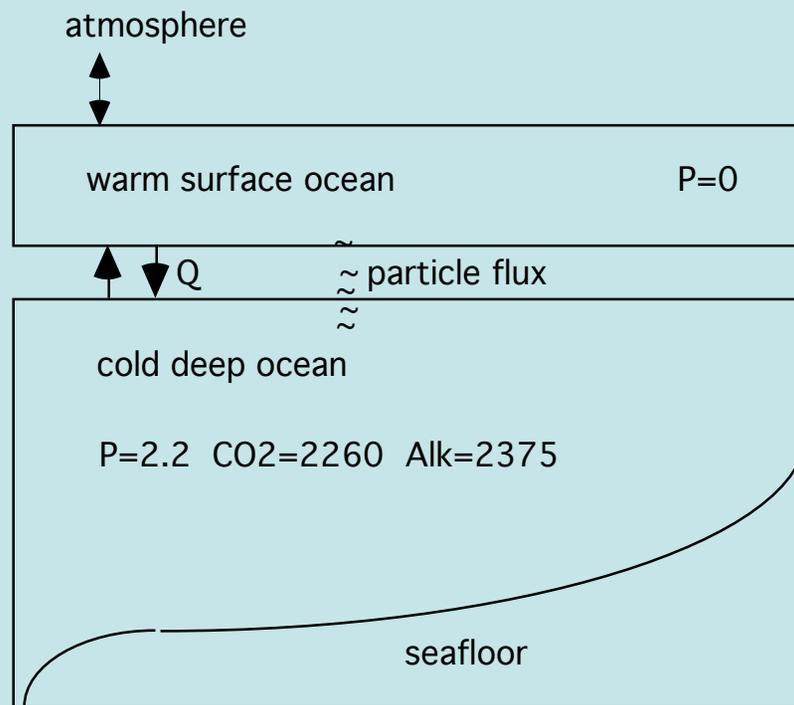
Role of Temperature in G/IG CO₂ cycles

- CO₂ is more soluble in cold water than in warm water - so if the ocean temperature cools during ice ages, atm. CO₂ should be lower because more ends up in the ocean.
- Given an estimate of ocean surface temperatures, we can readily calculate how much more CO₂ ends up in the ocean.
- Although our knowledge of ocean surface temperatures during the Last Glacial Maximum (LGM) is imperfect, we can make a reasonable estimate:
 - -5°C in low-latitude ocean (probably an extreme possibility)
 - -2.5 in high-latitude ocean (can't get any colder than the freezing point)
- This would lead to a -30 ppmV drop in atmospheric CO₂.
- This is significant but only ~ 30% of the total. *And..*

Factors offsetting the decrease due to cooler temperatures:

- The withdrawal of seawater into continental glaciers leave the ocean saltier, and CO_2 is less soluble in saltier waters (approximate magnitude: +6.5 ppmV)
- The glaciers and cooler climate also reduced the continental biomass putting more carbon in the ocean, and thereby *increasing* atmospheric CO_2 . Carbon isotope observations imply a whole-ocean $\delta^{13}\text{C}$ decrease of -0.35 ‰ during the LGM (presumed due to the oxidation and solubilization of the biomass) which would lead initially to a +15 ppmV increase in CO_2 .
- After taking all of these things into account, the decrease in atmospheric CO_2 due to all of these easy-to-estimate factors is 8.5 ppmV.
- We are a long way from accounting for glacial CO_2 !

Simple two-box ocean model



$$\text{CO}_2(\text{surface}) = \text{CO}_2(\text{deep}) - \begin{matrix} \text{organic C} \\ \downarrow \\ 106 \end{matrix} - \begin{matrix} \text{CaCO}_3 \\ \downarrow \\ 21 \end{matrix} * P(\text{deep})$$

$$\text{Alk}(\text{surface}) = \text{Alk}(\text{deep}) - \begin{matrix} \text{CaCO}_3 \\ \downarrow \\ 2 * 21 \end{matrix} - \begin{matrix} \text{NH}_3\text{oxidation} \\ \downarrow \\ 16 \end{matrix} * P(\text{deep})$$

Broecker's 2-box interglacial ocean:

ATMOSPHERE

$P_{CO_2} = 324$

SURFACE OCEAN

$T = 22$ $S = 34.7$ $P = 0$ $ALK = 2291$ $\Sigma CO_2 = 1967$ $\delta^{13}C = 2.2$

$CH_2O : CaCO_3 : NH_3 : P = 106 : 27 : 16 : 1 ; \delta^{13}C = -20$

DEEP OCEAN

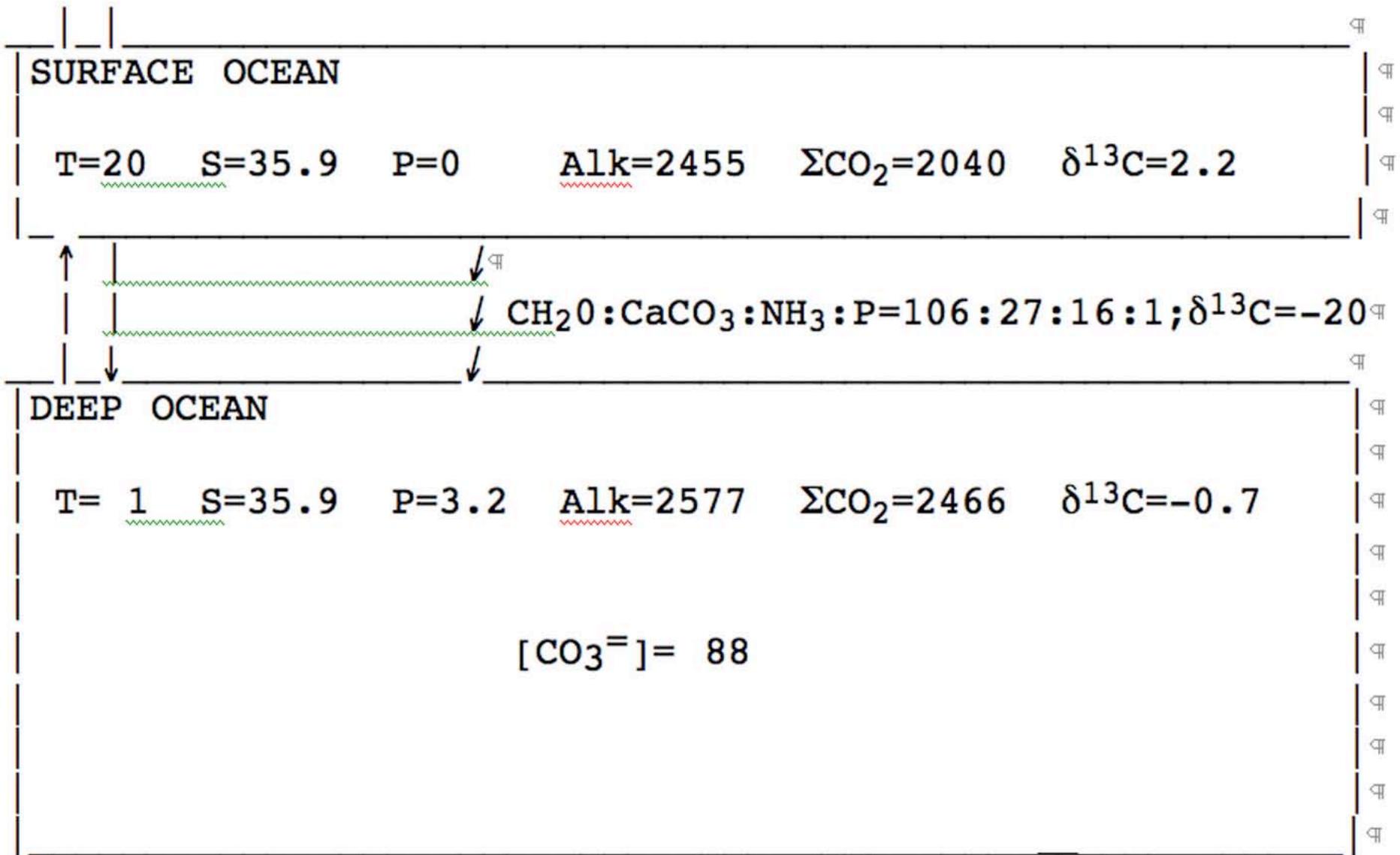
$T = 1$ $S = 34.7$ $P = 2.2$ $ALK = 2375$ $\Sigma CO_2 = 2260$ $\delta^{13}C = 0.0$

$[CO_3^{=}] = 85$

Broecker's 2-box glacial ocean:

ATMOSPHERE

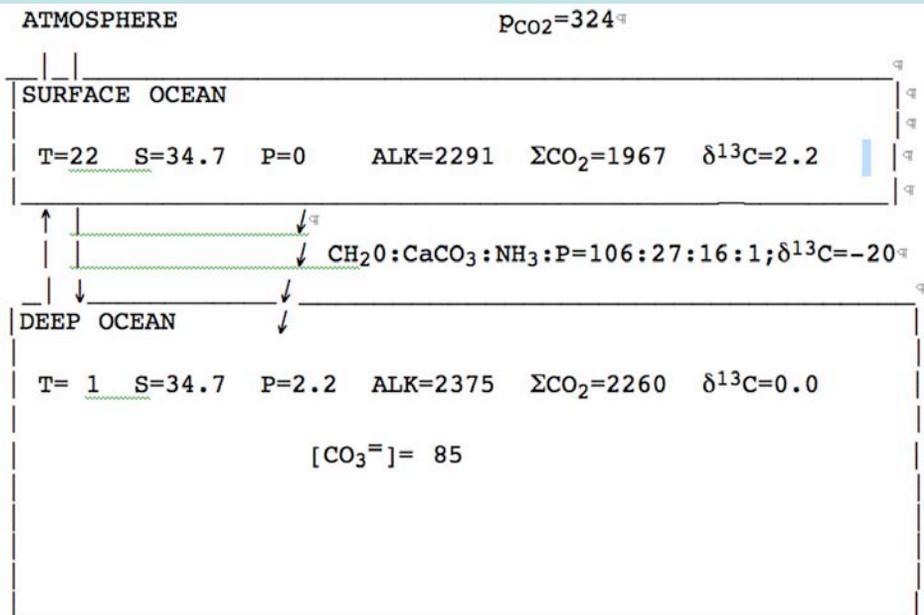
$$p_{\text{CO}_2} = 241$$



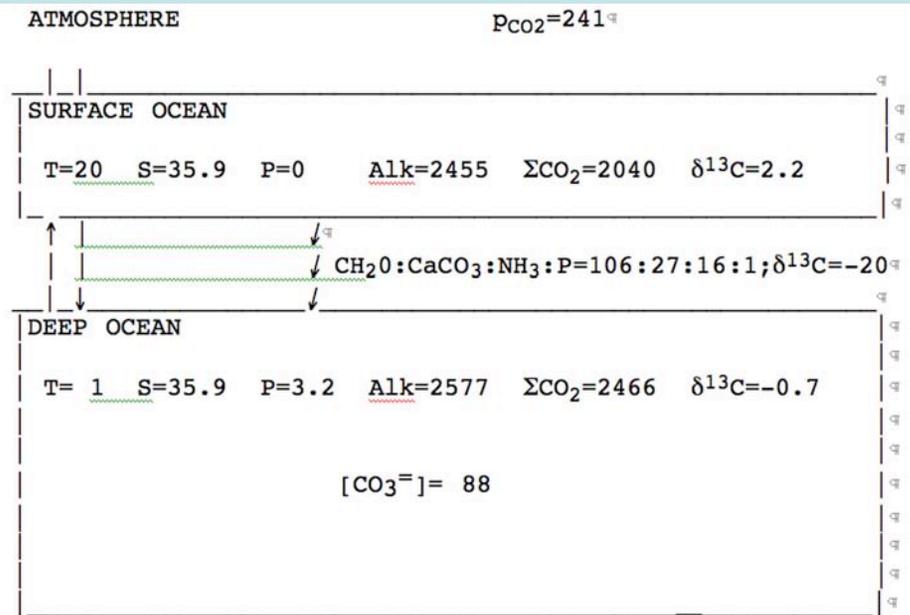
(Assumes that marine organic matter from continental shelf is oxidized and put into ocean and that sedimentary CaCO_3 dissolves to keep $[\text{CO}_3^{=}]$ of deep ocean approximately constant)

Broecker's interglacial/glacial oceans:

Interglacial



Glacial



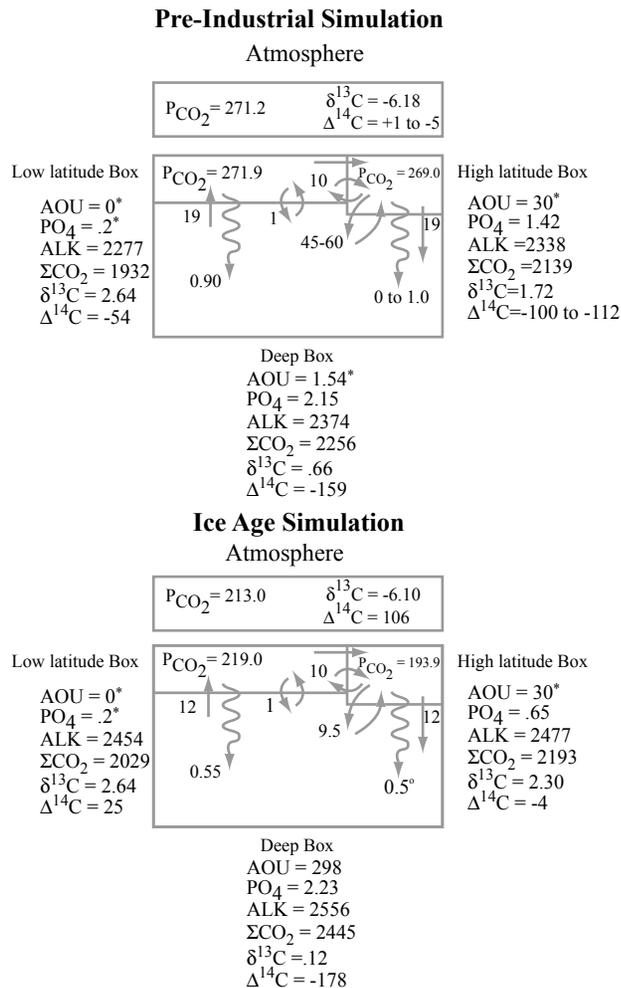
(Assumes that marine organic matter from continental shelf is oxidized and put into ocean and that sedimentary $CaCO_3$ dissolves to keep $[CO_3^{=}]$ of deep ocean is approximately constant)

Toggweiler-Sarmiento (1984) 3-box model for interglacial / glacial CO₂

see also: Knox and McElroy, Wenk and Siegenthaler

This model suggests that the pre-formed nutrient content of polar surface waters decreases during glacial period (often pointing to increased high-latitude stratification as the mechanism for achieving higher nutrient utilization).

An alternative proposal for the mechanism of nutrient depletion is the “Martin Hypothesis” that says that Fe limits Antarctic productivity and that this limitation is diminished during glacial periods by a higher dust flux to polar regions (see ice core data).



Steady state concentrations of model variables in the ocean and atmospheric boxes for the preindustrial and ice age simulations. Units are micromoles per kilogram for AOU, PO₄, and ΣCO_2 ; microequivalents per kilogram for alkalinity, parts per million for PCO₂; and parts per thousand (per mil) for $\delta^{13}C$ and $\Delta^{14}C$. Model transports between boxes are given in units of sverdrups (10⁶m³/s). Particle fluxes are given next to the wiggly arrows in units of moles C per square meter per year. Asterisks indicate values that are initial assumptions.

Fig. 7. Steady state concentrations of model variables in the ocean and atmospheric boxes for the preindustrial and ice age simulations. Units are micromoles per kilogram for AOU, PO₄, and ΣCO_2 ; microequivalents per kilogram for alkalinity, parts per million for PCO₂; and parts per thousand (per mil) for $\delta^{13}C$ and $\Delta^{14}C$. Model transports between boxes are given in units of sverdrups (10⁶ m³/s). Particle fluxes are given next to the wiggly arrows in units of moles C per square meter per year. Asterisks indicate values that are initial assumptions.

The nitrogen fixation / inventory hypothesis

(McElroy, Broecker, others...)

- This hypothesis assumes that N is the limiting nutrient (instead of P). In other words, that the C:N ratio is fixed but the C:P ratio is flexible.
- The residence time of NO_3^- in the ocean is on the order of thousands of years. If something perturbs the input/output balance, the nitrate concentration can respond relatively quickly.
- Things that could perturb the nitrate balance:
- More dust, more N fixation (until oxygen loss increases denitrification)
- Changes in ocean circulation that diminish the low- O_2 zones (inferred from $\delta^{15}\text{N}$ W. N. Pacific and Arabian Sea - possibly but not necessarily related to ocean nutrient deepening)
- Otherwise works the same as the “shelf phosphorus” model.

Some Reading

Broecker W. S. (1982) Ocean chemistry during glacial time. *Geochim. Cosmochim. Acta* 46, 1689-1705.

Sigman, D. and E. Boyle (2000) Glacial/Interglacial variations in atmospheric carbon dioxide, *Nature* 407:859-869.

Sarmiento, J.L. and R. Toggweiler (1984) A new model for the role of the oceans in determining atmospheric p_{CO_2} , *Nature* 308:621-624.