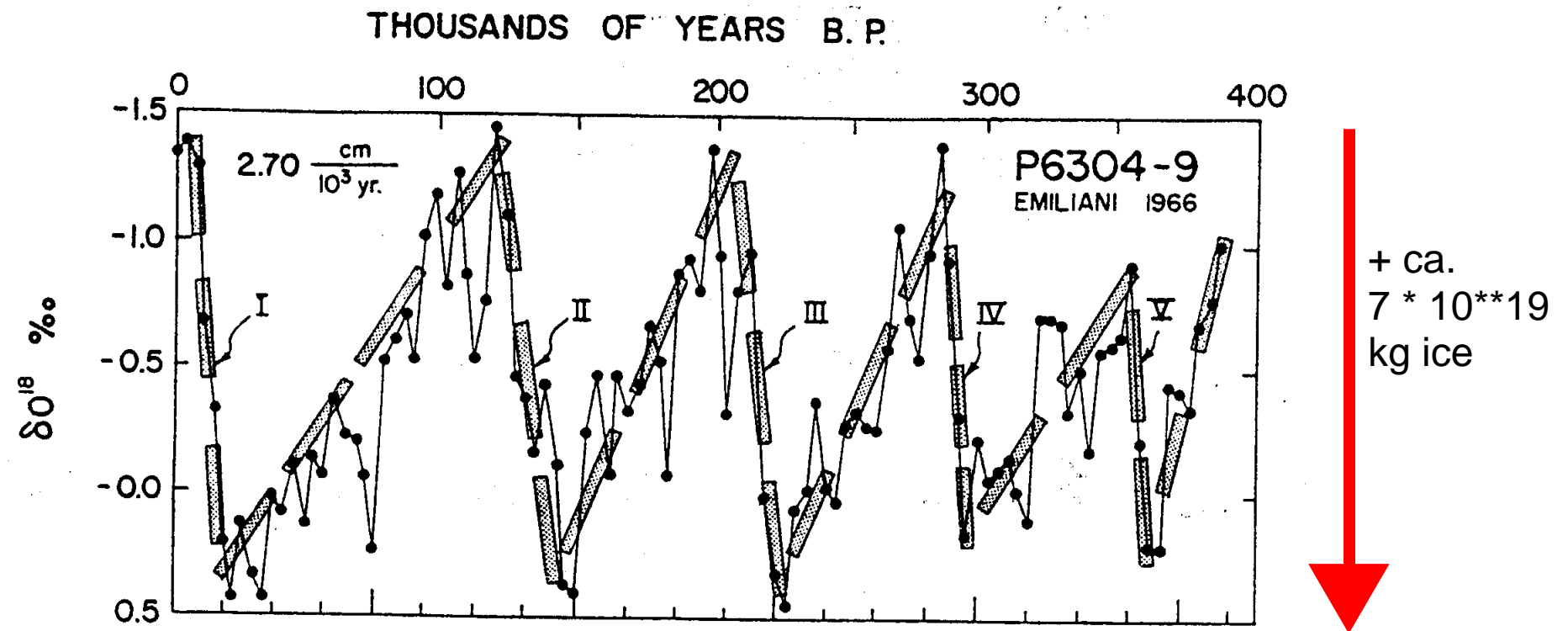


The leads and lags of CO₂

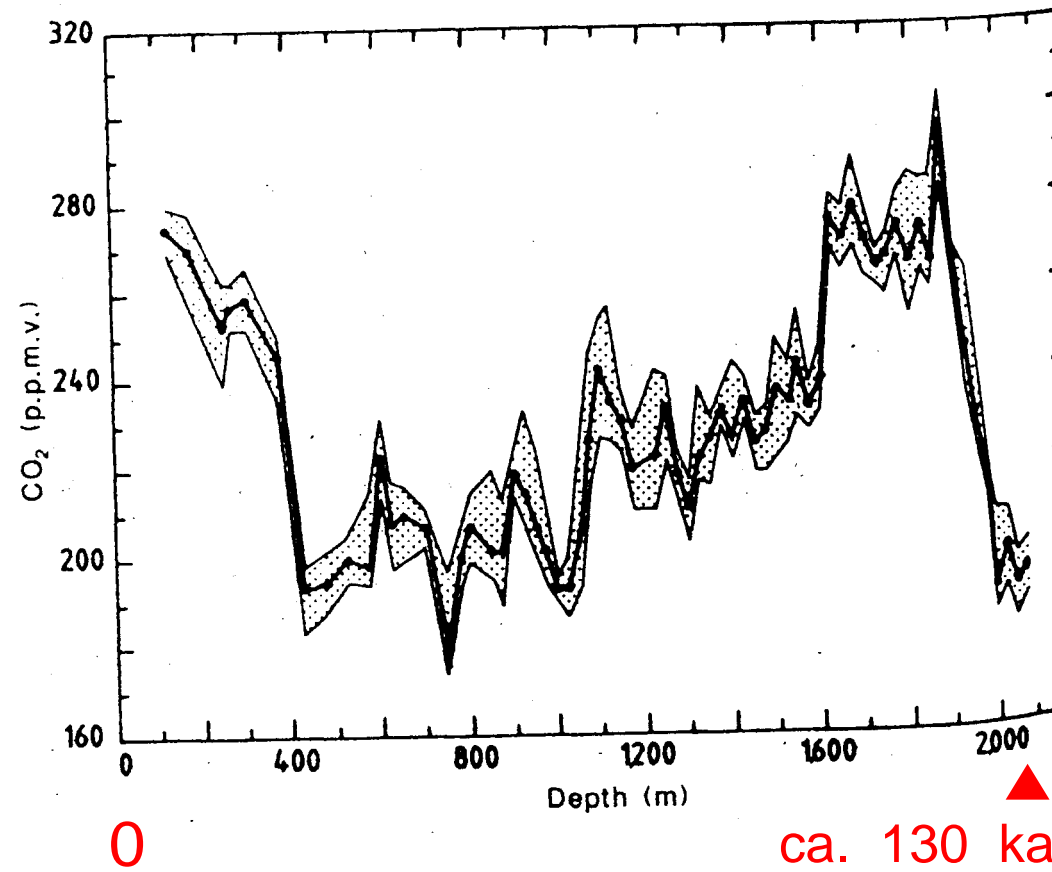
Manfred Mudelsee

Institute of Meteorology, University of Leipzig, FRG

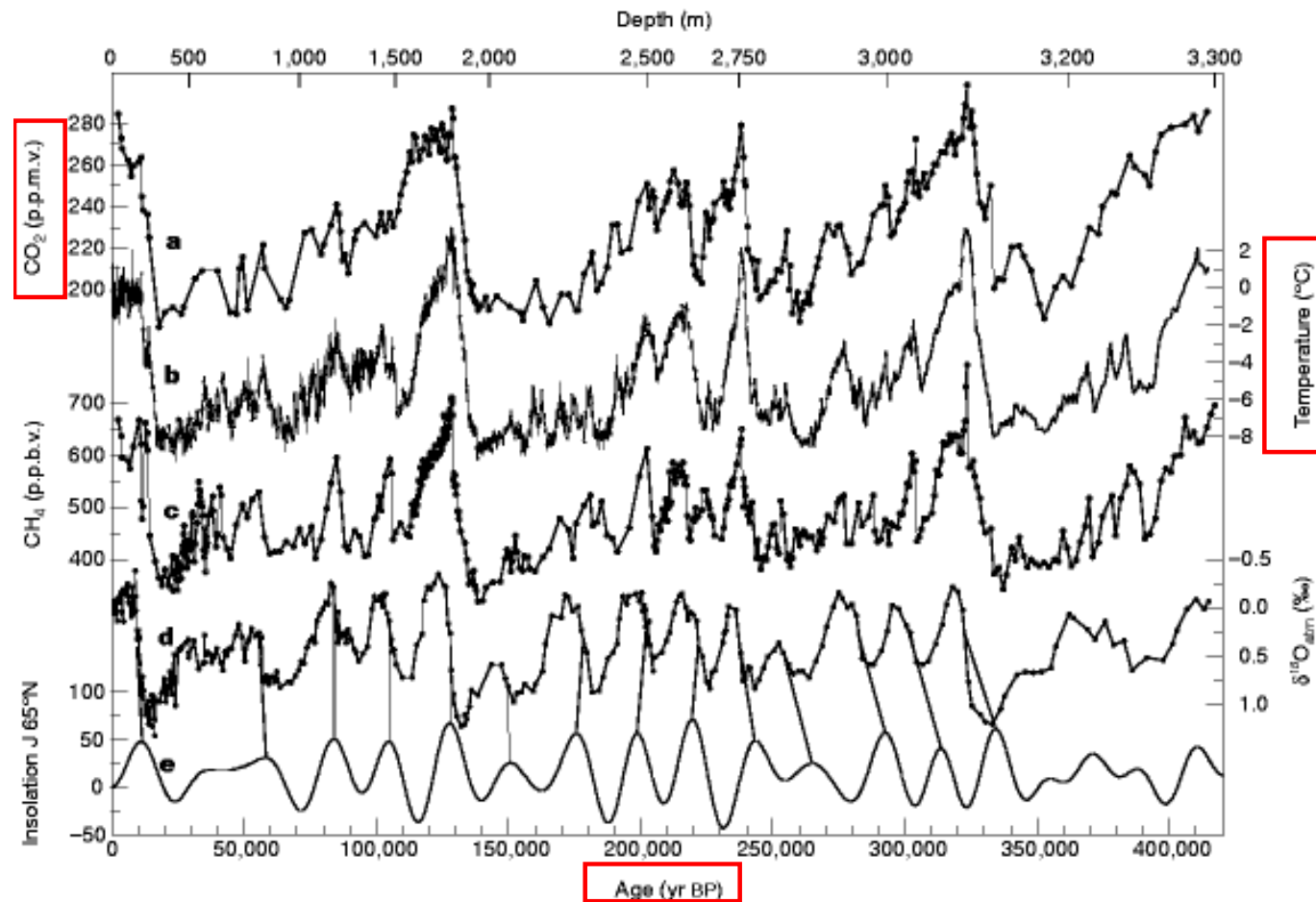
Work supported by: EU (Marie Curie Research Fellowship)
DFG (Research Fellowship)



(Broecker & van Donk 1970)



Vostok ice core (Barnola *et al.* 1987 *Nature* 329:408–414)



Complete Vostok ice core (Petit *et al.* 1999)

Table 1. Summary of Scenarios Put Forward to Account for the Lower CO₂ Content of the Atmosphere During Times of Glaciation

Model	Problems	Advantages	References
<i>Nutrient Based</i>			
Shelf hypothesis	linked to sea level		<i>Broecker</i> [1982]
Vertical redistribution	$\delta^{13}\text{C}$ change too late		<i>Boyle</i> [1988] <i>Keir</i> [1991]
<i>Shallow Ocean CaCO₃ Based</i>			
Coral reef hypothesis	linked to sea level		<i>Berger</i> [1982] <i>Berger and Keir</i> [1984] <i>Keir and Berger</i> [1985]
Shallow water CaCO ₃	linked to sea level		<i>Opdyke and Walker</i> [1992] <i>Milliman</i> [1993] <i>Opdyke and Wilkinson</i> [1993] <i>Walker and Opdyke</i> [1995]
<i>Northern Atlantic Based</i>			
Cooler glacial North Atlantic	warming post dated the rise in CO ₂		<i>Keir</i> [1993]
<i>Sediment Respiration Based</i>			
Increase in the ratio of organic carbon to CaCO ₃ in the material falling to the sea floor	mass balance	System response time is right (≈ 10 kyr)	<i>Sigman</i> [1997] <i>Archer and Maier-Reimer</i> [1994] <i>Sanyal et al.</i> [1995]
<i>Southern Ocean Based</i>			
Polar dominance	not seen in Southern Ocean paleoproductivity records and lacks mechanism for increased productivity	Southern Ocean	<i>Sarmiento and Toggweiler</i> [1984] <i>Siegenthaler and Wenk</i> [1984] <i>Knox and McElroy</i> [1984]
Polar alkalinity	not seen in Southern Ocean paleoproductivity records and lacks mechanism for increased alkalinity	Southern Ocean	<i>Broecker and Peng</i> [1989]
Southern Ocean solubility pump	effect on CO ₂ not large enough	timing fits with T change	
Iron hypothesis	not seen in Southern Ocean paleoproductivity records and response time too quick	agrees with dust flux change	<i>Martin</i> [1990]

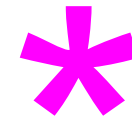
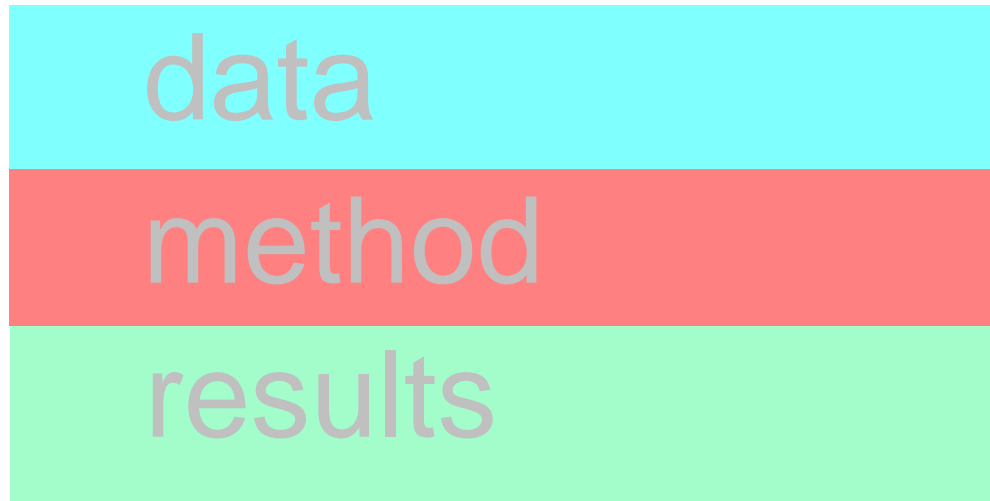
(Broecker & Henderson 1998)

Aim of this study: estimate **phase relations** (leads/lags) of CO₂ variations relative to variations of:

- global ice volume
- temperature

Problems caused by: • limited proxy quality, measurement noise

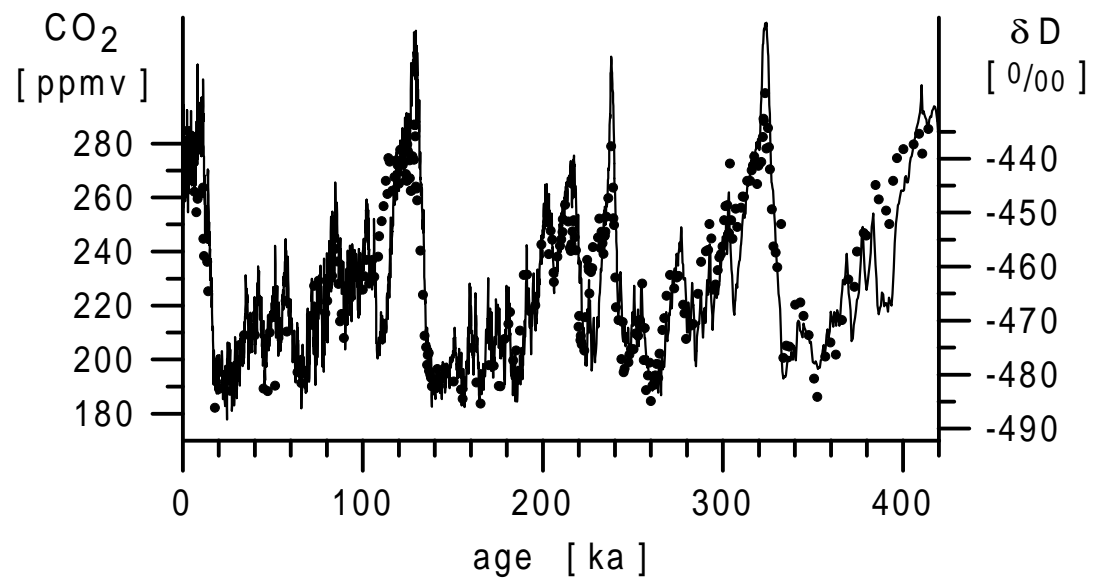
- uncertain timescales



excursion

Mudelsee M (2001) Quaternary Science Reviews 20:583–589.

<http://www.uni-leipzig.de/~meteo/MUDELSEE/>



CO₂ air bubbles

*
δD ice: temperature

ice-age ≠ air-age

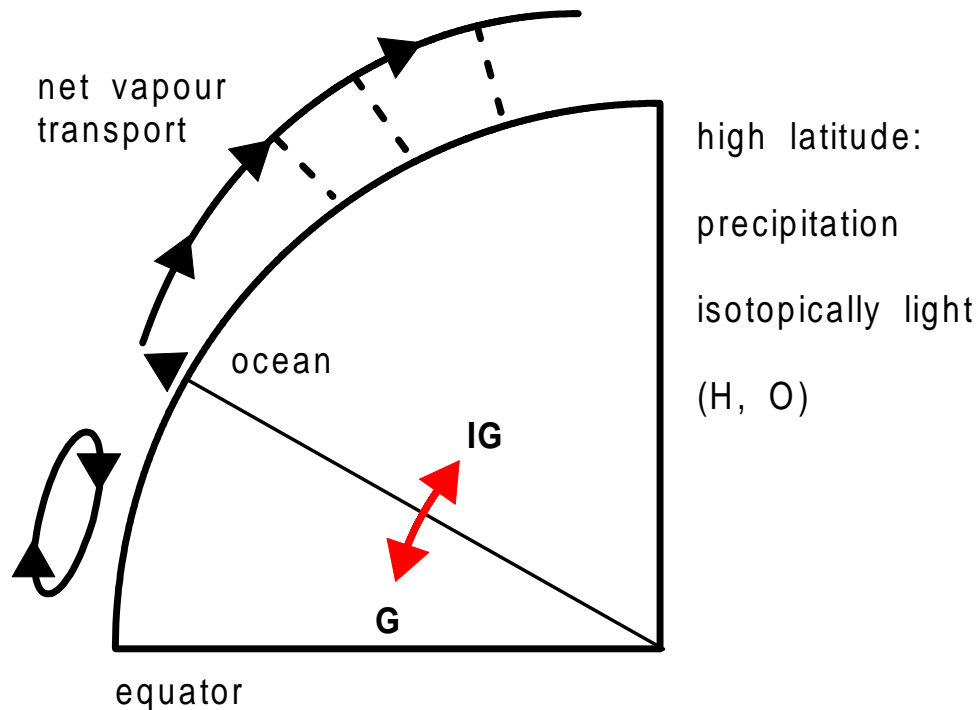


$$\delta D = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{standard}}}{(D/H)_{\text{standard}}} \times 1000 \text{ ‰}$$

data



Rayleigh condensation



glacial/cold:

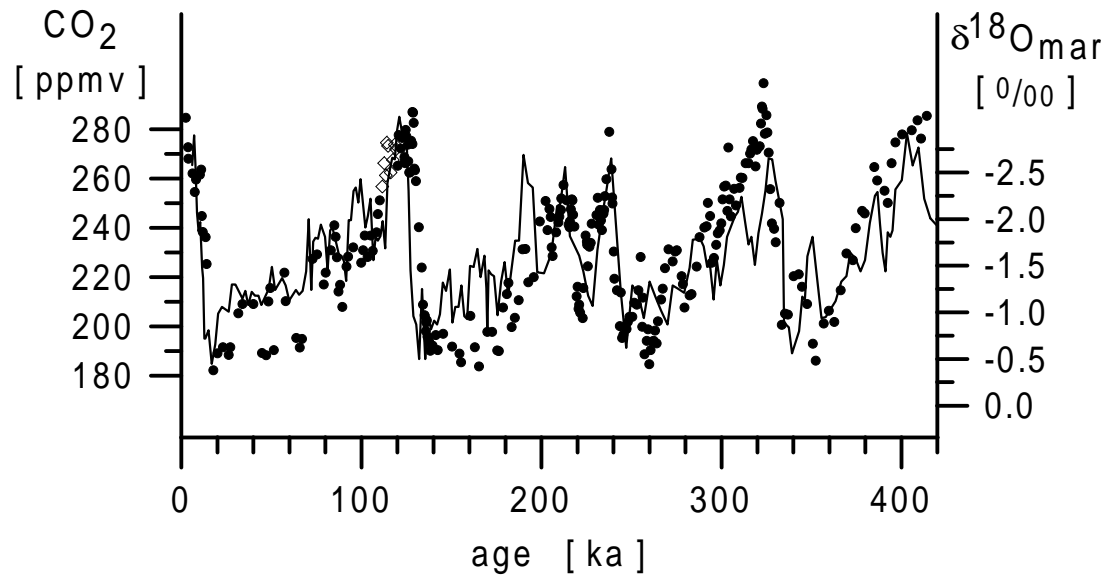
⇒ 'Rayleigh path' longer

⇒ ice isotopically lighter

other effects:

kinetic, sublimation etc.

Oeschger & Langway (Eds.)
(1989) The Environmental
Record in Glaciers and Ice
Sheets. Wiley, New York.

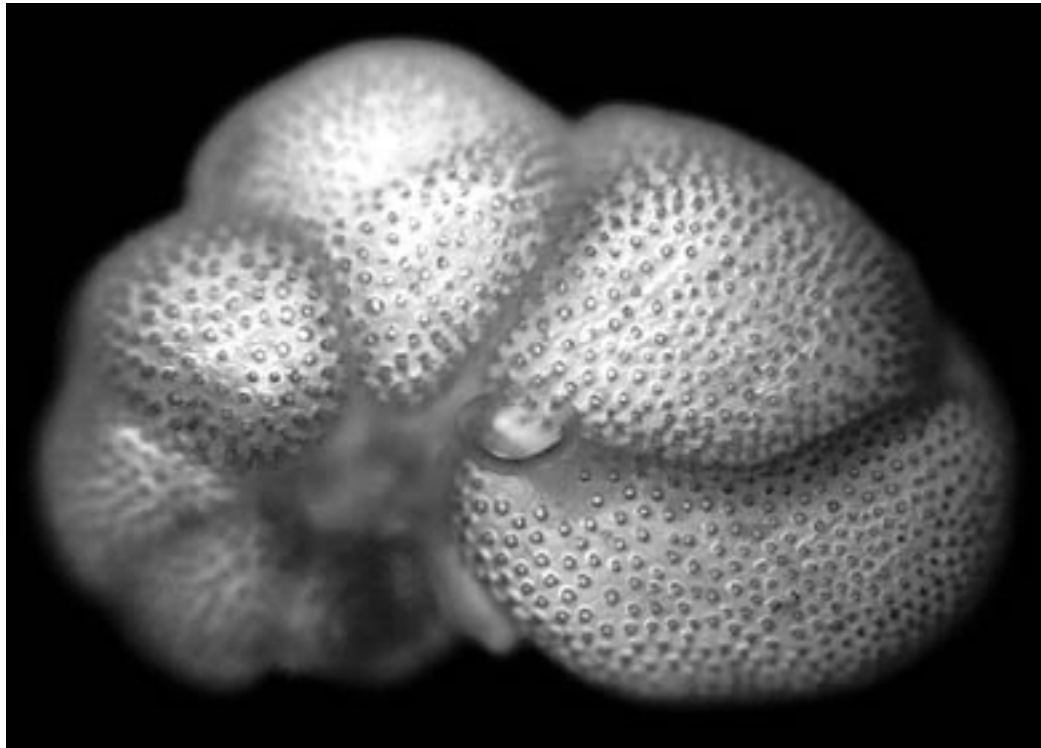


• CO₂ Vostok ice core
 – δ¹⁸O marine core MD 900963 (Bassinot *et al.* 1994)
 (benthic record)

foraminifera:
 plankton, carbonate

δ¹⁸O_{mar}:
 ice volume

problem:
 temperature signal



Foraminifera *Rosalina globularis*, size: ≈ 1.1 mm
(<http://www.microscopy-uk.org./mag/artmar/forwin.html>)



$$\delta^{18}\text{O} = \frac{\left(^{18}\text{O}/^{16}\text{O}\right)_{\text{sample}} - \left(^{18}\text{O}/^{16}\text{O}\right)_{\text{standard}}}{\left(^{18}\text{O}/^{16}\text{O}\right)_{\text{standard}}} \times 1000 \text{ ‰}$$

Rayleigh condensation \Rightarrow polar ice: isotopically light

	IG	G
$\delta^{18}\text{O}_{\text{mar}}$	low	high

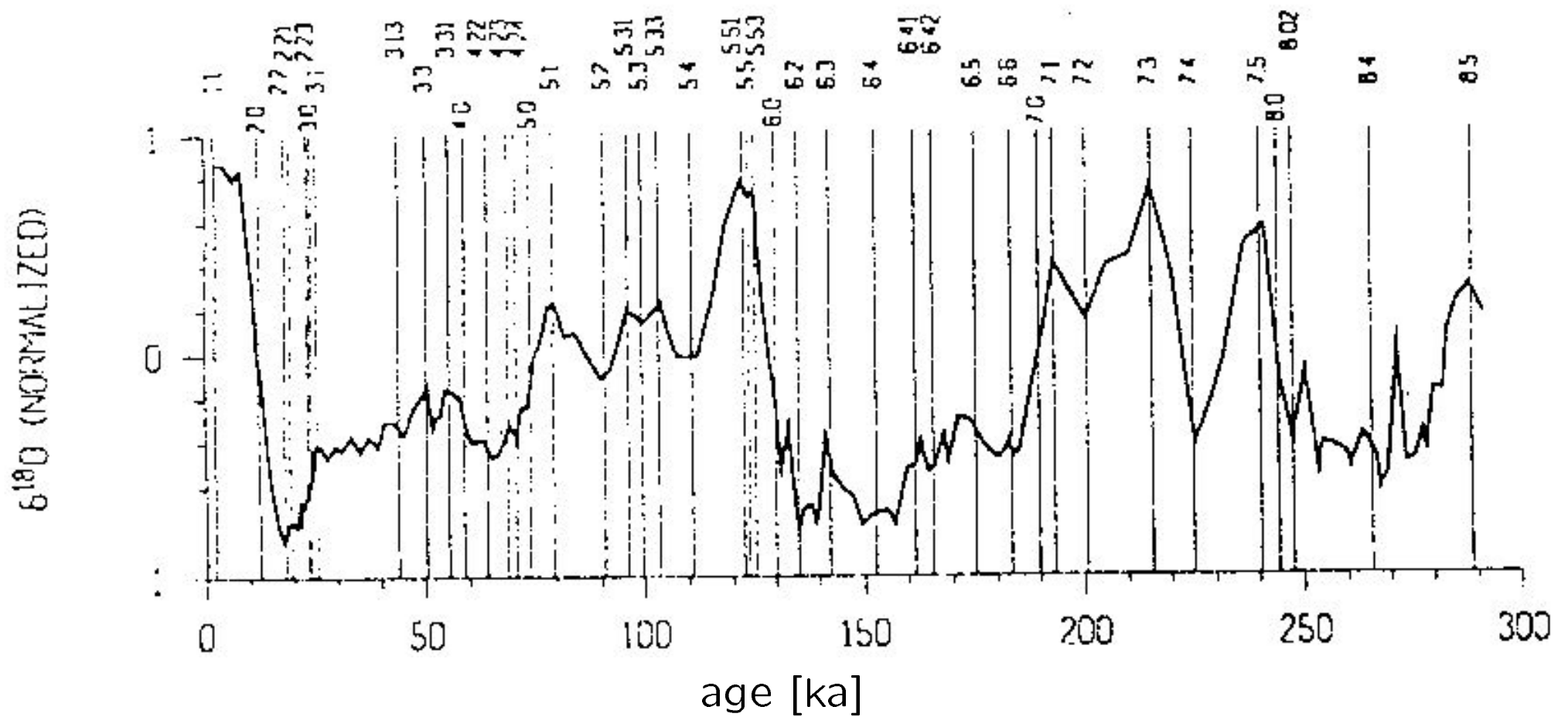
Shackleton N (1967) Nature 215:15-17.

Dansgaard W, Tauber H (1969) Science 166:499-502.

Because also temperature variations are recorded by $\delta^{18}\text{O}_{\text{mar}}$:

⇒ benthic records (as above, Bassinot)

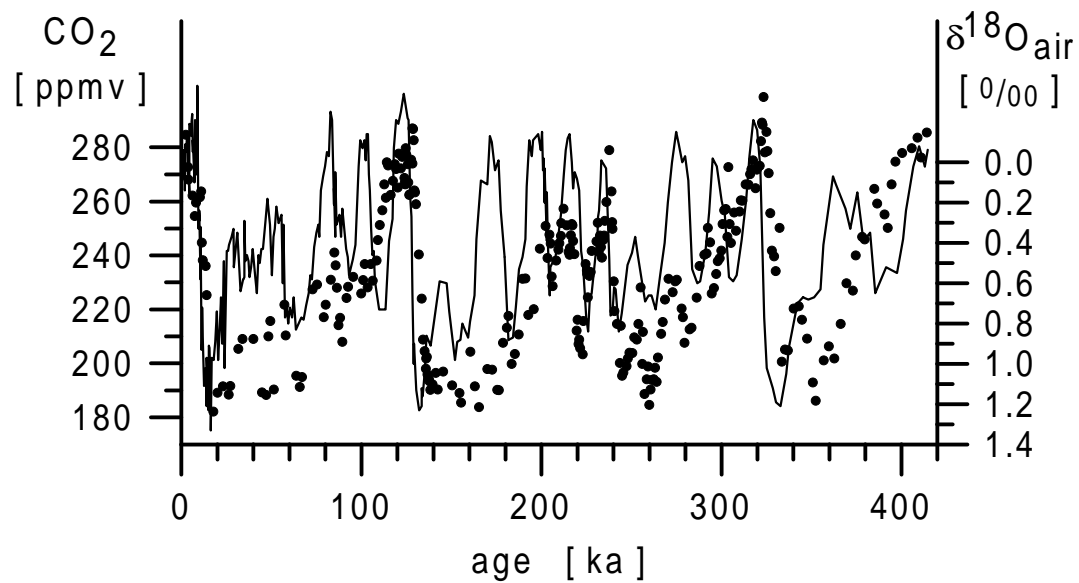
⇒ planktonic, tropical records (SPECMAP)



SPECMAP (Imbrie *et al.* 1984, Martinson *et al.* 1987)

marine timescale:

- fixpoint Termination II (≈ 127 ka)
- fixpoint geomagnetic reversal B/M (≈ 780 ka)
- interpolation
- orbital tuning (assumption: astronomical forcing)



• CO₂ Vostok ice core
 – δ¹⁸O Vostok ice core

δ¹⁸O_{air}: ice volume

problem:

Dole effect

(hydrological cycle & photosynthesis)



oceanic $\delta^{18}\text{O} \rightarrow \text{air, O}_2$

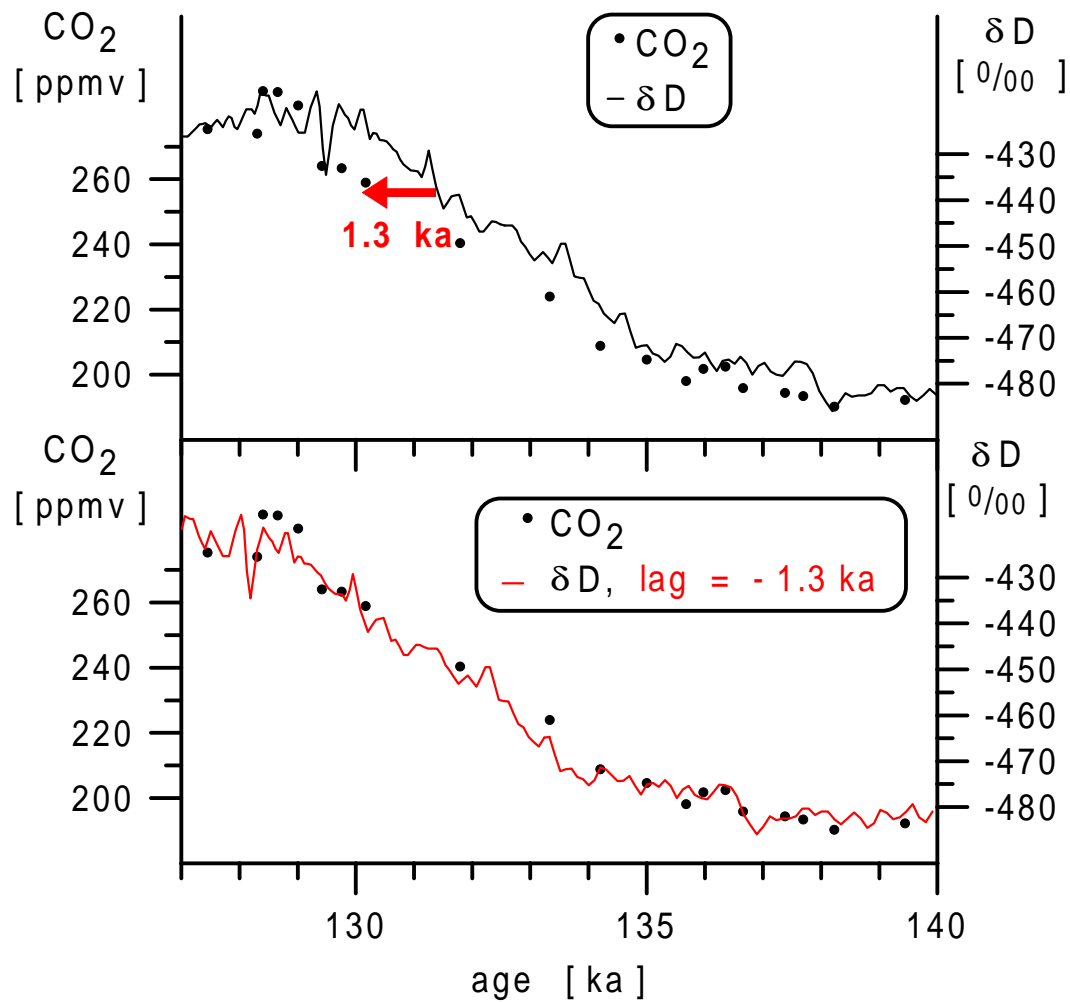
$\delta^{18}\text{O}_{\text{air}}$ lags $\delta^{18}\text{O}_{\text{mar}}$

atmospheric turnover time (O_2):

Bender *et al.* 1994: 1.2 ka

Sowers *et al.* 1991: 2–3 ka

here: 2 ± 1 ka



$$y_u = a + b x_{t+l} + c x_{t+l}^2 + \epsilon$$

y : CO₂

u : air – age

x : δD interpolated

t : ice – age

ϵ : error

a, b, c : regression
parameters

l : lag

$l < 0$: CO₂ lags

method

Estimation: generalized least squares (GLS):

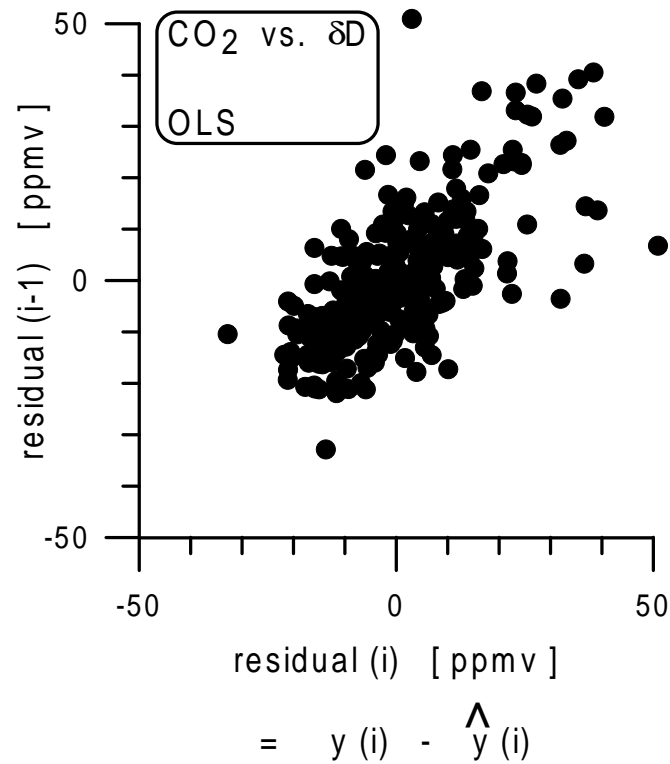
$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\epsilon} \quad \text{model}$$

$$\mathbf{y} = \begin{bmatrix} y(1) \\ y(2) \\ \vdots \\ y(n) \end{bmatrix} \quad y \text{ data} \qquad \mathbf{X} = \begin{bmatrix} 1 & x(1) & x(1)^2 \\ 1 & x(2) & x(2)^2 \\ \vdots & \vdots & \vdots \\ 1 & x(n) & x(n)^2 \end{bmatrix} \quad x \text{ data: lagged, interpolated}$$

$$\boldsymbol{\beta} = \begin{bmatrix} a \\ b \\ c \end{bmatrix} \quad \text{parameters} \qquad \boldsymbol{\epsilon} = \sigma_y \begin{bmatrix} r(1) \\ r(2) \\ \vdots \\ r(n) \end{bmatrix} \quad \text{error: homoscedastic, autocorrelated}$$

Montgomery & Peck (1992) Introduction to Linear Regression Analysis, 2nd Edition. Wiley, New York.

Sen & Srivastava (1990)



Autocorrelated errors (persistence)

$$r(i) = \exp\left(\frac{u(i) - u(i+1)}{\tau_y}\right) r(i+1) + \left[1 - \exp\left(2\frac{u(i) - u(i+1)}{\tau_y}\right)\right] \zeta(i)$$

$$\zeta(i) \stackrel{\text{i.i.d.}}{\sim} N(0, 1)$$

τ_y = autocorrelation time, 'memory'

(Robinson 1977)

$V_{i,j} = \exp(-||u(i) - u(j)|| / \tau_y)$ correlation matrix

$\hat{\beta} = (X'V^{-1}X)^{-1} X' V^{-1}y$ estimation

$\chi^2 = (y - X\hat{\beta})' V^{-1} (y - X\hat{\beta})$ sum of squares

$\chi_\nu^2 = \chi^2 / (n - n_p)$ reduced sum of squares

n_p = number of parameters (= 4 for parabolic model)

$\Rightarrow \chi_\nu^2$ allows fit comparison

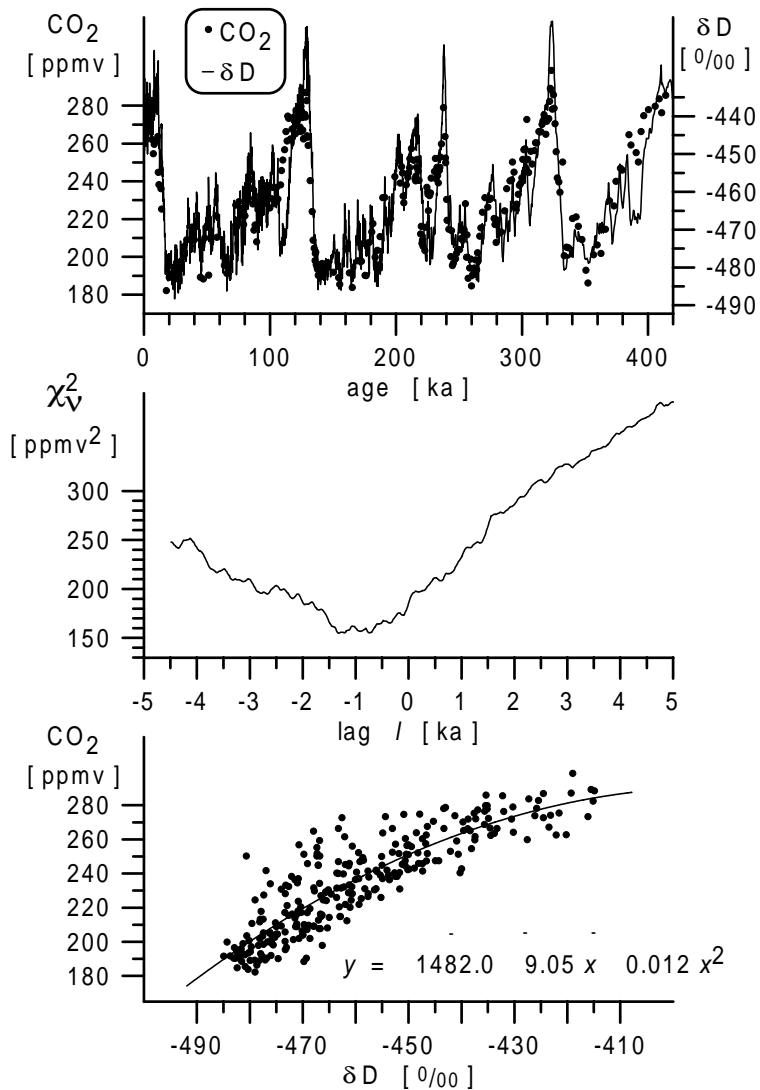
2 search loops: • 'memory' τ_y (0.01 ka increments)

• lag l (0.005 ka increments)

result: • minimal reduced sum of squares, χ^2_ν

• best lag l

- advantages:
- GLS uses persistence information \Rightarrow precise estimation
 - all CO₂ data points contribute \Rightarrow efficient estimation



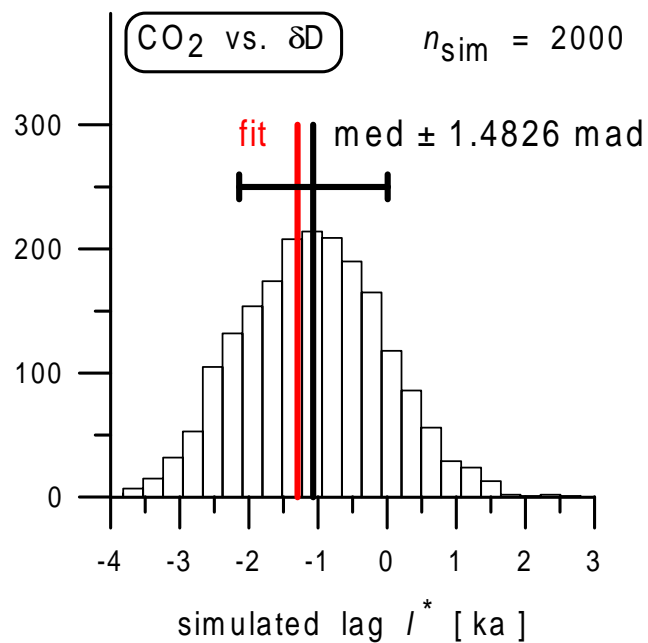
CO₂ versus δD

$$\text{lag } l = -1.3 \pm 1.0 \text{ ka}$$

$$\chi_v^2 = 154.8 \text{ ppmv}^2$$

lag \approx constant (long-term)

results



Bootstrap simulations:

$y = \text{CO}_2$ vs. $x = \delta D$

$u = \text{air-age}$, $t = \text{ice-age}$

$y^* \sim N(\mu = y, \sigma = 2.5 \text{ ppmv}, \tau_y = 0.92 \text{ ka})$

$x^* \sim N(\mu = x, \sigma = 1.0 \text{ ‰}, \tau_x = 2.1 \text{ ka})$

$\left. \begin{matrix} u^* \\ t^* \end{matrix} \right\}$ sedimentation uncertainty

effective: uncertainty (1 ka) of
ice-age/air-age difference

$\text{mad}(l^*) = \text{med}(| l^* - \text{med}(l^*) |)$
 \Rightarrow 'robust std' (Tukey 1977)



τ_x determination:

detrending of $x(i)$,

removal of harmonic components,

AR(1) fits (uneven time spacing)

Mudelsee (2000) TAUEST: a persistence estimation computer program for unevenly spaced weather/climate time series. Computers & Geosciences. [submitted]

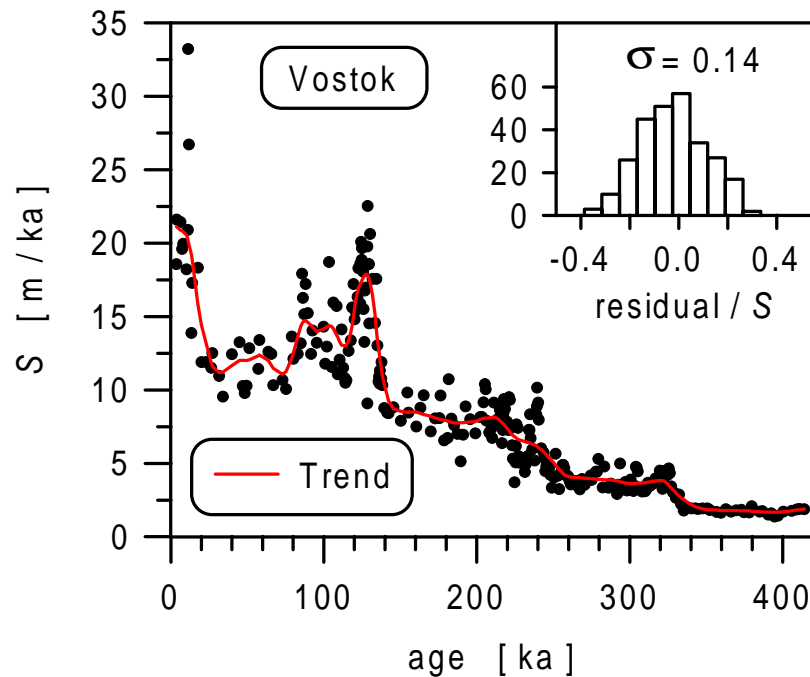
Sedimentation uncertainty

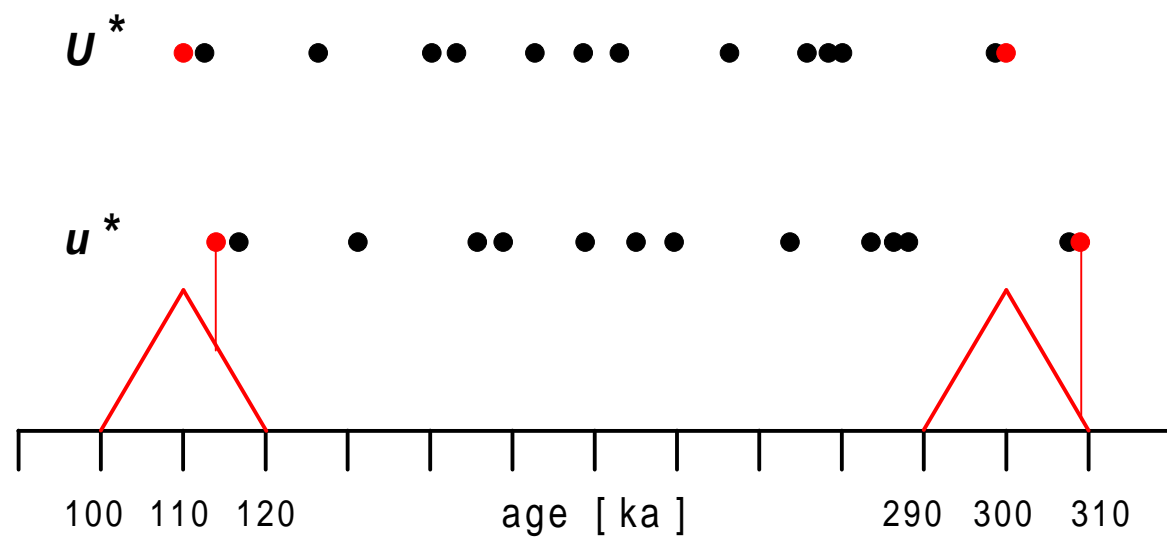
S^* (via depth) $\Rightarrow U^*$

U^* fitted into error range $\Rightarrow u^*$

error range (Petit *et al.* 1999):

- ≤ 5 ka [0; 110 ka] *
- ≤ 10 ka]110 ka; 300 ka]
- ≤ 15 ka]300 ka; 420 ka]





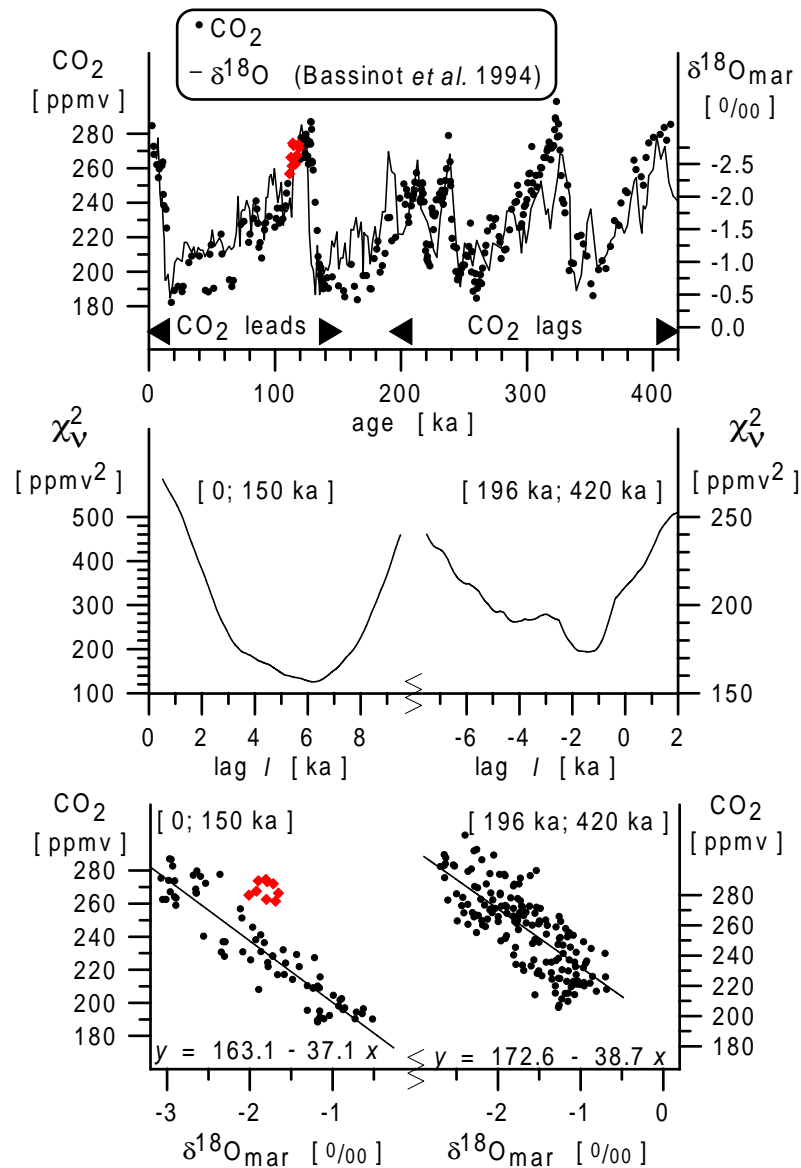
Triangular probability distributions

CO₂ versus temperature

via δD : lag $l = -1.3 \pm 1.0$ ka (CO₂ lags)

CO₂ versus $\delta^{18}\text{O}_{\text{mar}}$

lag change?



$$l = +6.2 \pm 2.7 \text{ ka} \quad [0; 150 \text{ ka}]$$

$$\chi_{\nu}^2 = 127.4 \text{ ppmv}^2$$

$$l = -1.4 \pm 3.7 \text{ ka} \quad [196 \text{ ka; } 420 \text{ ka}]$$

$$\chi_{\nu}^2 = 173.5 \text{ ppmv}^2$$

NB: outliers (substage 5e)

Bootstrap simulations:

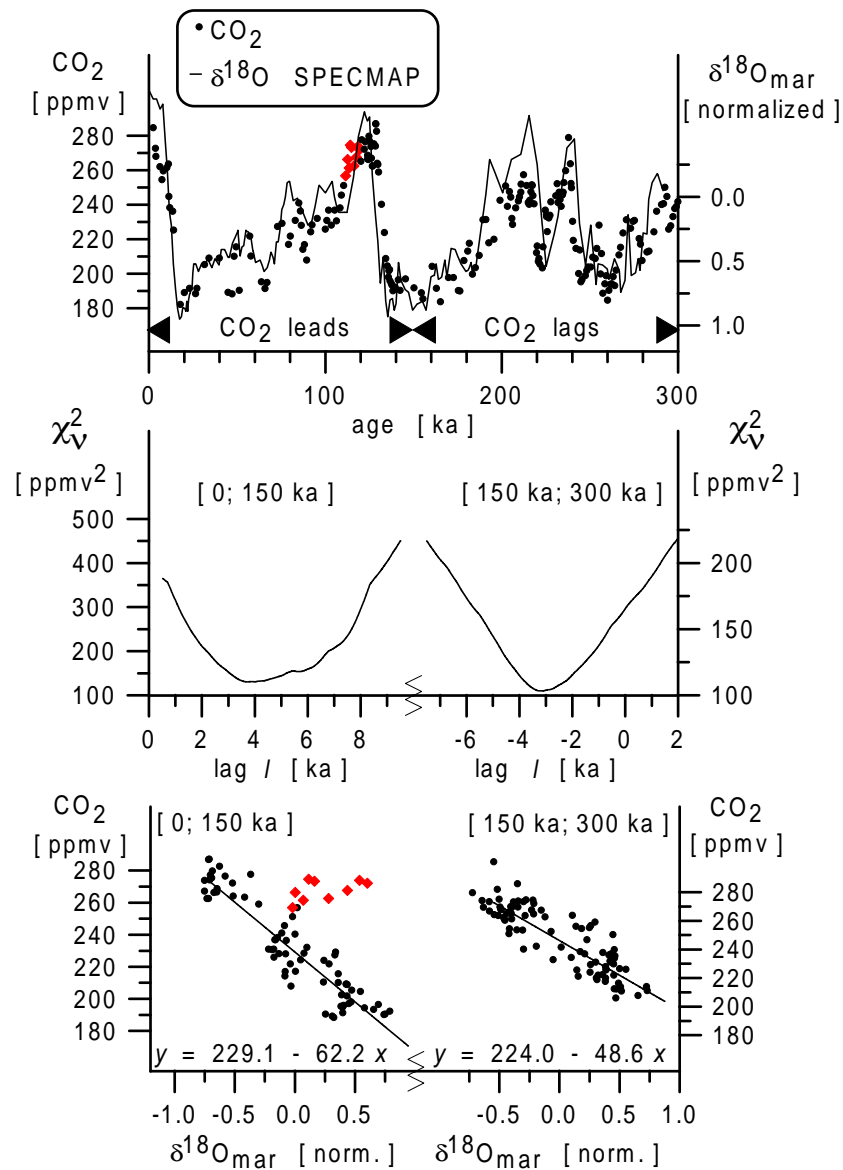
$y = \text{CO}_2$ vs. $x = \delta^{18}\text{O}_{\text{mar}}$ (Bassinot *et al.* 1994)

u = air-age, t = sediment age

$$x^* \sim \text{N}(\mu = x, \sigma = 0.05 \text{ ‰}, \tau_x = 1.9 \text{ ka})$$

$$\left. \begin{matrix} u^* \\ t^* \end{matrix} \right\} \text{ independent}$$

$$t \text{ error} = 5.0 \text{ ka (Bassinot } et al. 1994)$$



CO₂ versus δ¹⁸O_{mar}

lag change?

$$l = +3.7 \pm 2.8 \text{ ka} \quad [0; 150 \text{ ka}]$$

$$\chi^2_\nu = 130.3 \text{ ppmv}^2$$

$$l = -3.2 \pm 4.0 \text{ ka} \quad [150 \text{ ka; } 420 \text{ ka}]$$

$$\chi^2_\nu = 103.3 \text{ ppmv}^2$$

NB: outliers (substage 5e)

results

Bootstrap simulations:

$y = \text{CO}_2$ vs. $x = \delta^{18}\text{O}_{\text{mar}}$ (SPECMAP)

$u = \text{air-age}$, $t = \text{sediment age}$

$$x^* \sim \text{N}(\mu = x, \sigma = 0.045 \text{ ‰}, \tau_x = 1.2 \text{ ka})$$

$$\left. \begin{matrix} u^* \\ t^* \end{matrix} \right\} \text{ independent}$$

t error = 7.0 ka (conservative value)

CO₂ versus $\delta^{18}\text{O}_{\text{air}}$

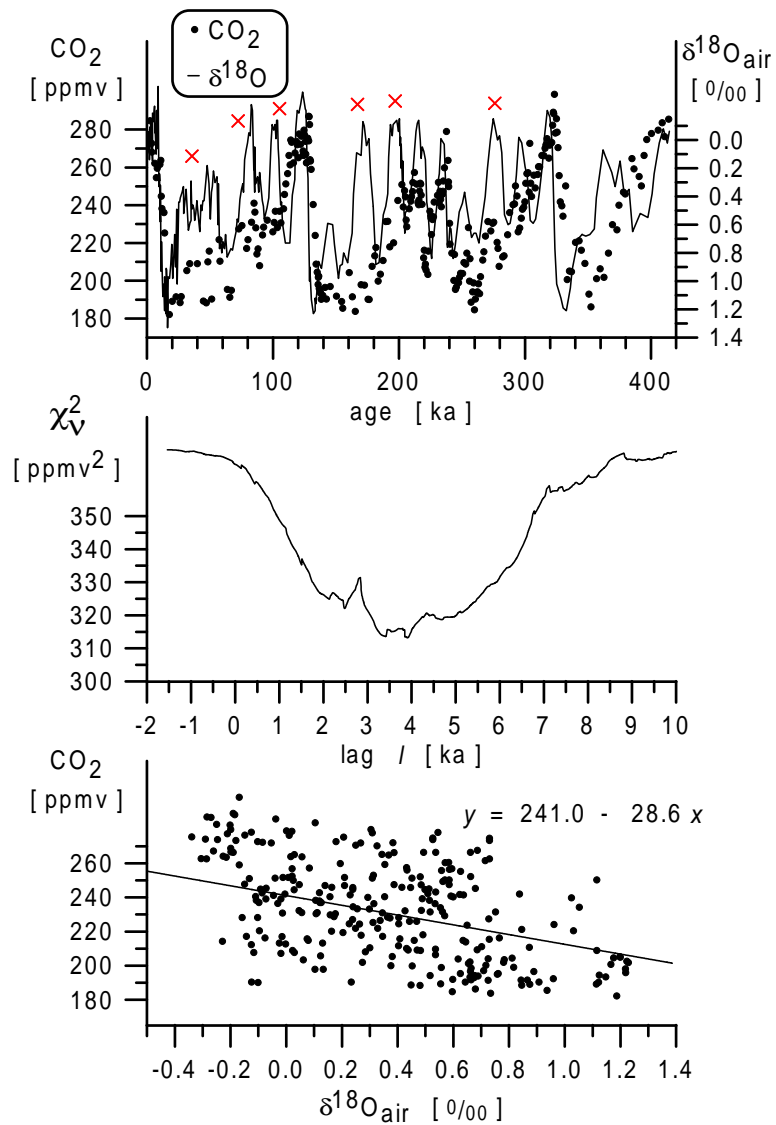
no lag change

$$l = 3.9 \pm 0.5 \text{ ka}$$

high stratigraphic accuracy

$$\chi^2_{\nu} = 313.2 \text{ ppmv}^2$$

\Rightarrow poor fit (Dole effect) ✗



results

Bootstrap simulations:

$$y = \text{CO}_2 \text{ vs. } x = \delta^{18}\text{O}_{\text{air}}$$

$$u = \text{air-age, } t = \text{air-age}$$

$$x^* \sim N(\mu = x, \sigma = 0.1 \text{ ‰}, \tau_x = 4.8 \text{ ka})$$

σ : conservative value

$$\left. \begin{matrix} u^* \\ t^* \end{matrix} \right\} \text{ totally dependent}$$

CO₂ versus $\delta^{18}\text{O}_{\text{air}}$ -derived ice volume

subtract atmospheric turnover time (O₂) of 2 ± 1 ka

\Rightarrow lag $l = 1.9 \pm 1.1$ ka (CO₂ leads)

CO₂ versus $\delta^{18}\text{O}_{\text{mar}}$ -derived ice volume

core MD900963, young interval: $l = 6.2 \pm 2.7$ ka

SPECMAP, young interval: $l = 3.7 \pm 2.8$ ka

average: $l = 5.0 \pm 1.9$ ka

CO₂ versus ice volume

via $\delta^{18}\text{O}_{\text{air}}$: lag $l = 1.9 \pm 1.1$ ka

via $\delta^{18}\text{O}_{\text{mar}}$, young interval: lag $l = 5.0 \pm 1.9$ ka

- interpolation error/poor fit quality might explain discrepancy
- $\delta^{18}\text{O}_{\text{air}}$: stratigraphic accuracy outweighs limited proxy quality
- no lag change: timescale errors in early part > than reported

Best guess: average:

\Rightarrow CO₂ leads over ice volume by $l = 2.7 \pm 1.3$ ka

Conclusion:

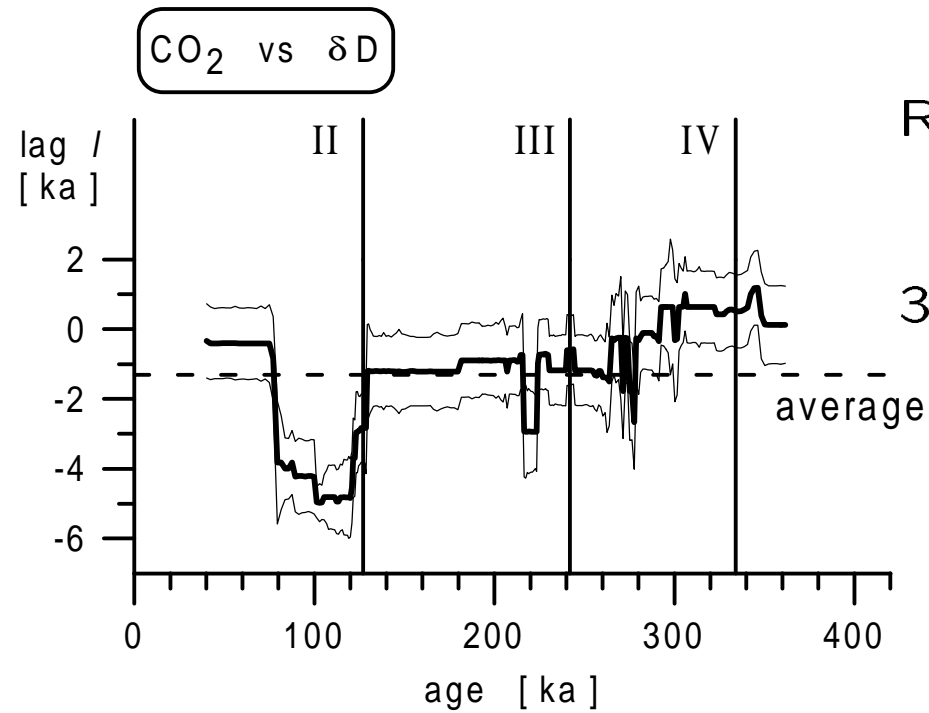
in the last 420 ka:

CO₂ variations lag behind temperature (δD) variations:

$$l = -1.3 \pm 1.0 \text{ ka}$$

CO₂ variations lead over ice-volume (via $\delta^{18}\text{O}_{\text{air}}$, $\delta^{18}\text{O}_{\text{mar}}$) variations:

$$l = 2.7 \pm 1.3 \text{ ka}$$



Running window:

38 points (55 ka on average)

results

Shackleton (2000)

- $\delta^{18}\text{O}_{\text{air}}$ better ice-volume proxy than $\delta^{18}\text{O}_{\text{mar}}$
- CO_2 and temperature in phase
 - \Leftarrow his estimation error (2.5 ka) too large to detect lag of CO_2 (1.3 ka)
- CO_2 leads ice volume by 14 ± 2.5 ka
 - \Leftarrow his estimations relative to ETP—lost accuracy (CO_2 vs. $\delta^{18}\text{O}_{\text{air}}$)
 - \Leftarrow timescale uncertainties taken into account?
 - \Leftarrow here: lag $l = \text{average}$ over periods of variation