

ESS 431 PRINCIPLES OF GLACIOLOGY
ESS 505 THE CRYOSPHERE

**Geochemistry of Ice Cores:
Stable Isotopes, Gases, and
Past Climate**

NOVEMBER 23, 2016

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Sources

Lecture notes by

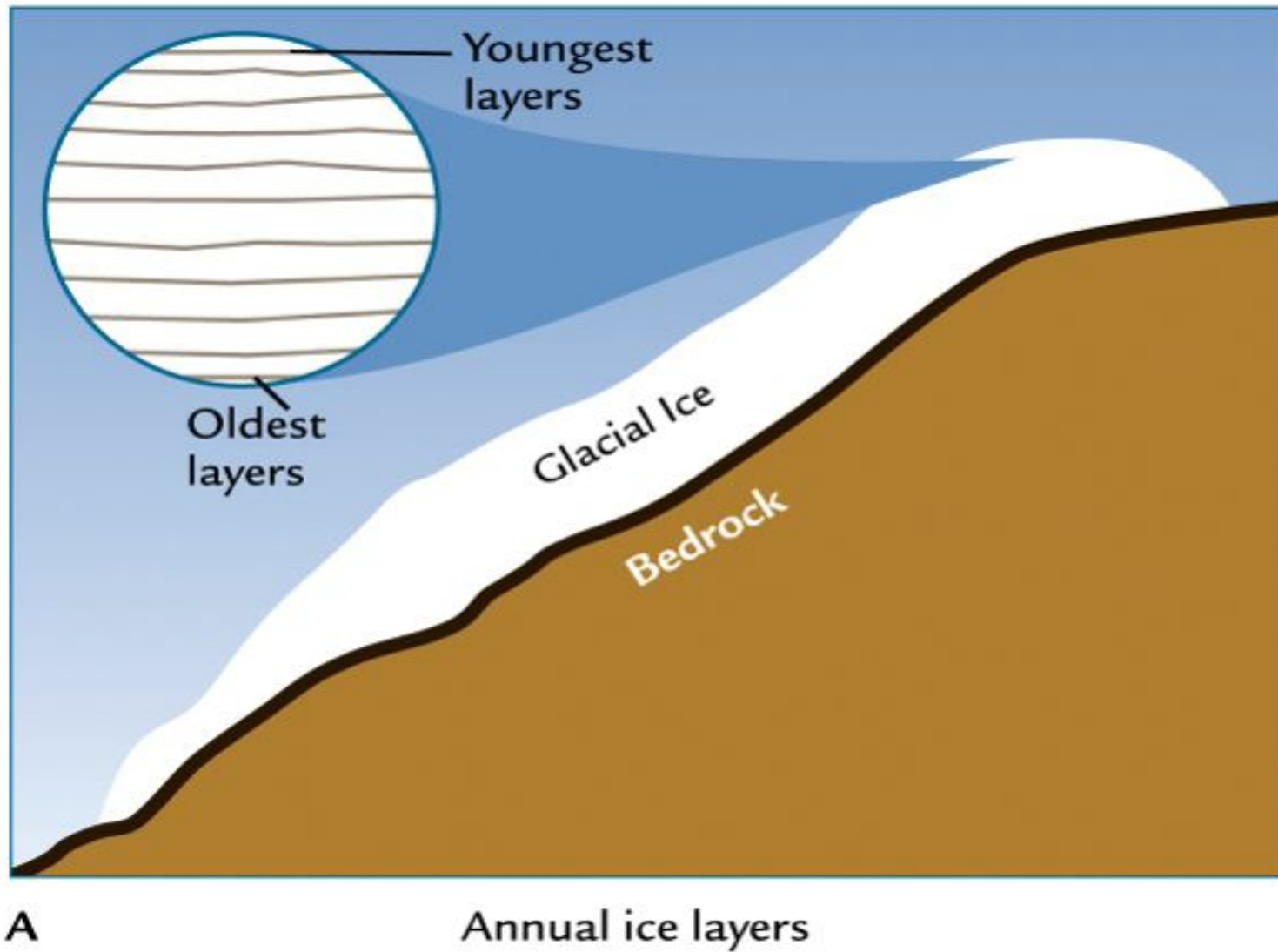
- Eric Steig
- Steve Warren

Many publications in

- *Nature*
- *Science*
- *Journal of Glaciology*
- *Annals of Glaciology*
- *Journal of Geophysical Research*
- *Climate of the Past*

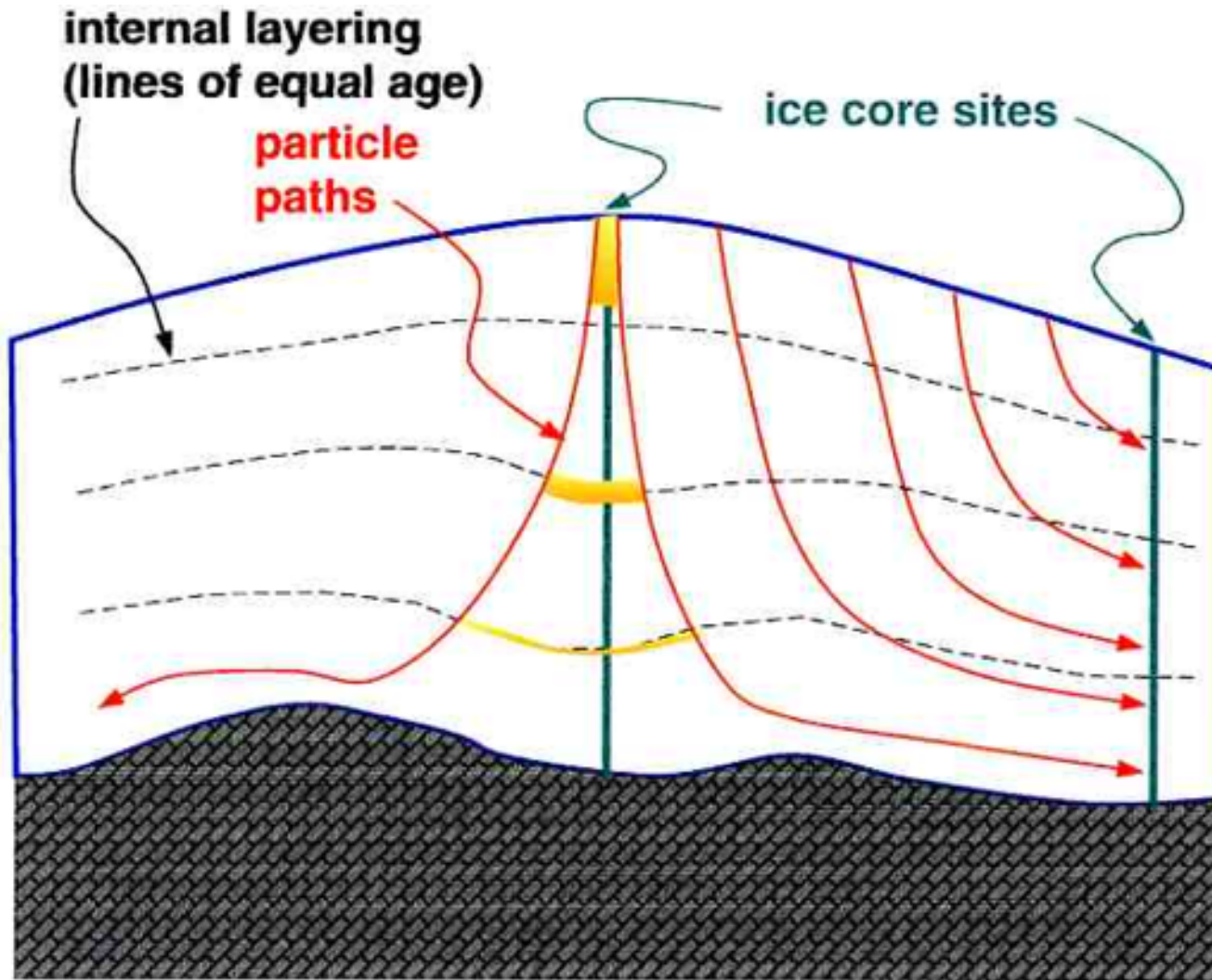
Conversations with many colleagues

Ice Cores



Choosing an Ice-Core Site

Near the summit is good.



- Ice is colder
- Climate signal relates to the same place for ice of all ages.

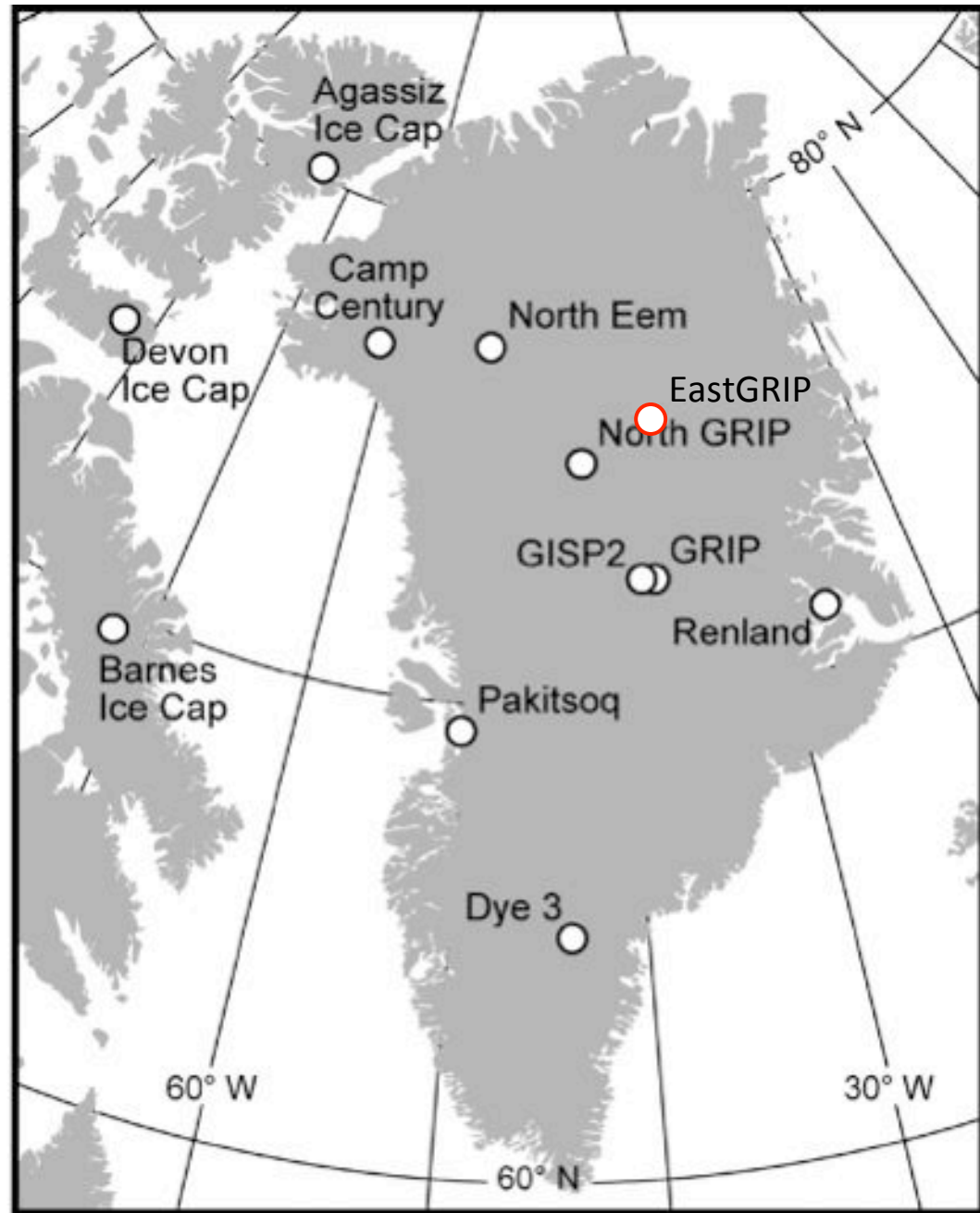
Layers get thinner over time due to flow.

- When are layers too thin to resolve annual signal?

Arctic Ice-core Sites

Cuffey and Paterson 2010.
The Physics of Glaciers.
Fig. 15.1

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Ice Core at Greenland Summit

- Greenland Ice Sheet Project 2 (GISP2)
- The drill inside this dome reached bedrock 3 km (10,000 ft) below the ice-sheet surface.
- The science team recovered a record of past climate going back more than 100,000 years.





Inside the GISP2 Drill Dome

- The drill is lowered into the hole on a long cable.
- It brings up a 6-meter-long piece of ice core on each run.



Where Are All the Scientists?

- This is not what you think it is.
- All the scientists are hard at work underground.
- This is the front door to the GISP2 Science Laboratory.





Science in a Labyrinth

- Ice cores are analyzed in Labs connected by tunnels under the snow.



UW Stable Isotope Lab

- All the comforts of the UW campus at -30 degrees C.
- These scientists will determine how cold it was in Greenland in the Last Ice Age.



Electrical Conductivity Method (ECM)

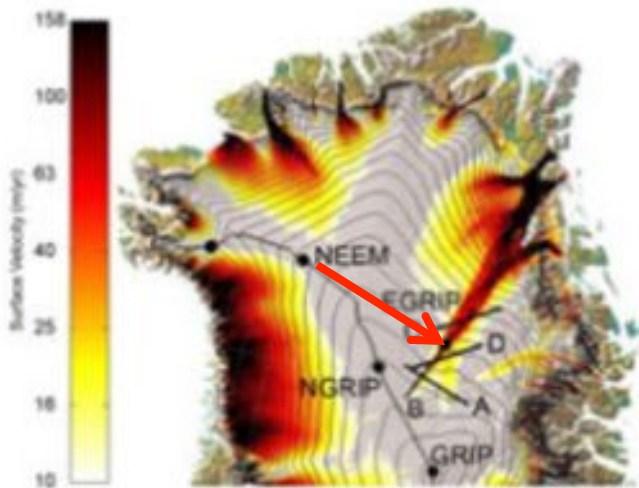
- This experiment detects *volcanic ash* in the ice.
- It also detects *ammonia* released by gigantic prehistoric forest fires – (But where? Probably not in Greenland).



A Natural Freezer

- The cores are stored in a cave dug in the snow, where the temperature is always -30° Celsius.
- oops ... the ceiling is sagging a little bit after 3 years ...

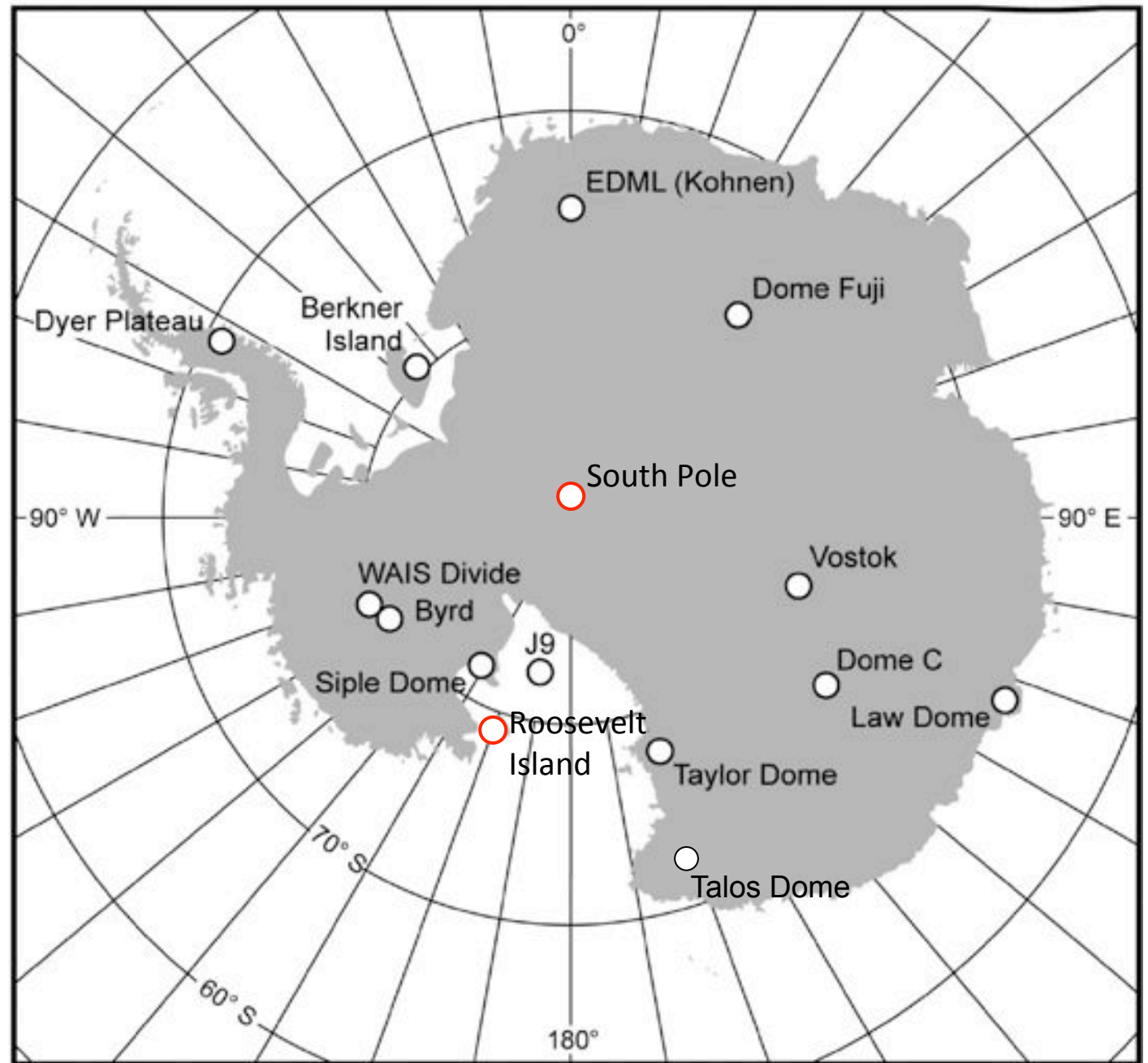
EastGRIP core site 2016



In 2015, the NEEM drill dome was hauled by tractor 440 km to eGRIP, eliminating the need to take it apart, fly it to the coast, then fly it back onto the ice sheet and rebuild it the next summer.

<http://eastgrip.org/>

b



Base map:
Cuffey and Paterson
2010. *The Physics of
Glaciers*. Fig. 15.1

Where might this
be?

Vostok Station,
East Antarctica



S.G.Warren photo

Vostok Station,
East Antarctica



S.G.Warren



S.G.Warren



S.G.Warren





S.G.Warren



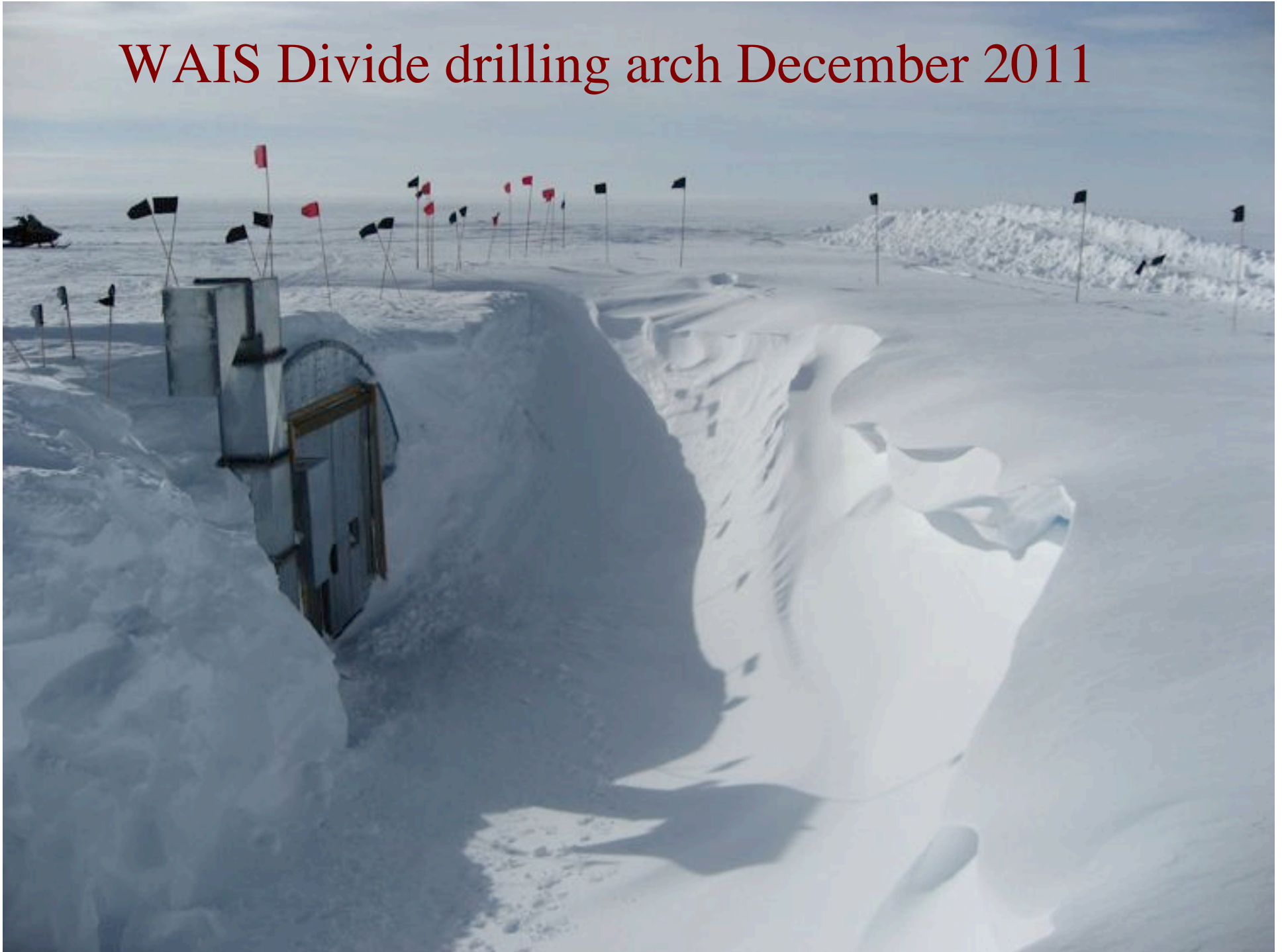
S.G.Warren

WAIS Divide drilling arch Jan 2006



WAIS <http://www.waisdivide.unh.edu/>

WAIS Divide drilling arch December 2011



WAIS Tilting-Tower drill



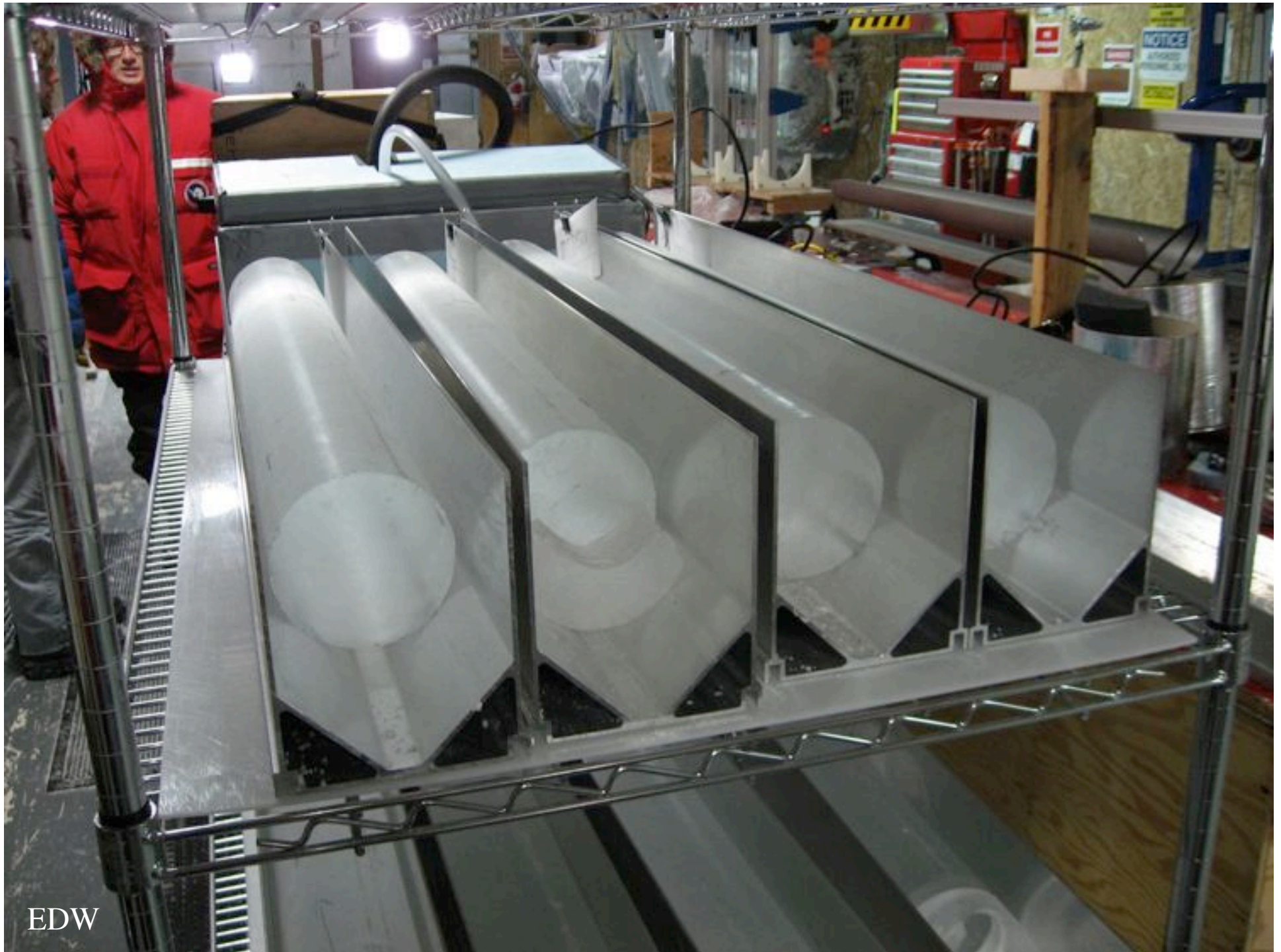
WAIS <http://www.waisdivide.unh.edu/>



EDW



EDW



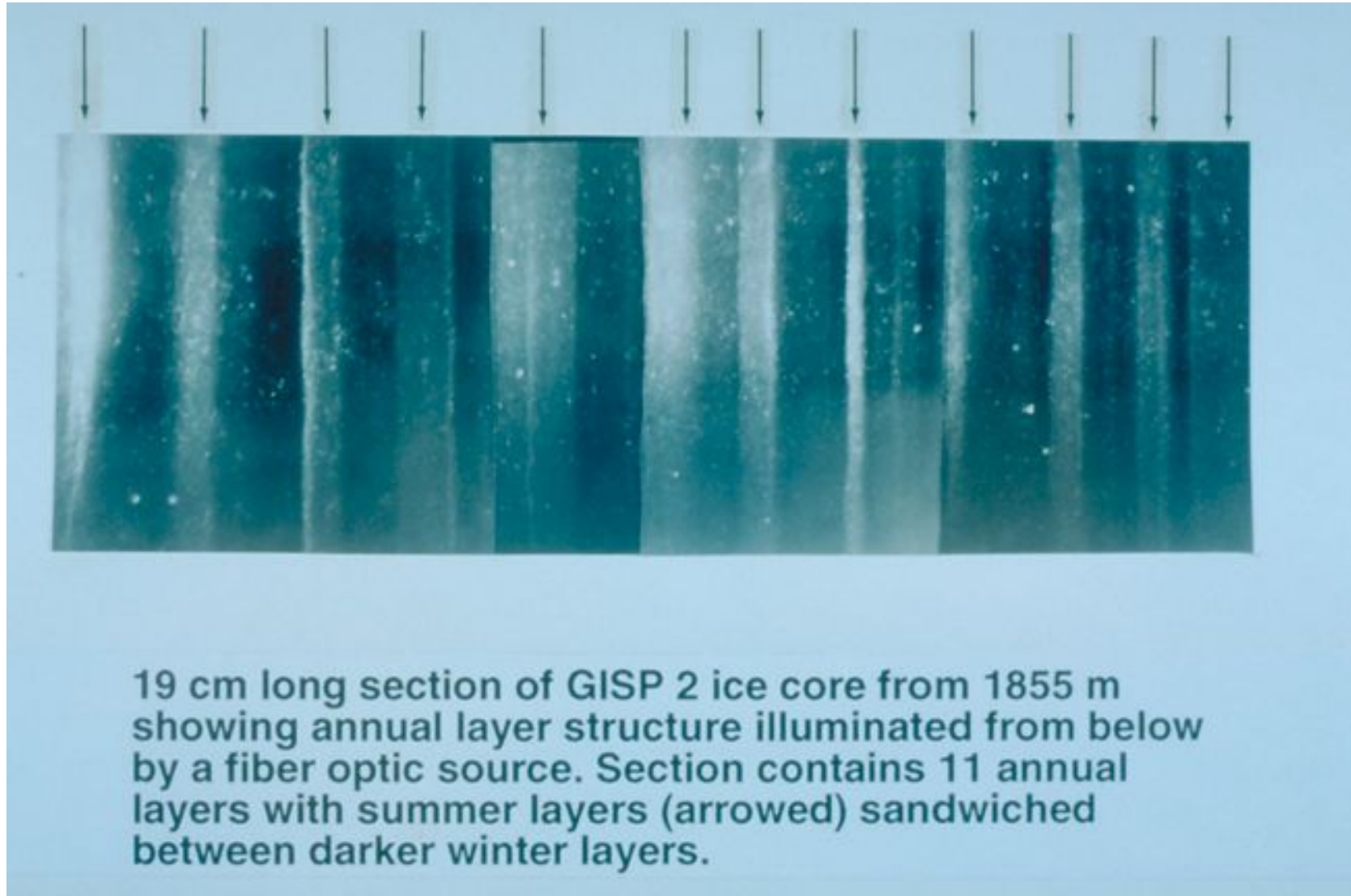
EDW

Ash layer in WAIS core

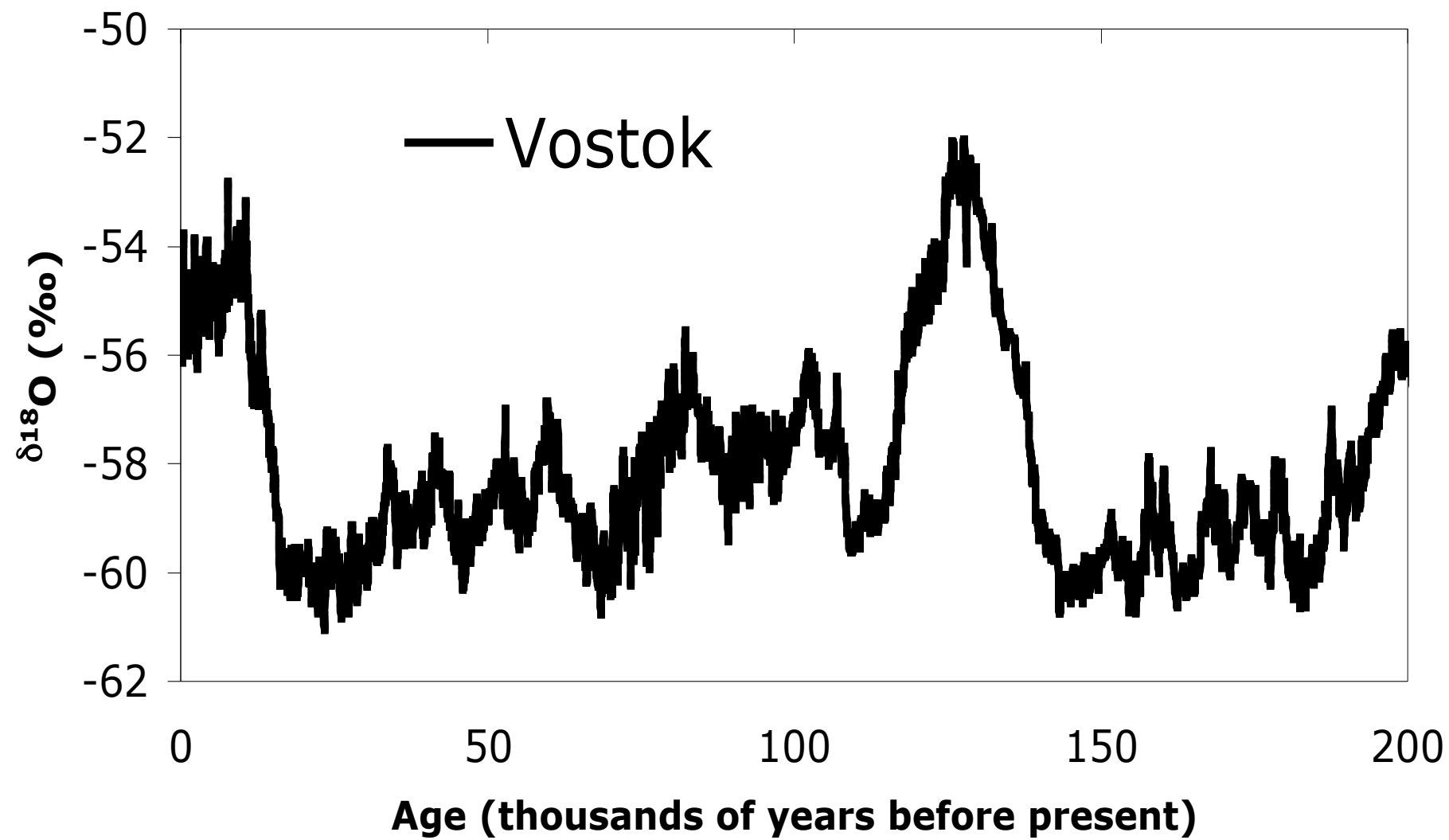


WAIS <http://www.waisdivide.unh.edu/>

Dating an Ice Core



GISP2 ice core, ~20,000 years old



^{18}O – What is it?

- Normal Oxygen is ^{16}O , with 8 neutrons.
- ^{18}O has 2 extra neutrons

H																		He
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub							
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Oxygen isotopes in ice cores

H₂O is composed of both H₂¹⁶O and H₂¹⁸O

$$\delta^{18}O_{ice} = \frac{\left(\frac{H_2^{18}O}{H_2^{16}O}\right)_{ice} - \left(\frac{H_2^{18}O}{H_2^{16}O}\right)_{SMOW}}{\left(\frac{H_2^{18}O}{H_2^{16}O}\right)_{SMOW}} \times 1000 \text{ ‰}$$

Deuterium isotopes in ice cores

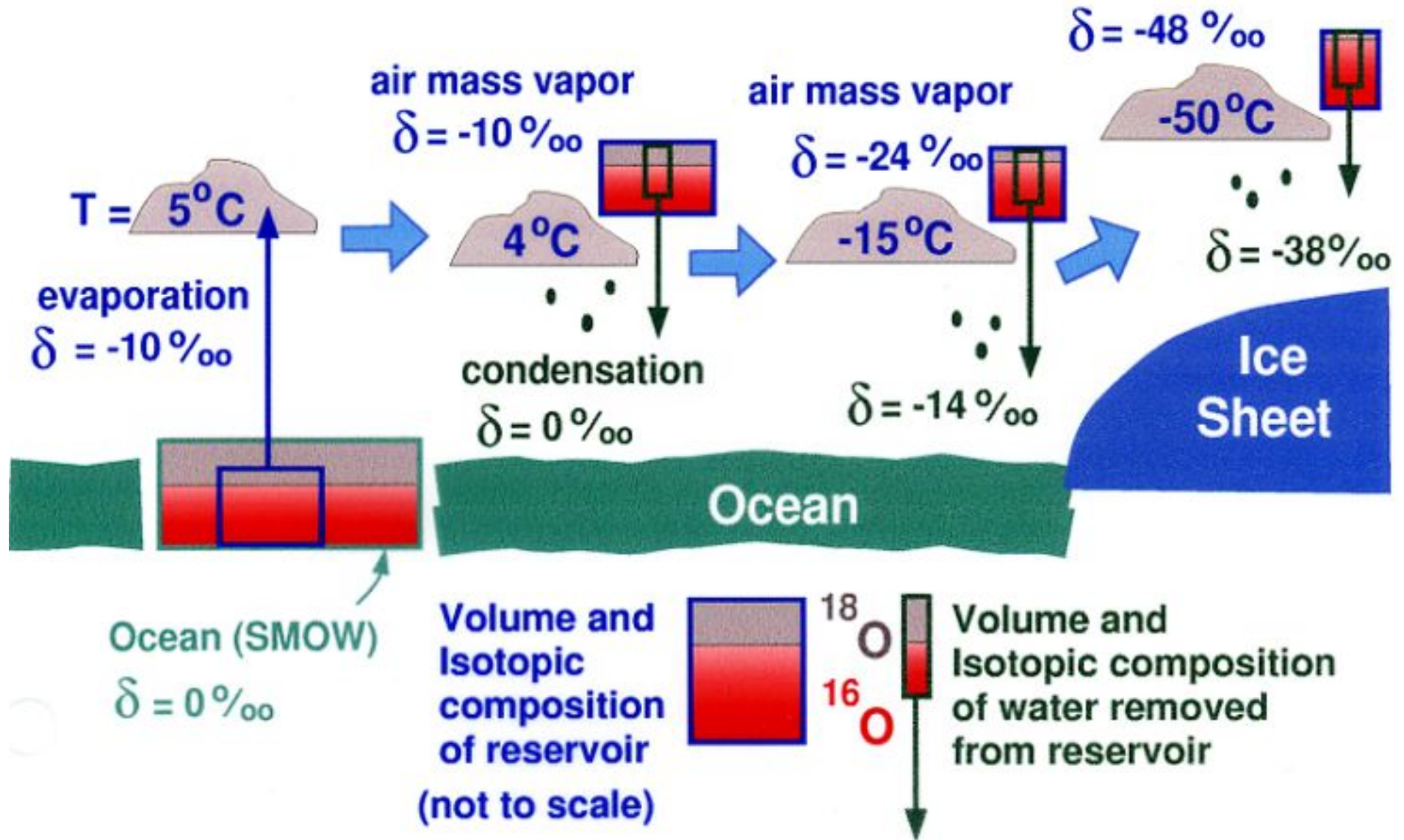
H₂O also contains heavy hydrogen (²H), also known as deuterium (D).

$$\delta D_{ice} = \frac{\left(\frac{D}{H}\right)_{ice} - \left(\frac{D}{H}\right)_{SMOW}}{\left(\frac{D}{H}\right)_{SMOW}} \times 1000 \text{ ‰}$$

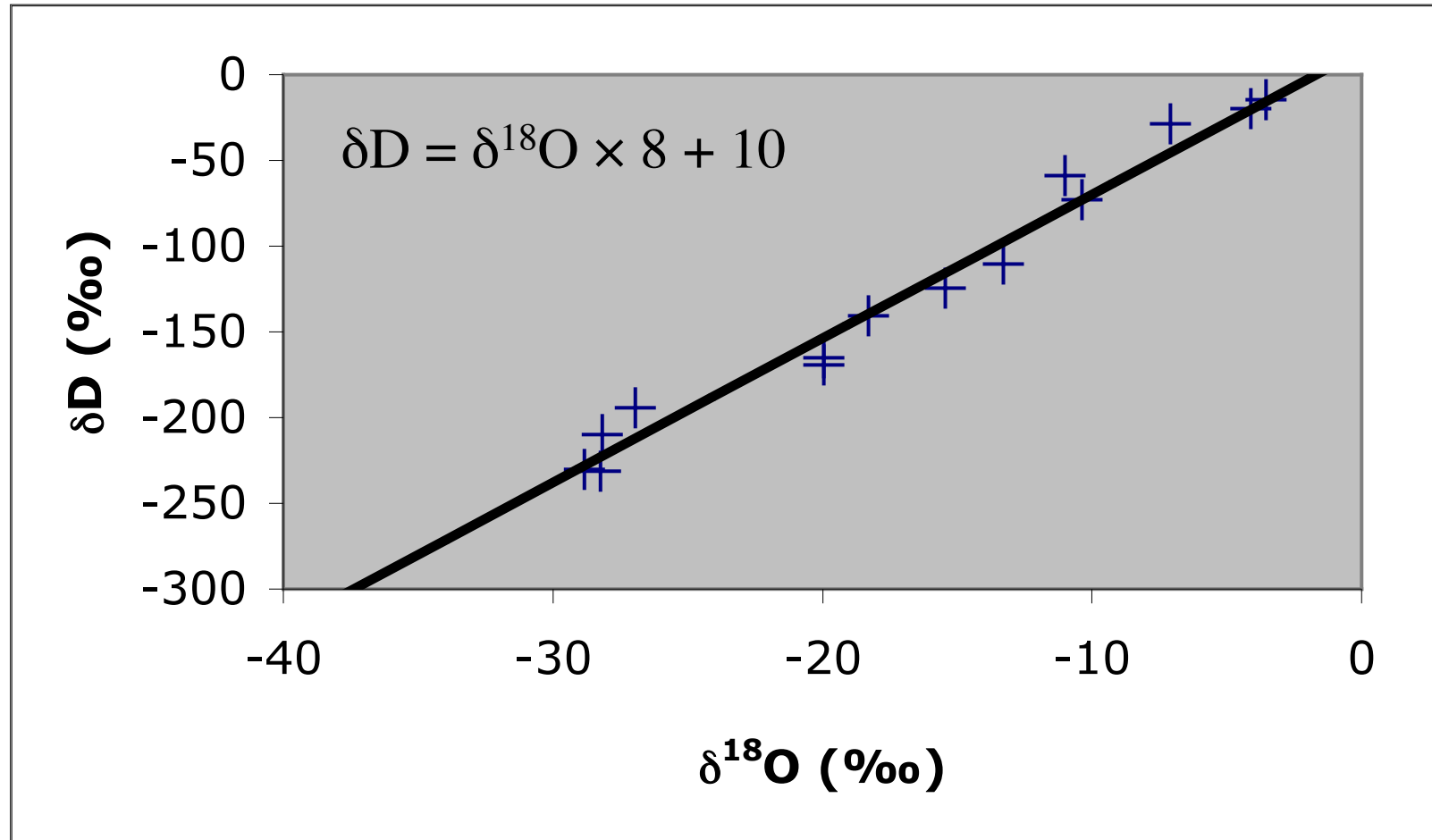
What is fractionation?

- ^{18}O and ^{16}O act the same way in chemical reactions (they are both oxygen molecules)
- They differ in subtle ways during phase changes.
- ^{18}O has a slightly greater tendency to be in the lower-energy state.
- During evaporation, the vapor is slightly depleted in ^{18}O relative to the water.
- During condensation, the condensing water is slightly enriched in ^{18}O relative to the vapor.

$\delta^{18}\text{O}$ as a Temperature Proxy

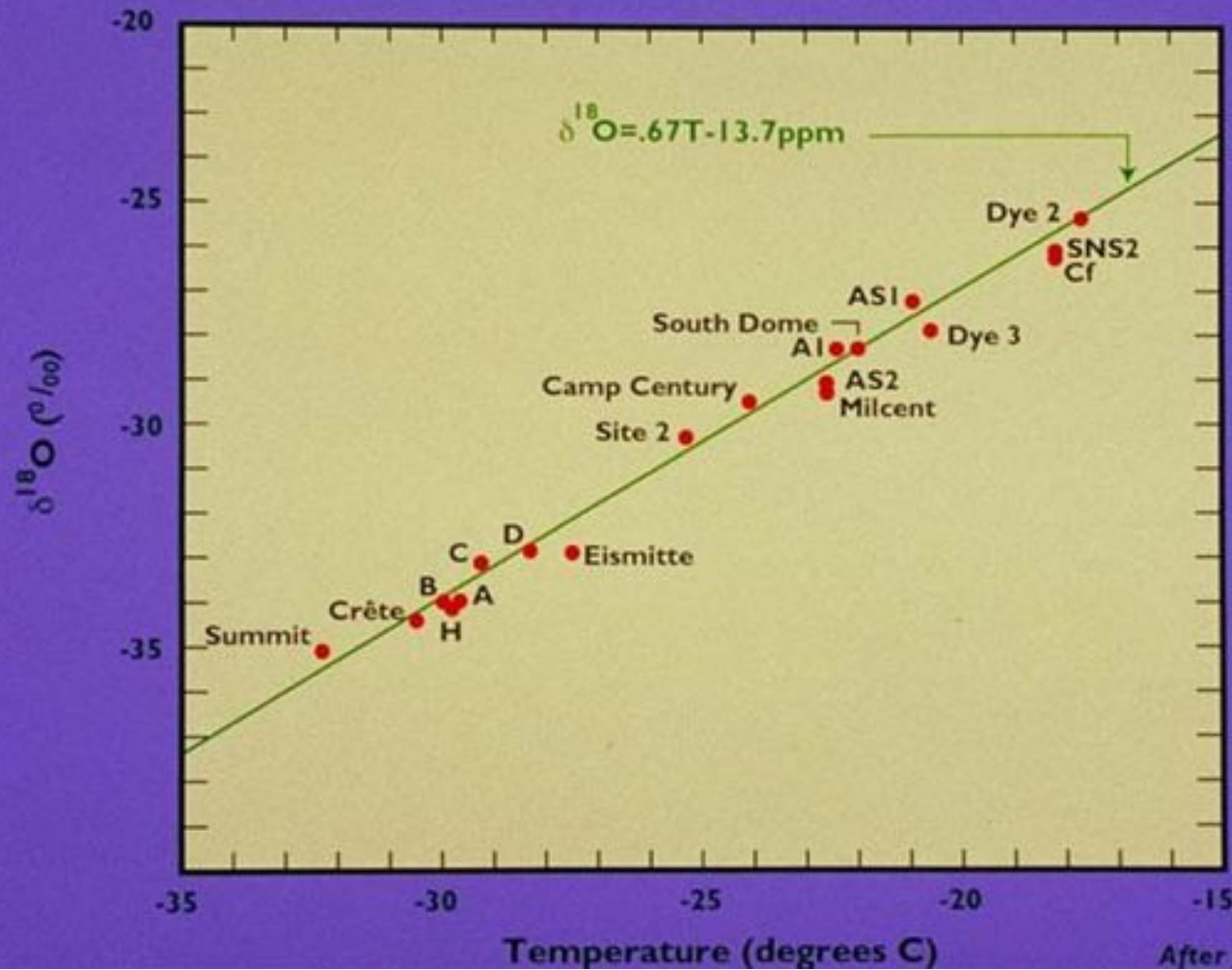


Global Meteoric Water Line



$$\text{deuterium excess} = d = \delta\text{D} - \delta^{18}\text{O} \times 8$$

Modern mean annual values of $\delta^{18}\text{O}$ and snowpack temperature from the Greenland Ice Sheet show an extremely close correspondence.



After Johnsen et al. (1988)

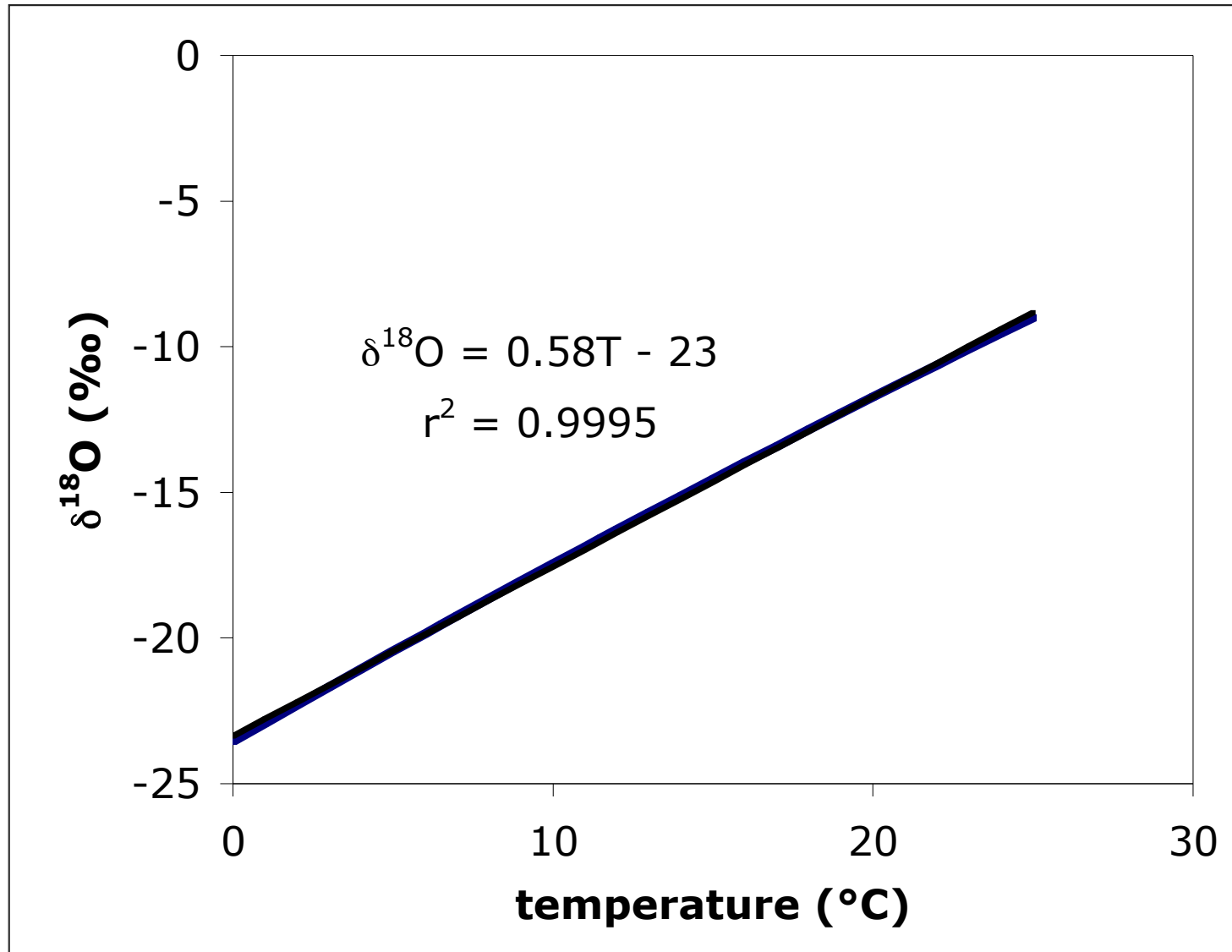
Rayleigh Distillation

Start with a saturated air mass above the ocean surface

Assume that:

- 1) As the air travels poleward, it cools adiabatically.
- 2) The amount of water vapor remaining in the air at any point is determined by the saturation vapor pressure of water.
- 3) All isotopic exchange occurs in equilibrium.
- 4) Once water condenses, it does not re-evaporate.
- 5) No new water is added to the air mass.**

$\delta^{18}\text{O}$ vs air temperature



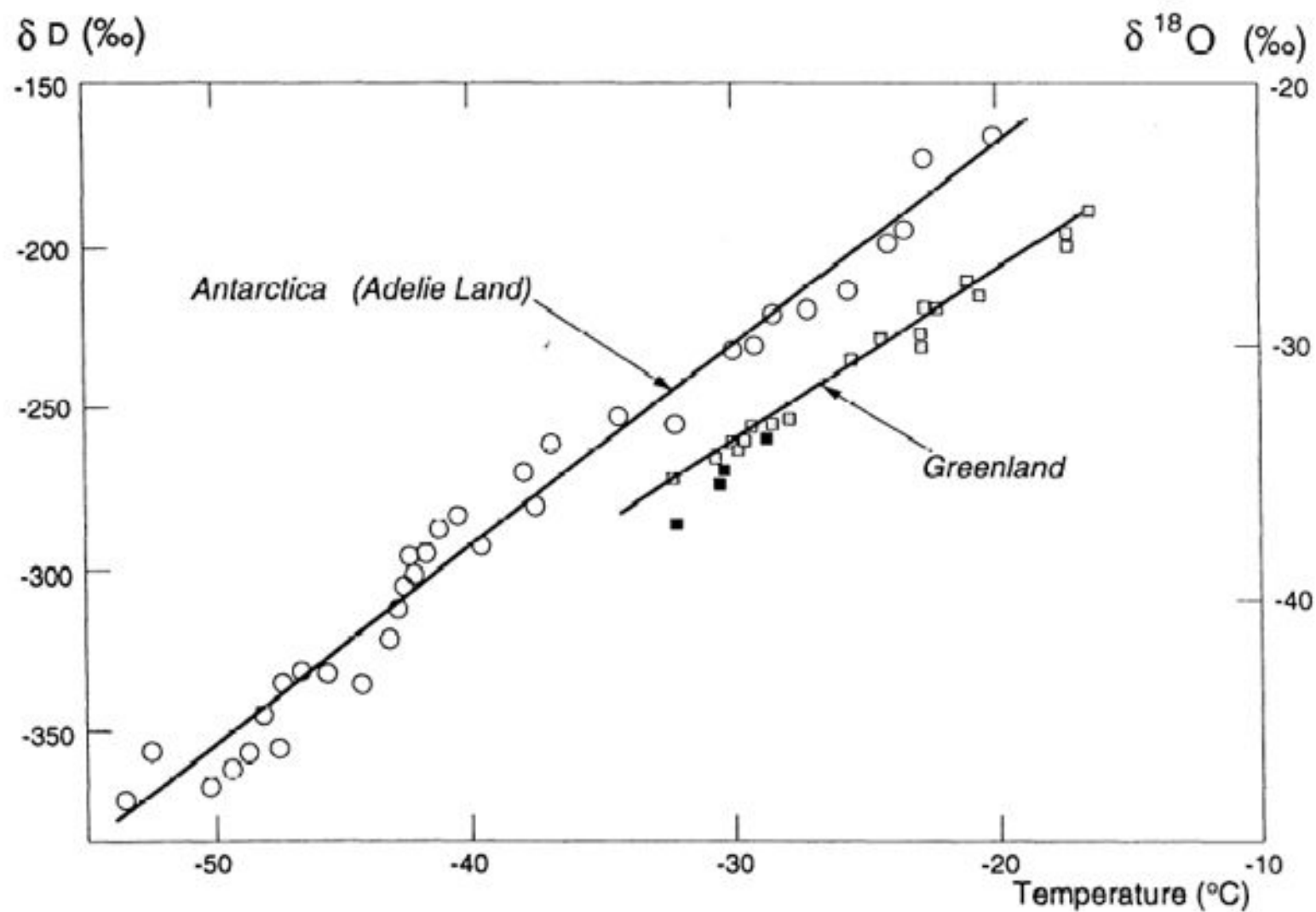
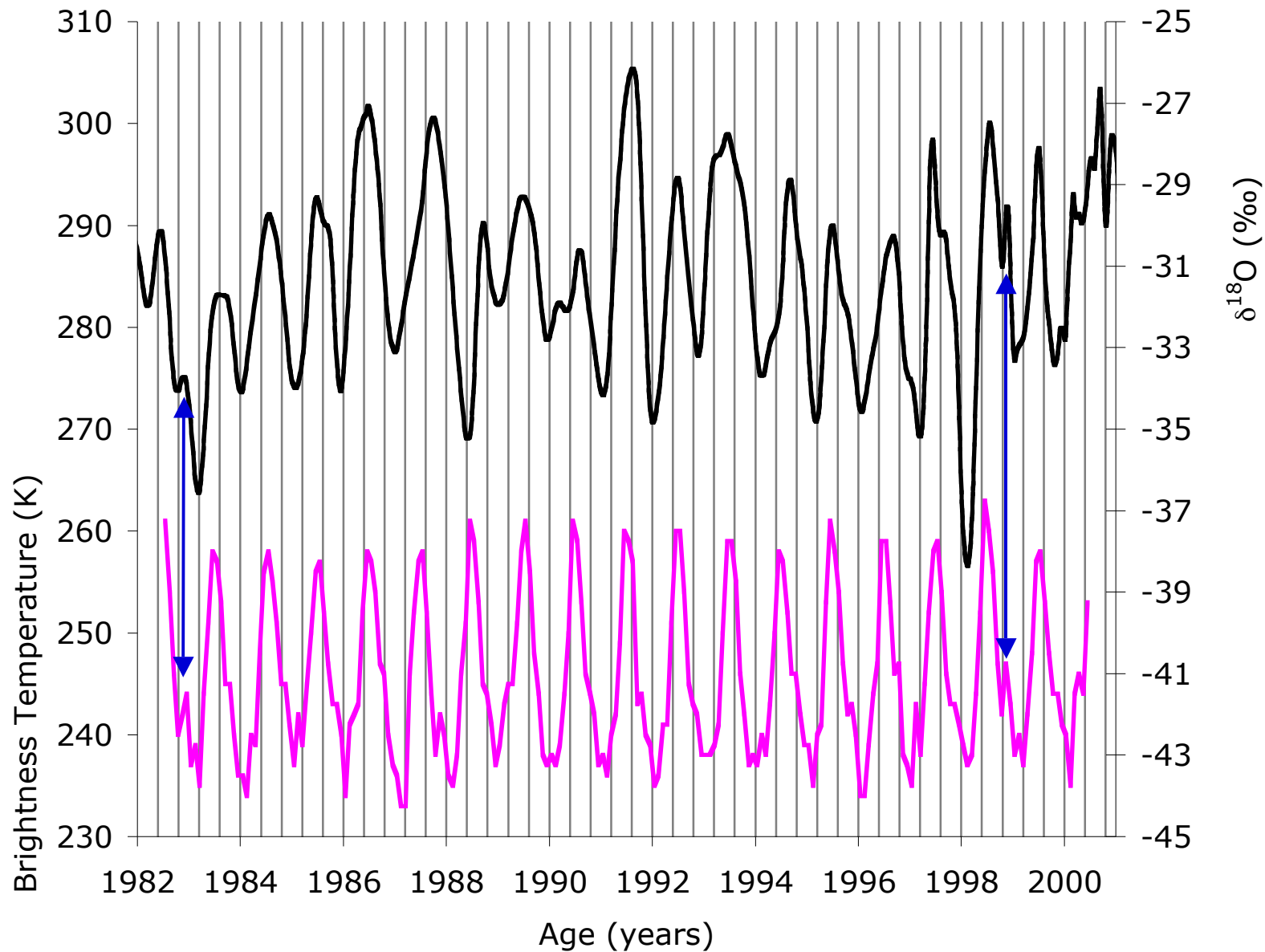
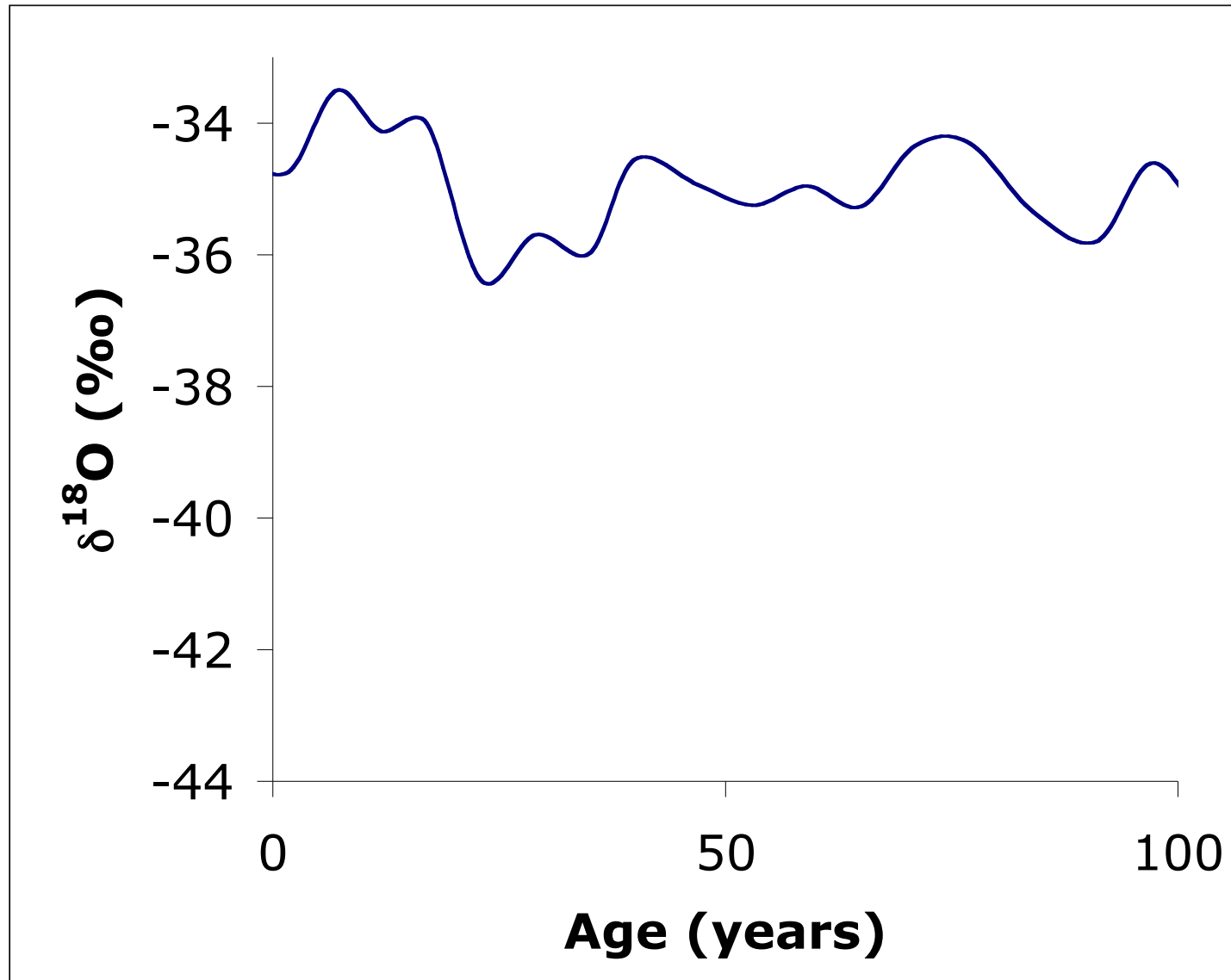


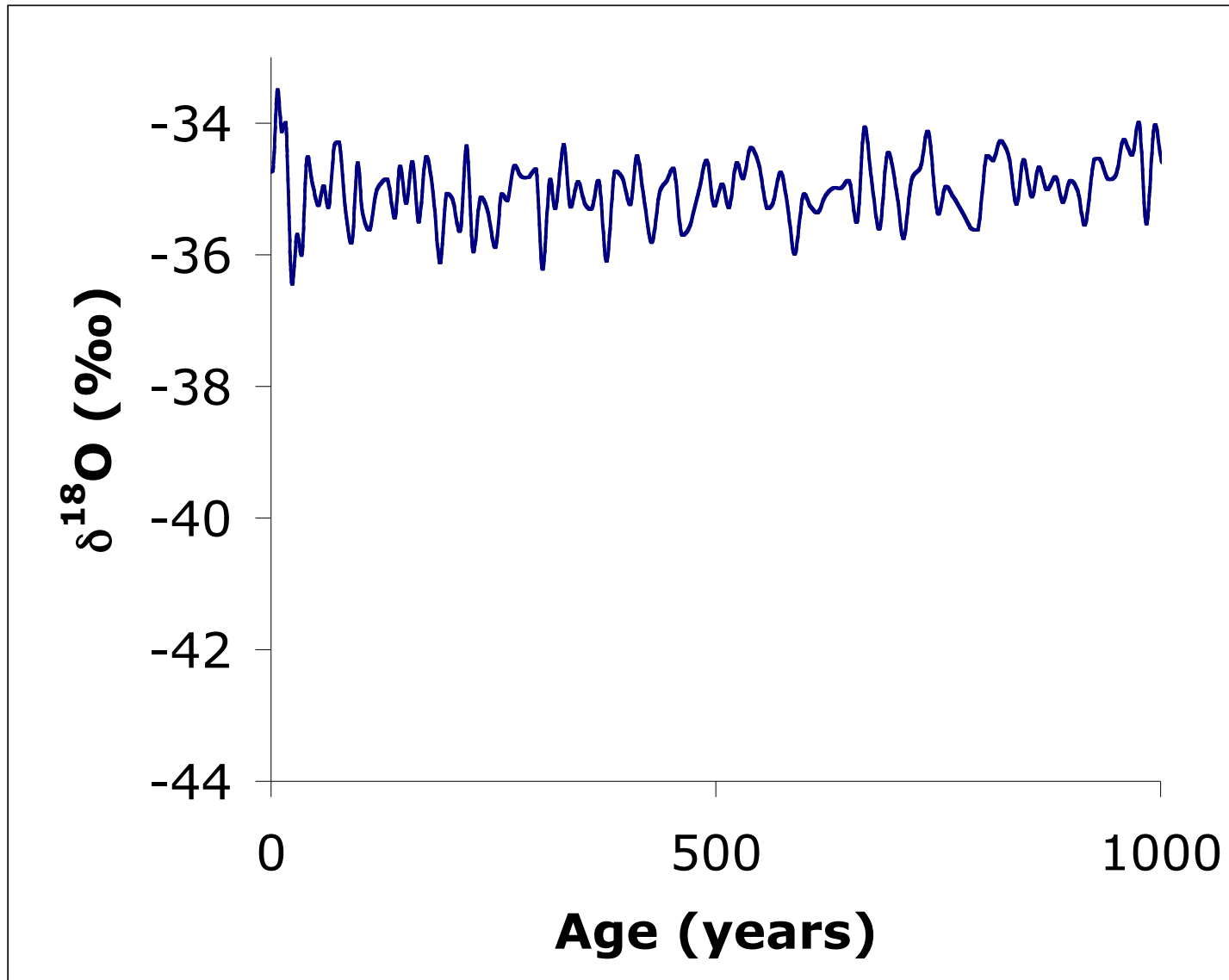
Figure 1. Isotope content of snow versus local surface temperature (annual average). Antarctic data (δD , left scale) are from *Lorius and Merlivat [1977]*, and Greenland data ($\delta^{18}O$, right scale) are from *Johnsen et al. [1989]*.



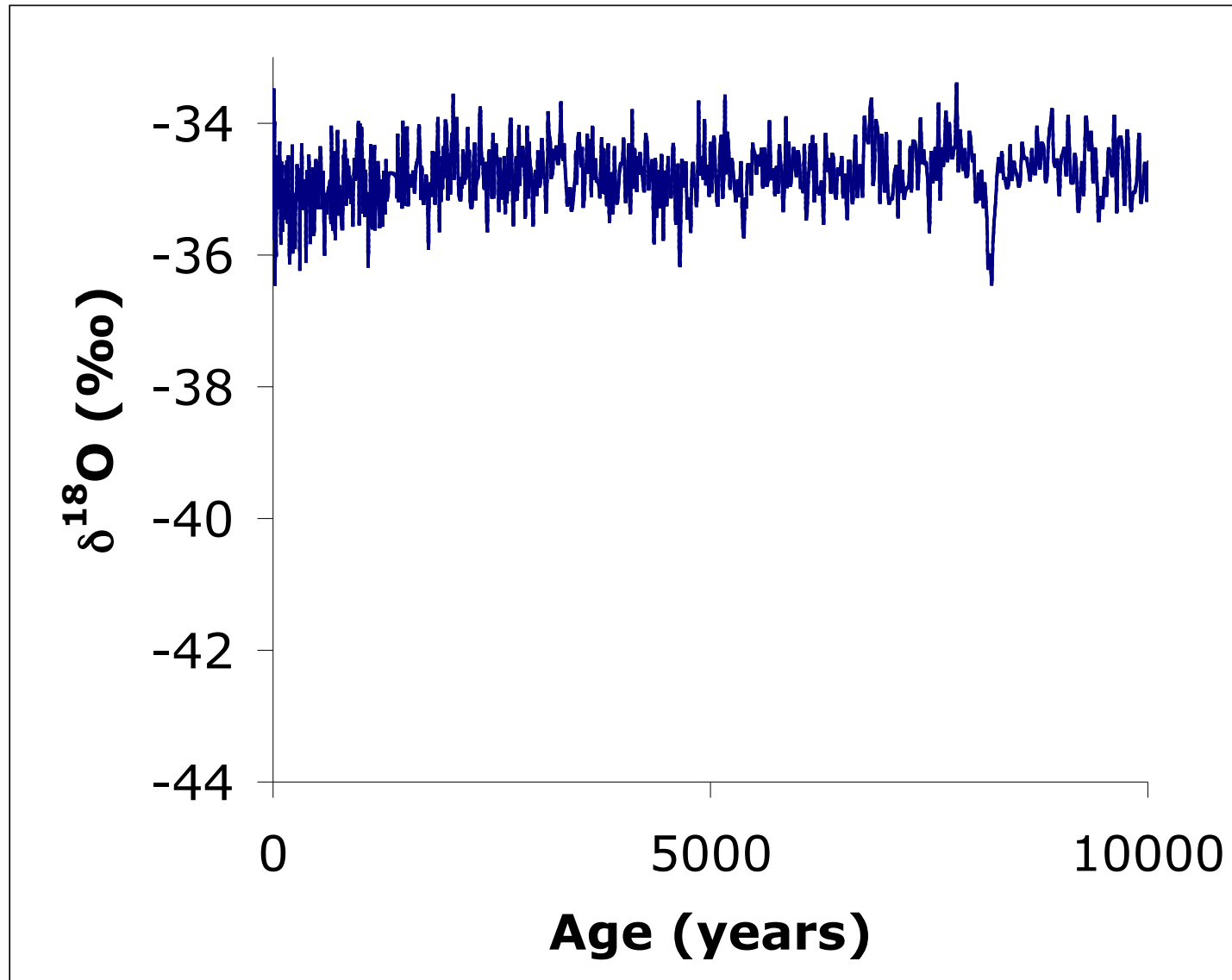
Surface temperature from satellites generally agrees with temperatures inferred from $\delta^{18}\text{O}$ in shallow ice cores covering the same time period.



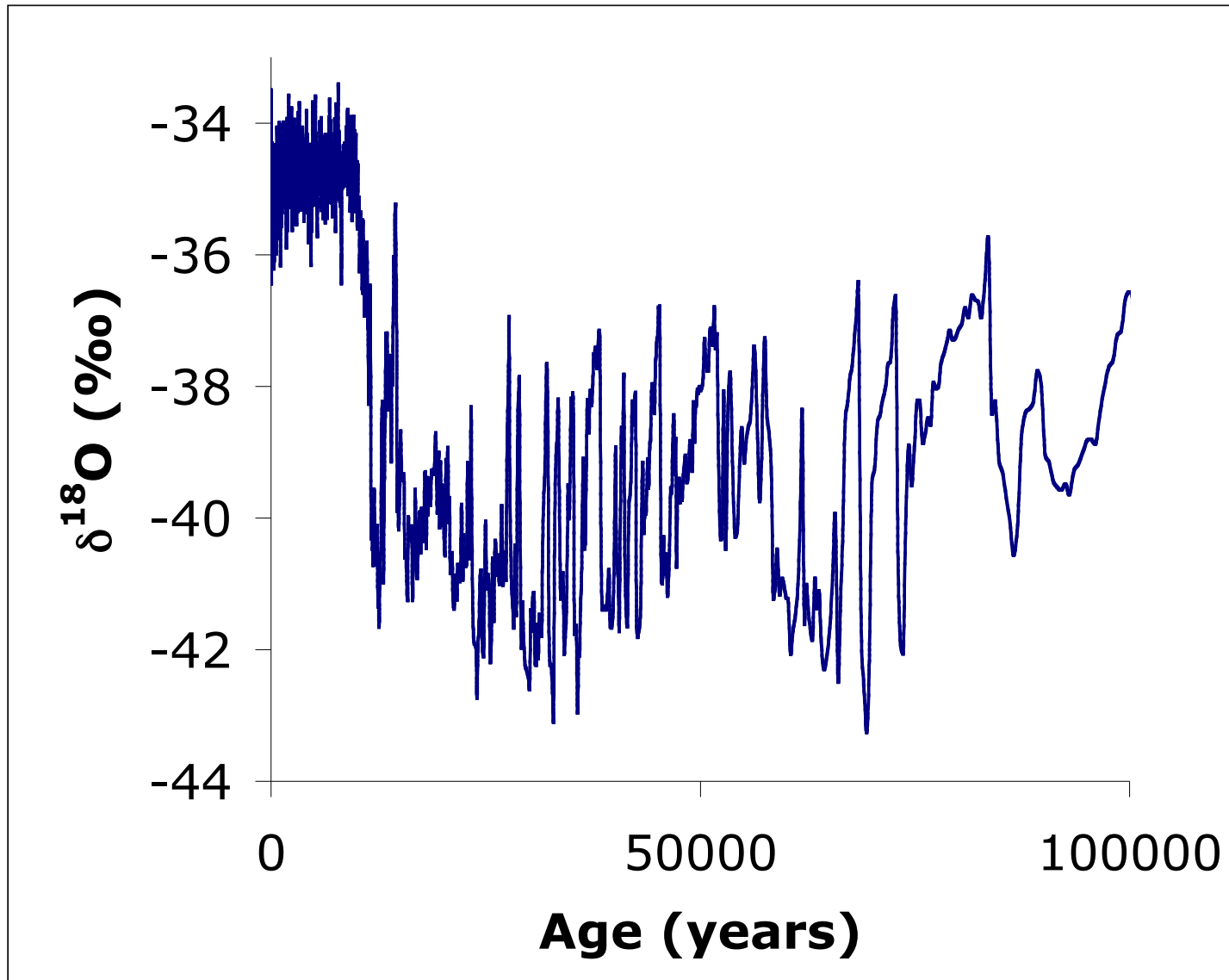
$\delta^{18}\text{O}$ in GISP2 ice core (central Greenland)



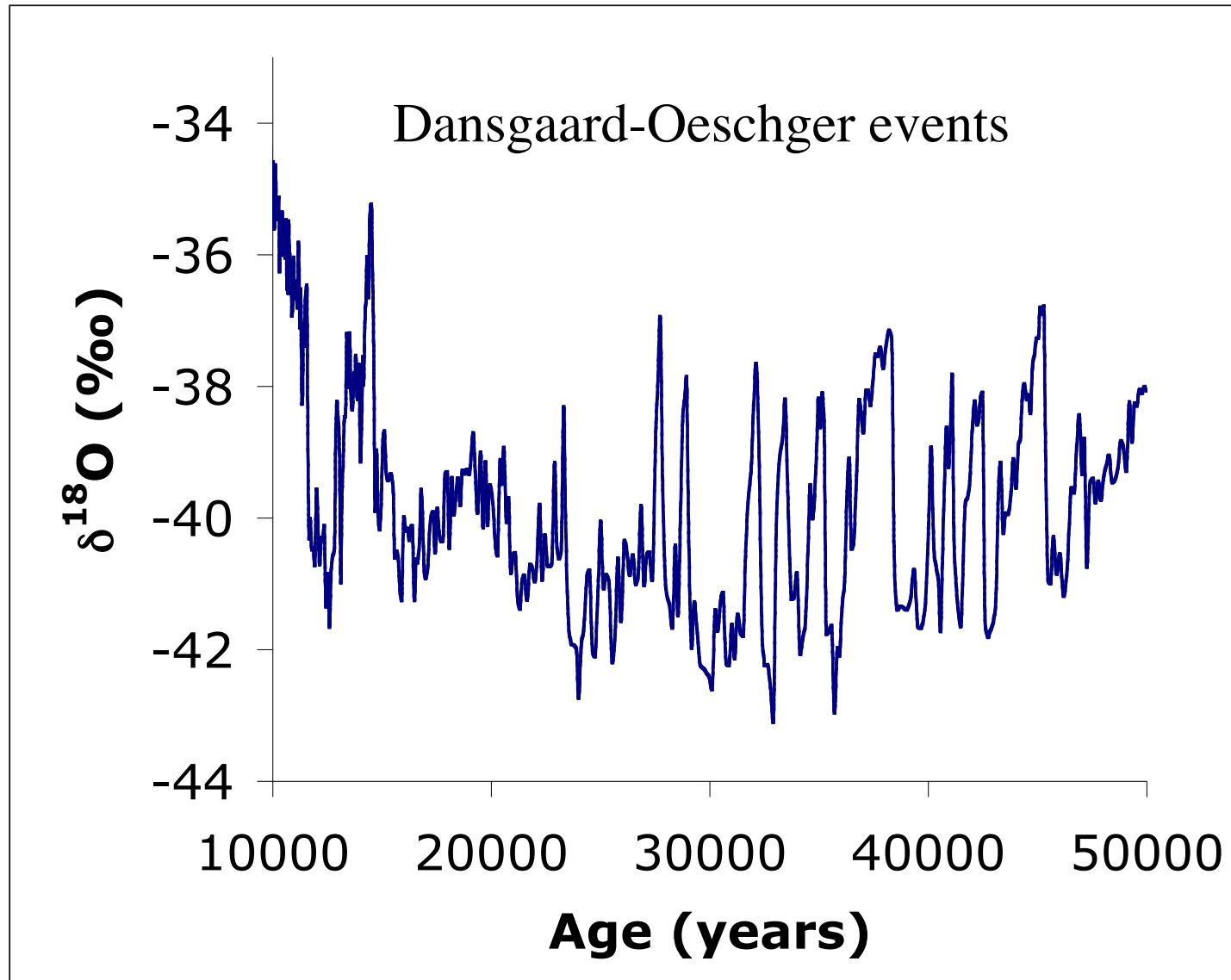
$\delta^{18}\text{O}$ in GISP2 ice core (central Greenland)



$\delta^{18}\text{O}$ in GISP2 ice core (central Greenland)



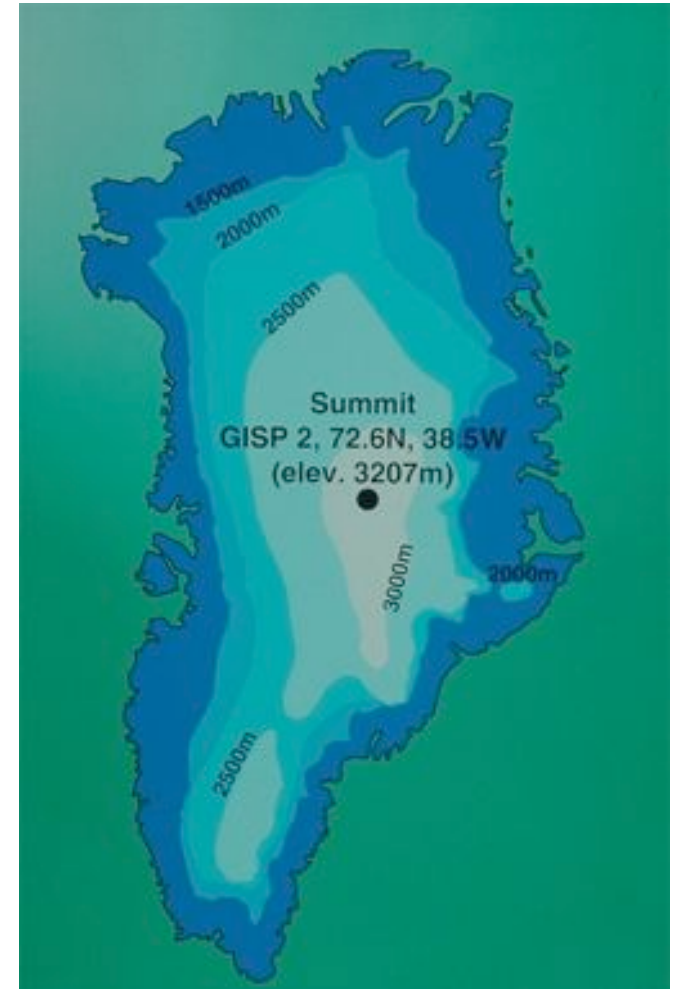
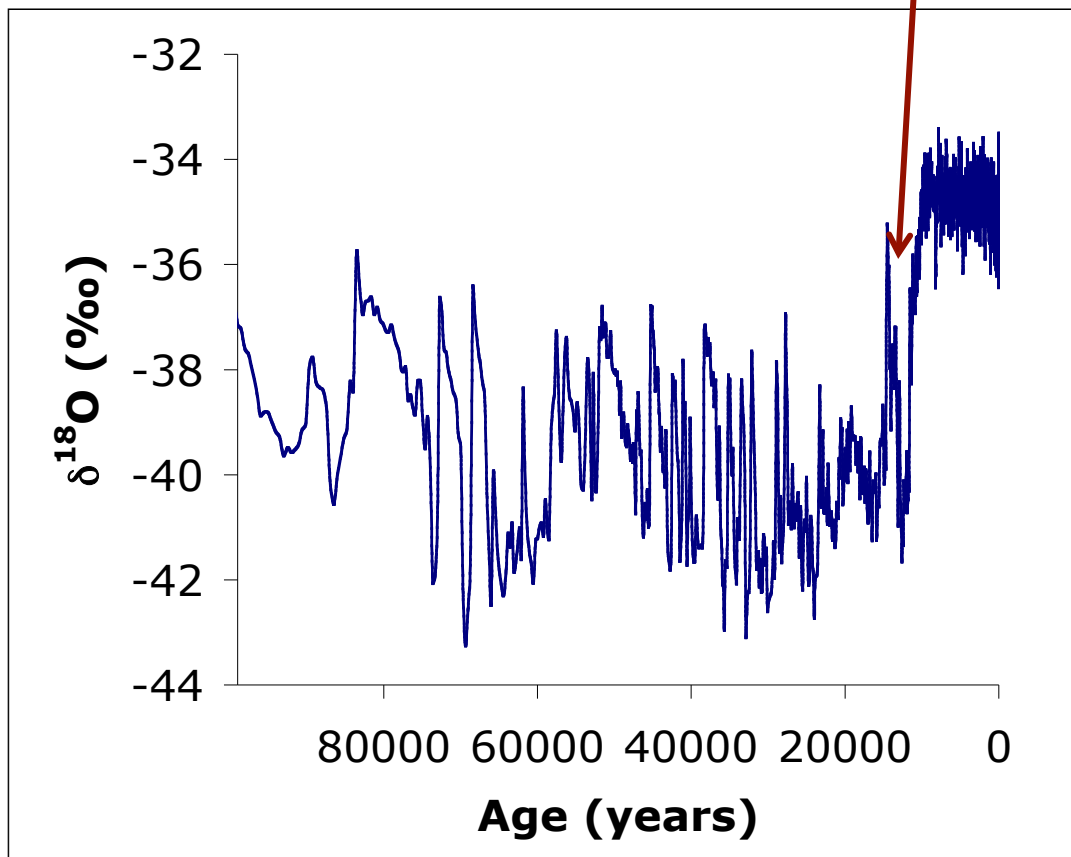
$\delta^{18}\text{O}$ in GISP2 ice core (central Greenland)



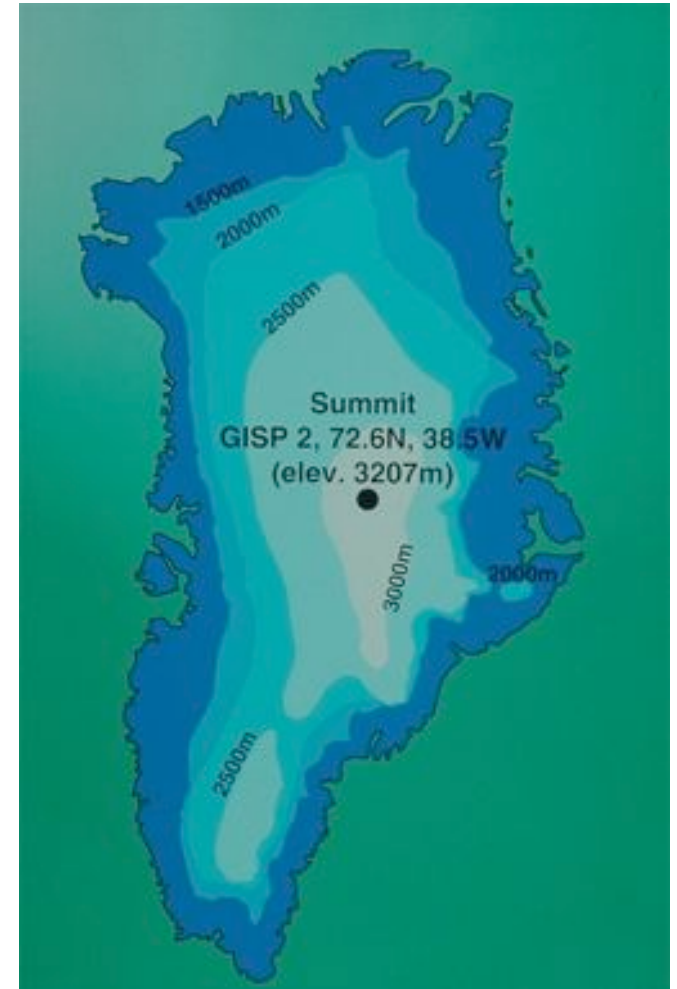
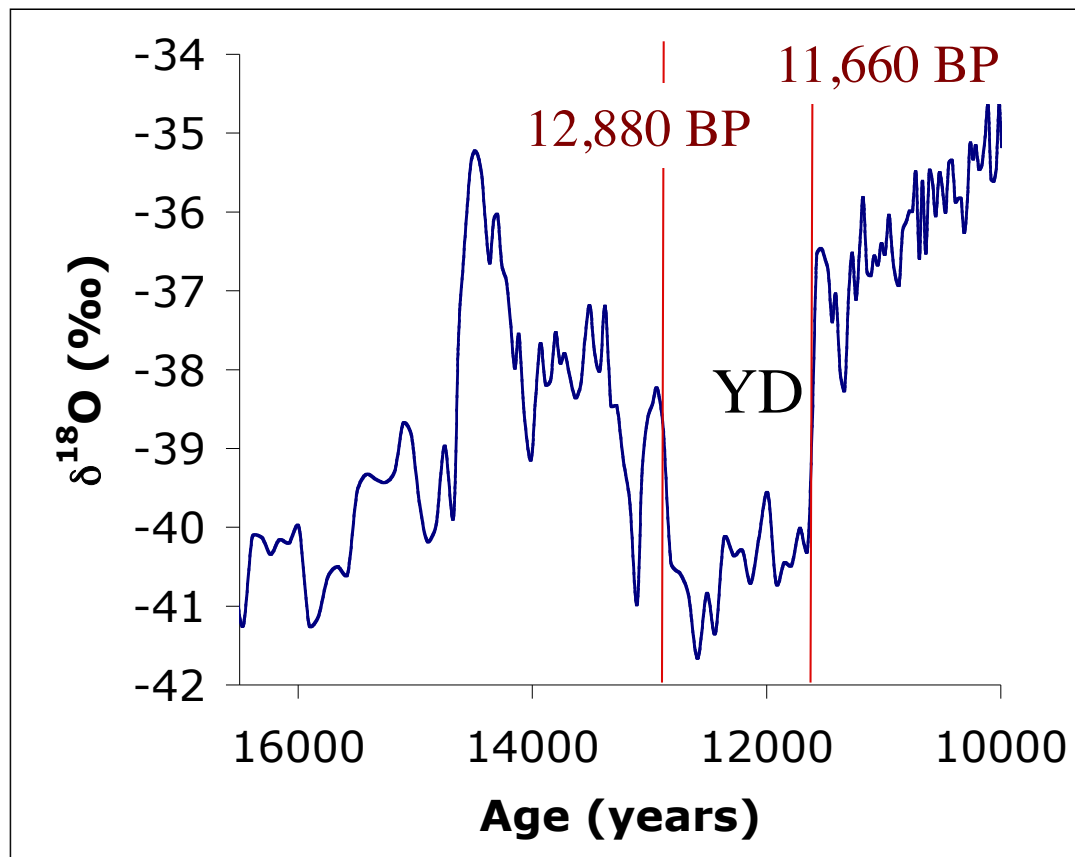
$\delta^{18}\text{O}$ in GISP2 ice core (central Greenland)

Central Greenland Ice Cores

Younger Dryas
cold event



Central Greenland Ice Cores



Temperature and Accumulation Rate

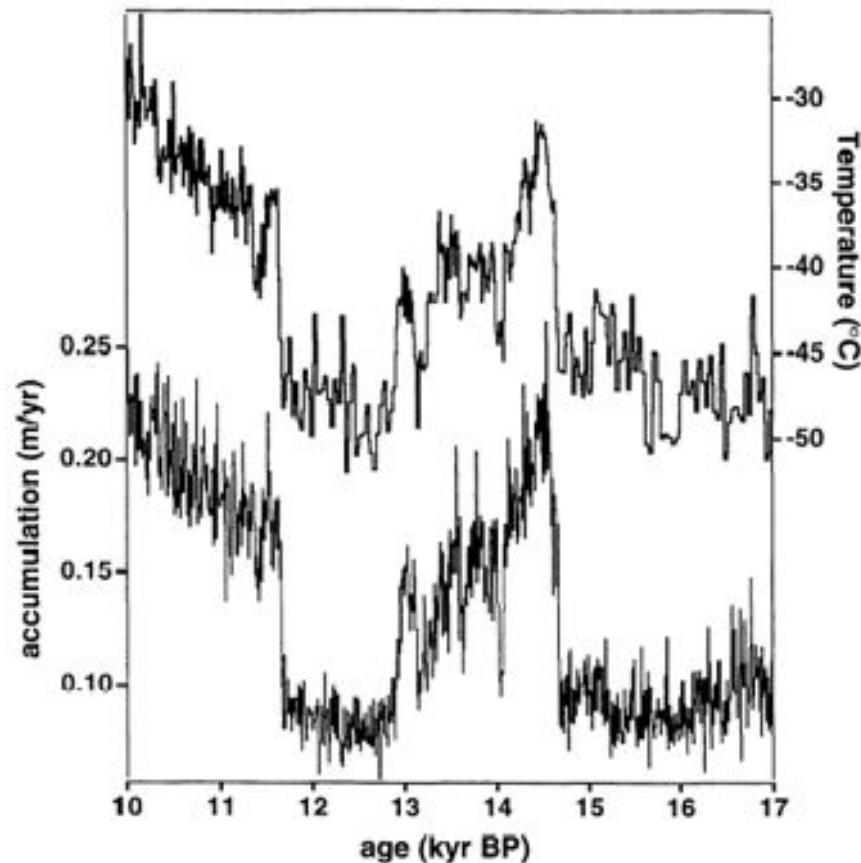
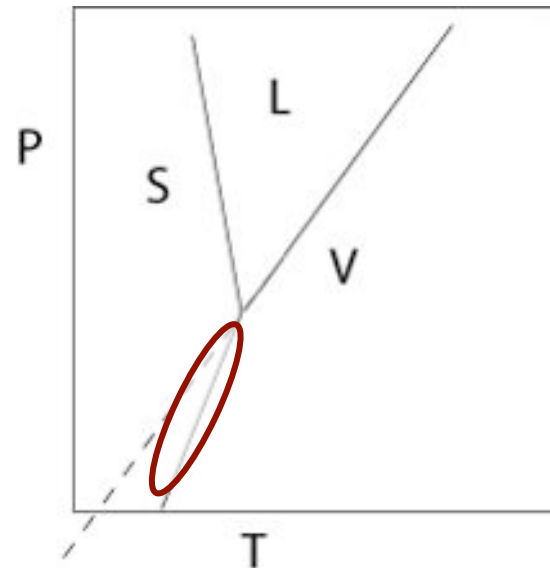
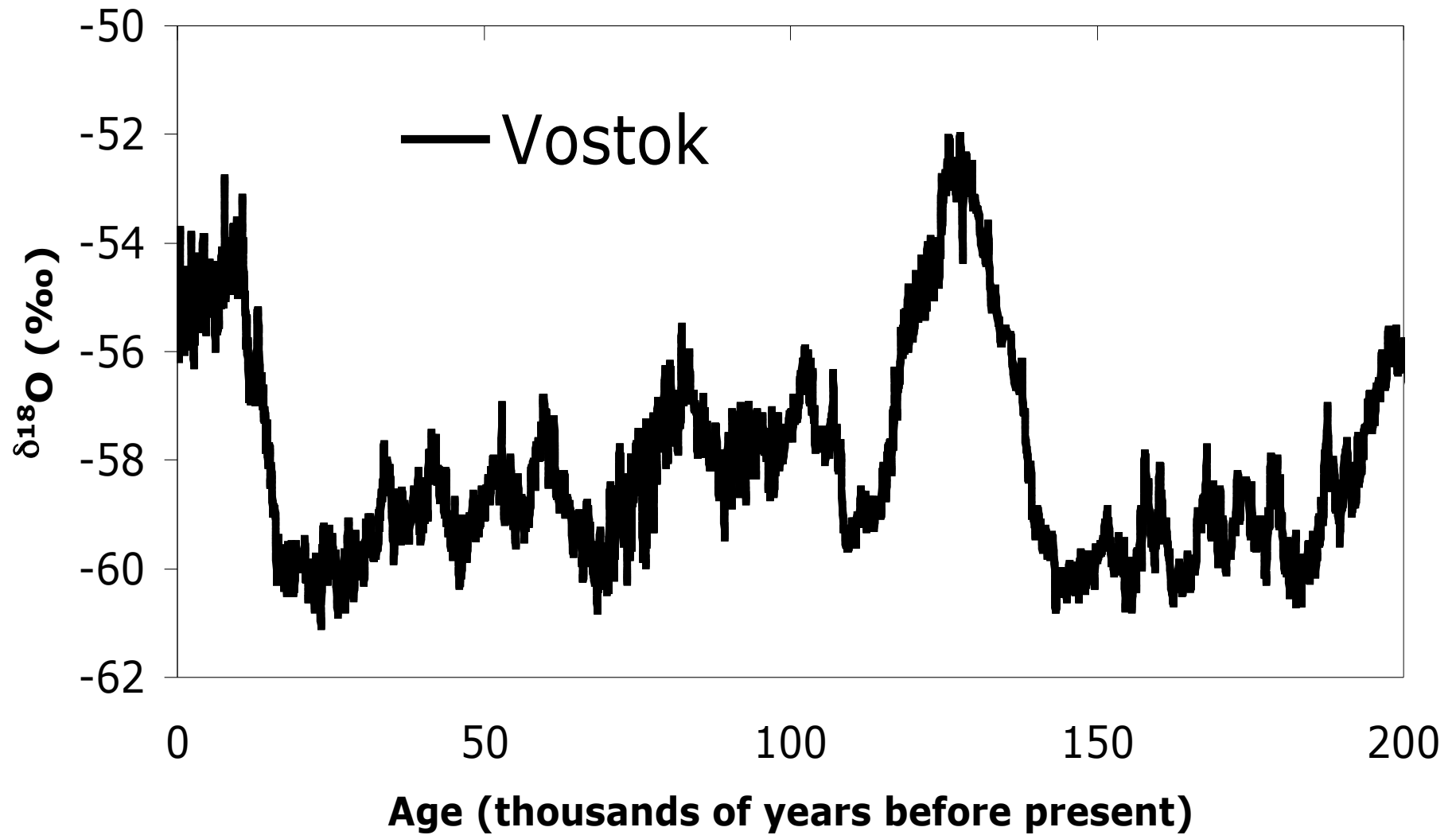


Figure 4. Comparison of the accumulation and δ records at the GISP2 site for the period between 18 and 10 kyr B. P. (adapted with permission from *Nature* [Kapsner et al., 1995]; copyright Macmillan Magazines Limited), in using a calibration of $0.33\text{‰}/^{\circ}\text{C}$ instead of $0.53\text{‰}/^{\circ}\text{C}$ (see text).

Was snowfall controlled by saturation vapor pressure?

Remember the phase diagram for H_2O





$\delta^{18}\text{O}$ also indicates past temperatures over longer time scales

$\delta^{18}\text{O}$ in Ocean vs. Atmosphere

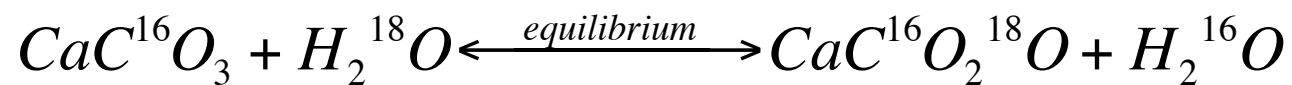
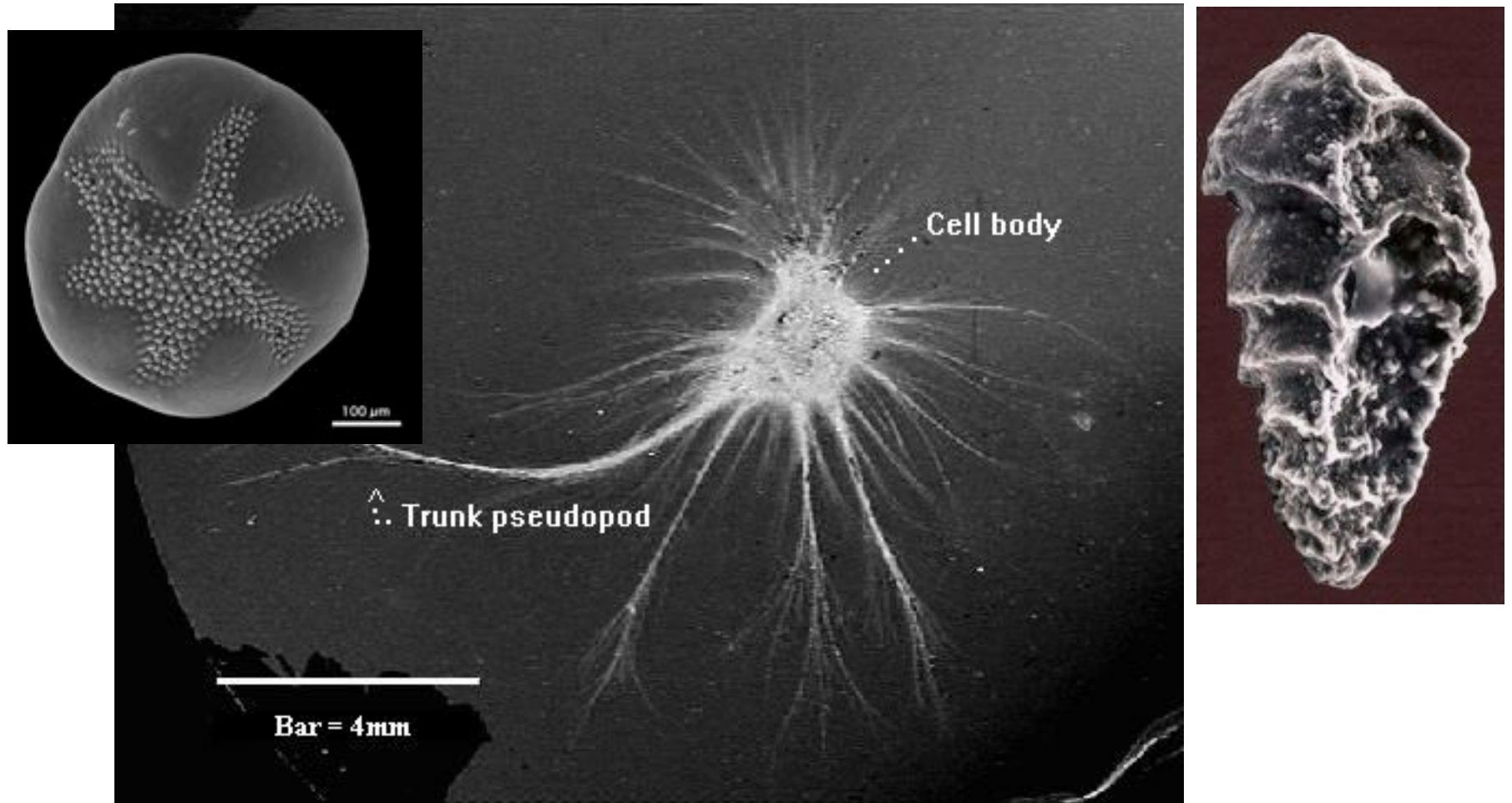
As the ice sheets build up during glaciations, they are preferentially made up of lighter isotopes.

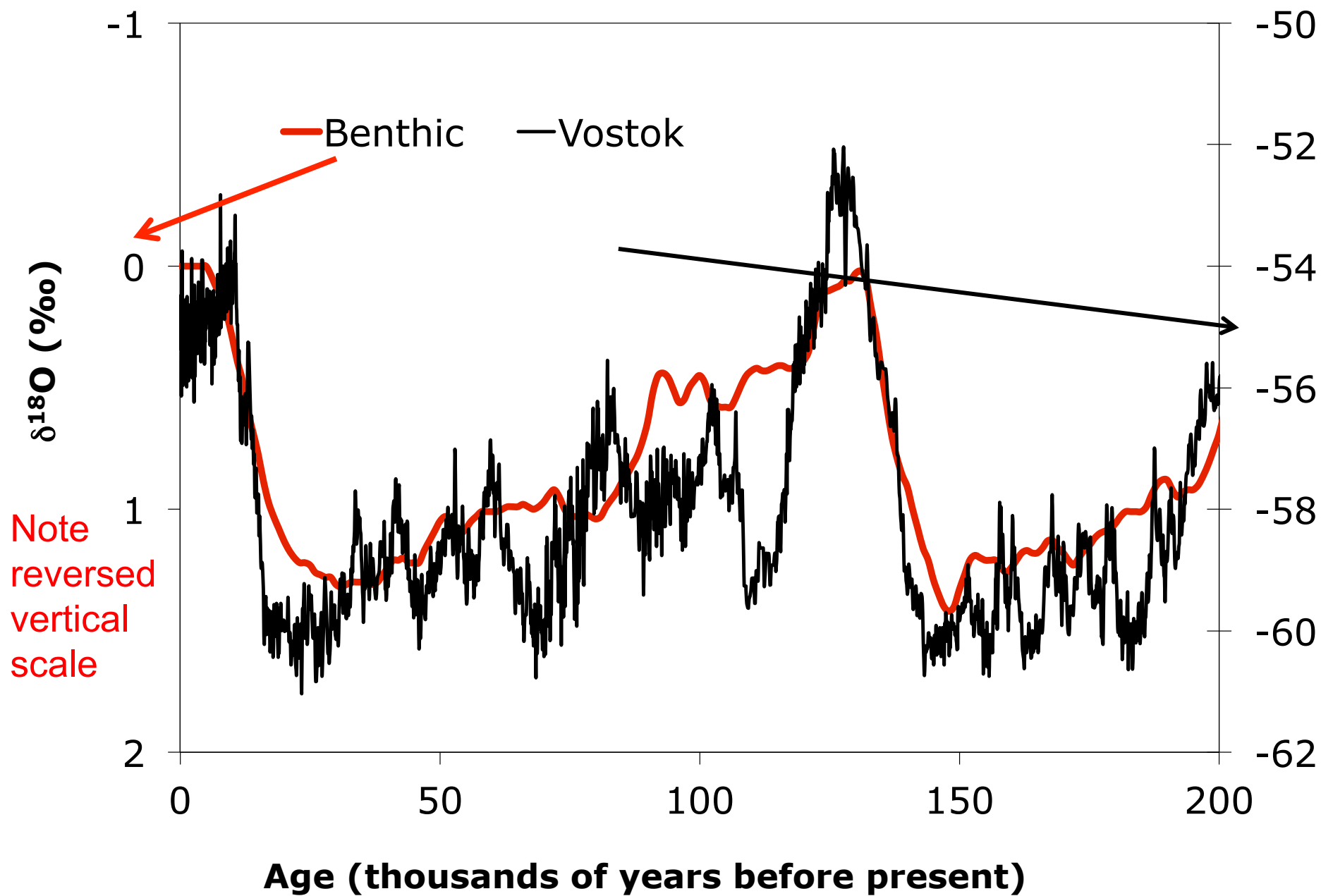
The consequence is that the ocean gets isotopically heavier as ice sheets grow.

Core color changes and changes in isotopic content in foram shells indicate climate shifts.



Planktonic and Benthic Foraminifera



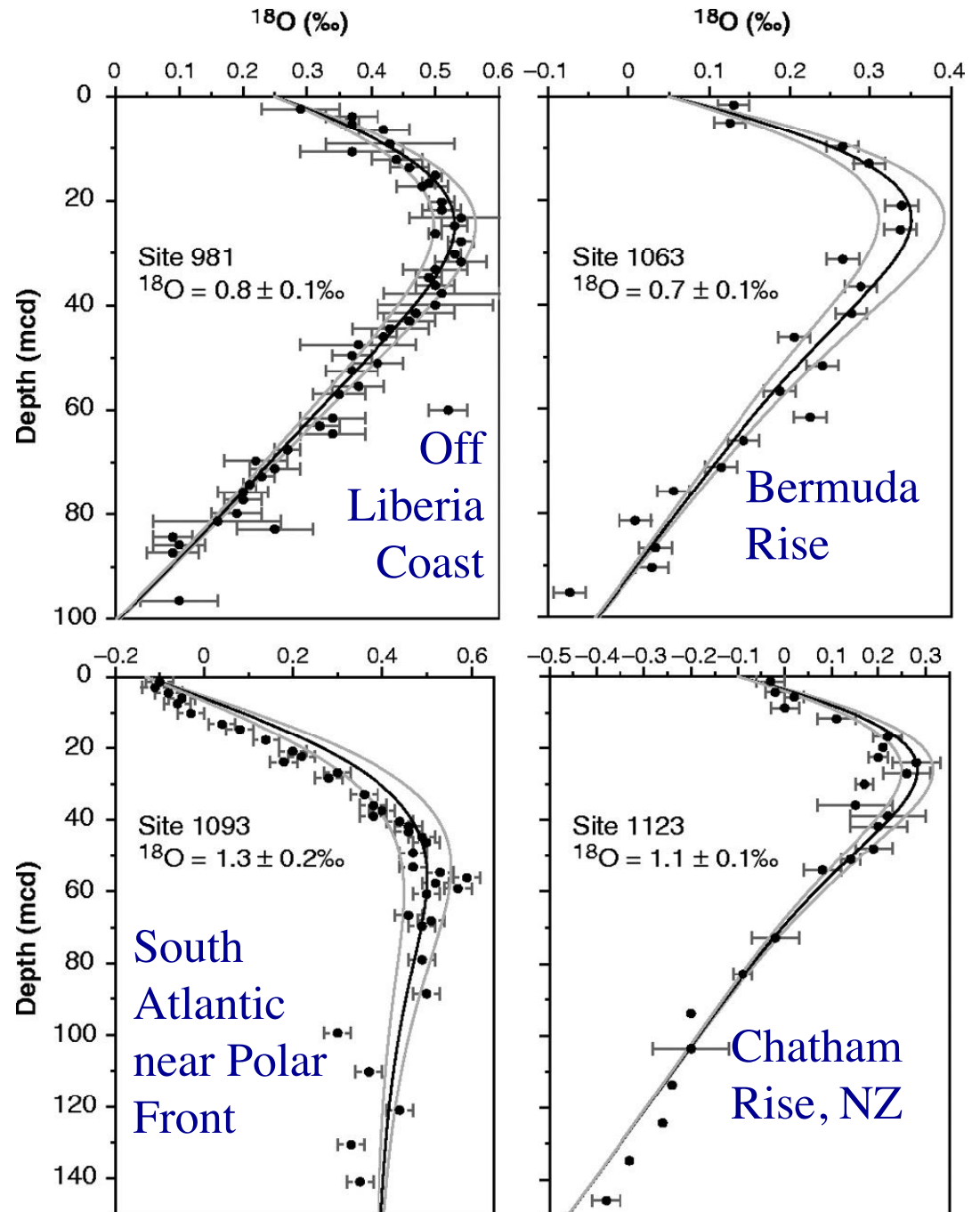


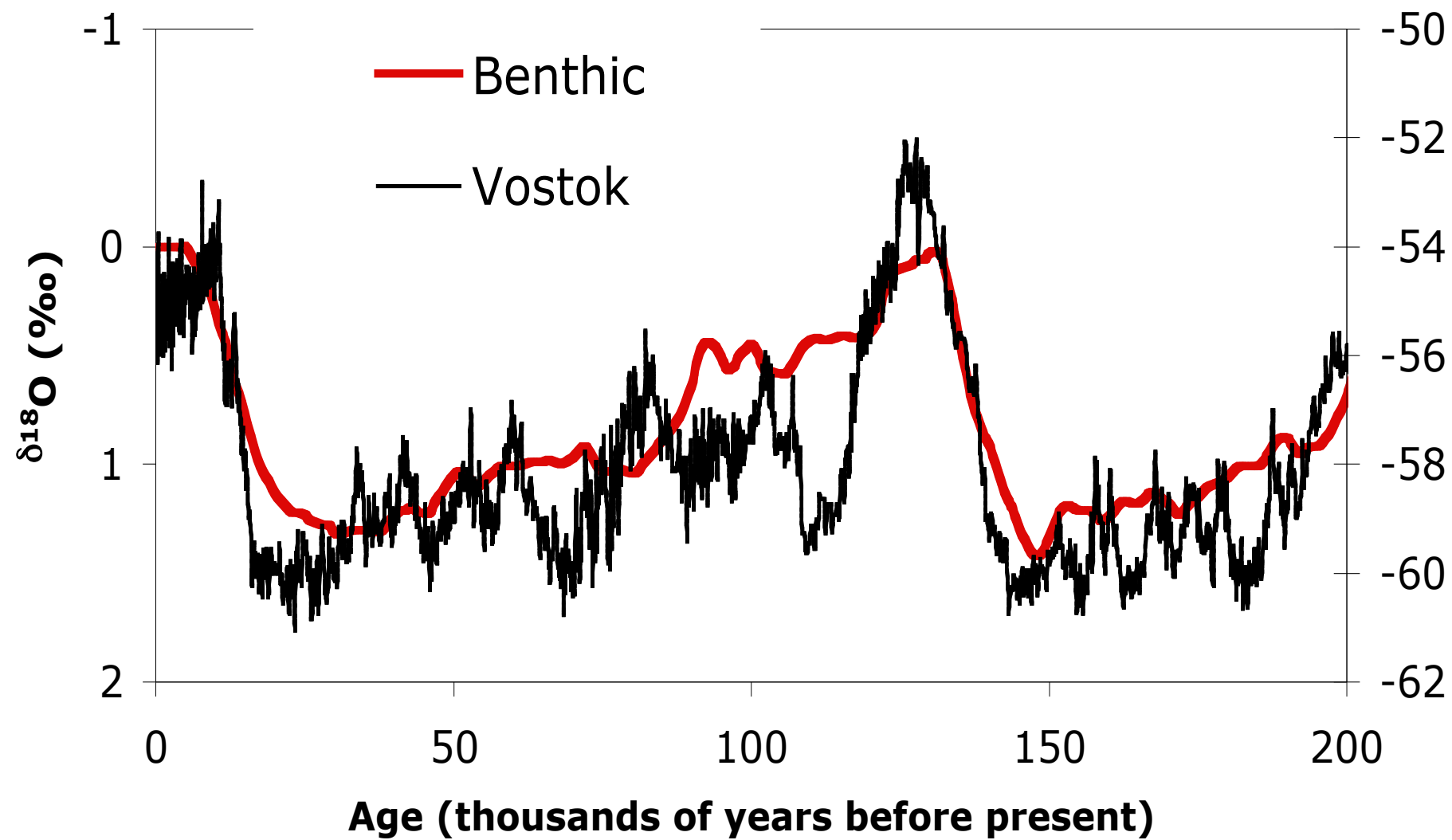
mcd = meters composite core depth

Marine sediment cores
at site 981 (Reunion)
deposition rate is high.
(~ 1 to 2 mm yr^{-1})

That's ~ 1 to 2 m ka^{-1}

What is causing the
high values of $\delta^{18}\text{O}$ in
the sediments and pore
water at 20-40 meters?





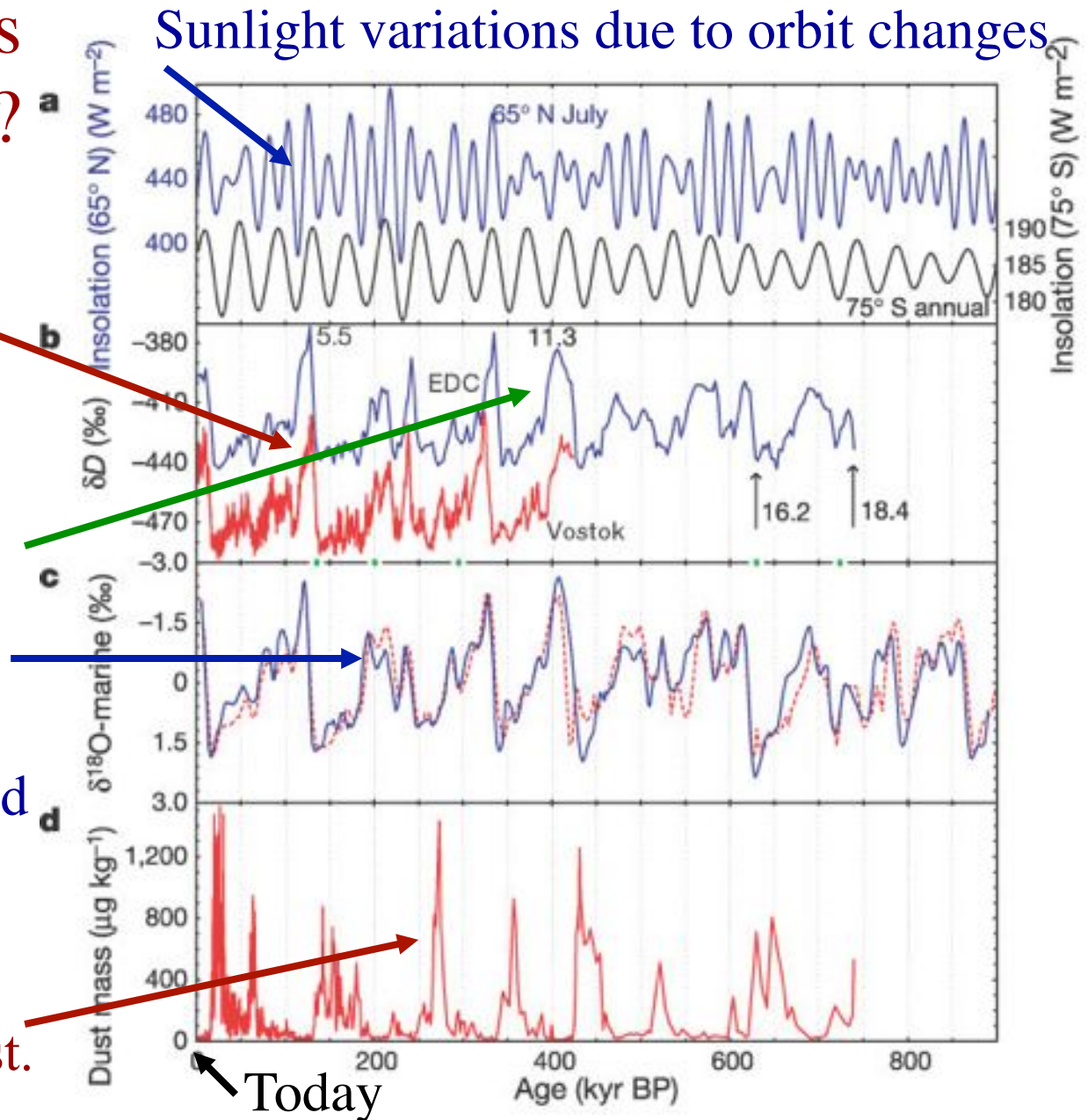
What story Does Antarctica Tell?

Vostok Station

- 4 glacial cycles

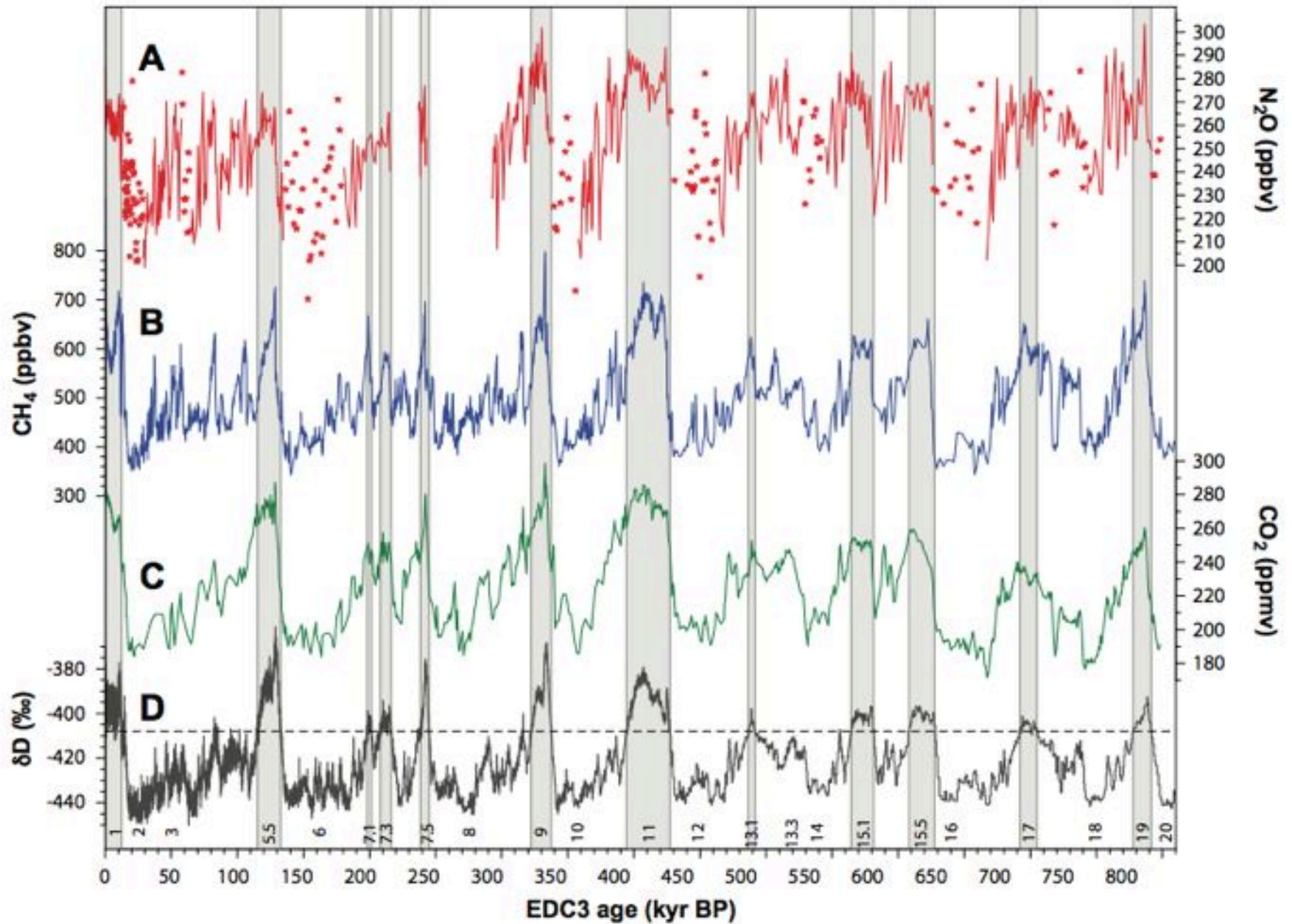
EPICA Dome C

- 8 glacial cycles
- Isotopes from ocean floor record the volume of ice on land in ice sheets.
- Dust in ice reveals windiness in the past.



Nature 429, 623-628 (10 June 2004) Eight glacial cycles from an Antarctic ice core

Epica Dome C – 800 ka



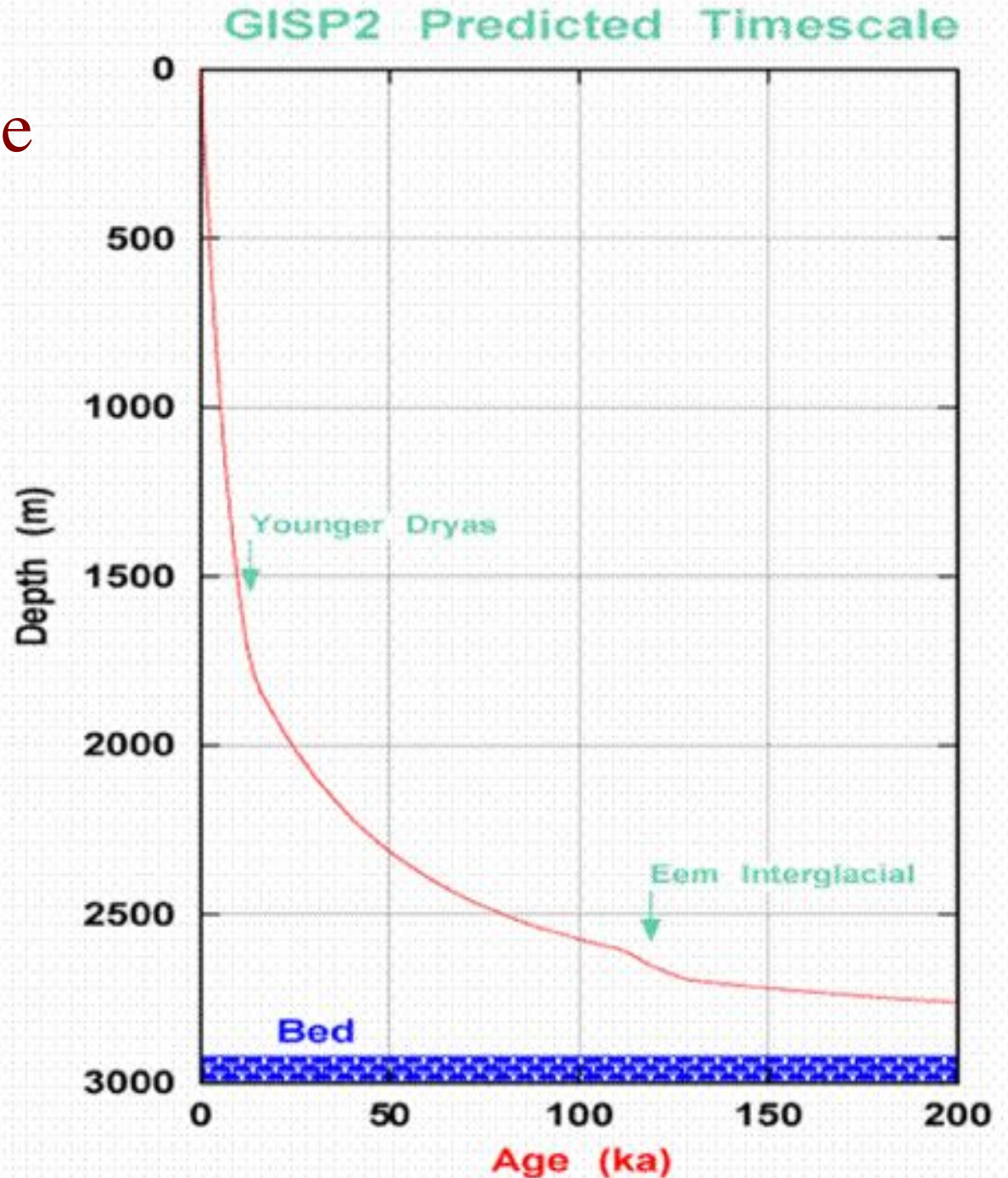
Dating ice cores

Approaches

- Model-based time scales
- Layer counting
- Matching well-dated cores with cores elsewhere (gas-based chronologies)

GISP2 depth-age

Predicted by an ice-flow model before the core was drilled, with a good guess at the history of net snowfall.



Layer counting - the concept

Seasonal timing of parameters being measured

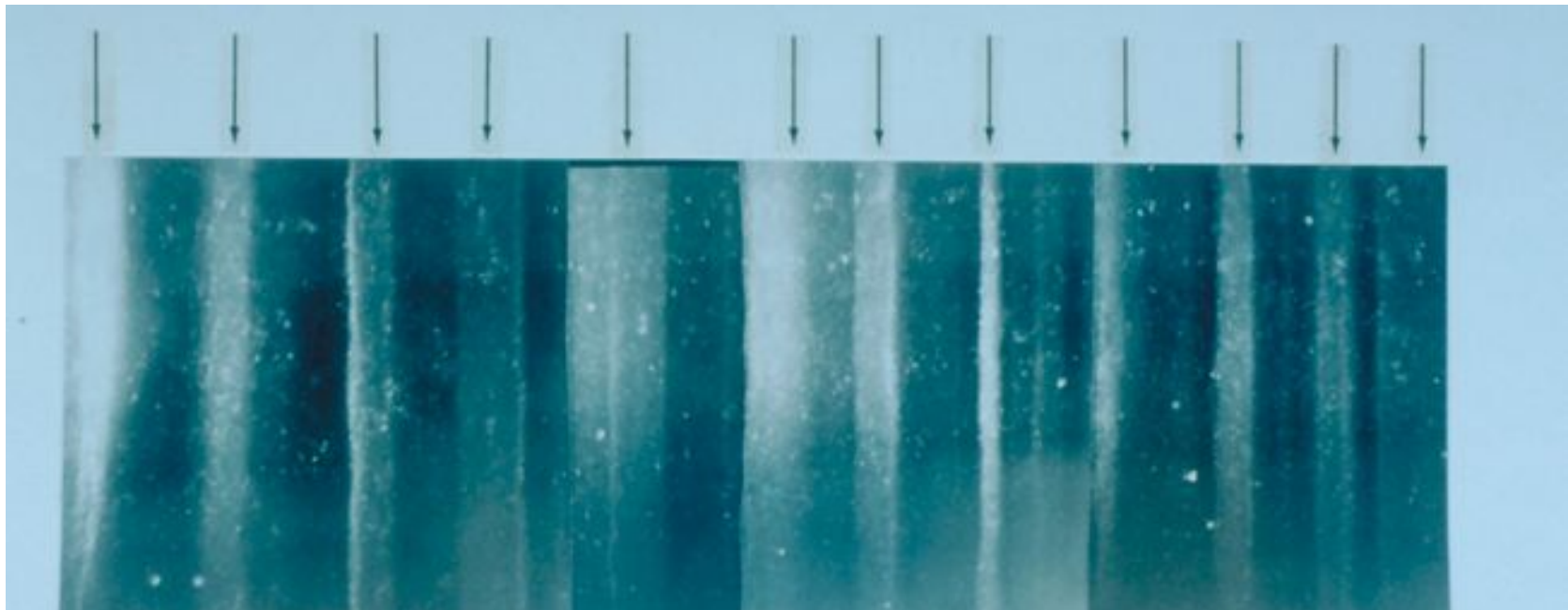
- e.g. $\delta^{18}\text{O}$ higher in summer than winter
- Dust varies seasonally with exposed bare ground (sources) and with wind speed (transport).
- Many others ...

Validation/correction with stratigraphic markers

- e.g. volcanic events of known age (rocks dated at the volcano)

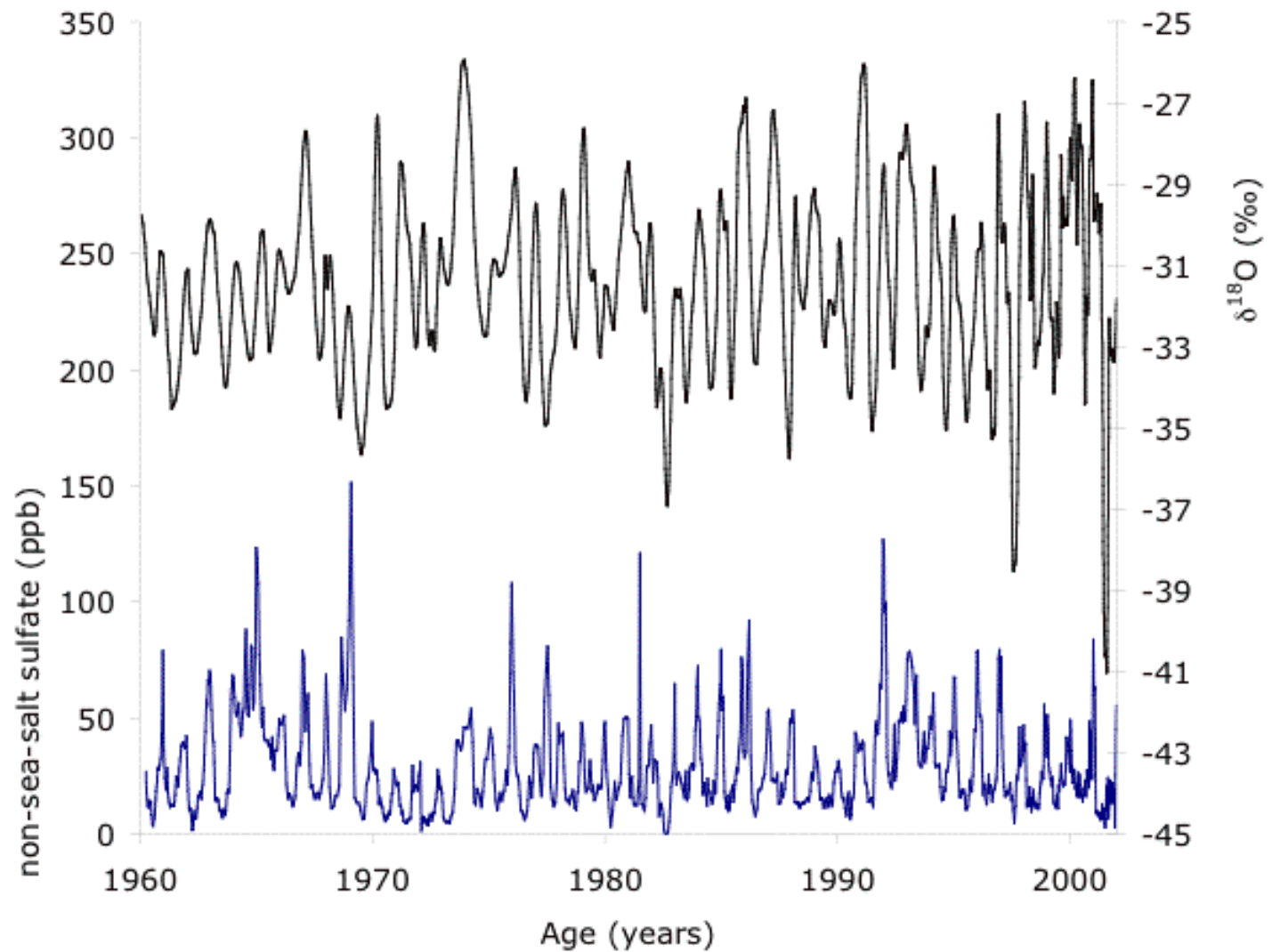
Layer counting - the practice

Summer layers, GISP2, Greenland ~20 kyr



Seasonal Cycles

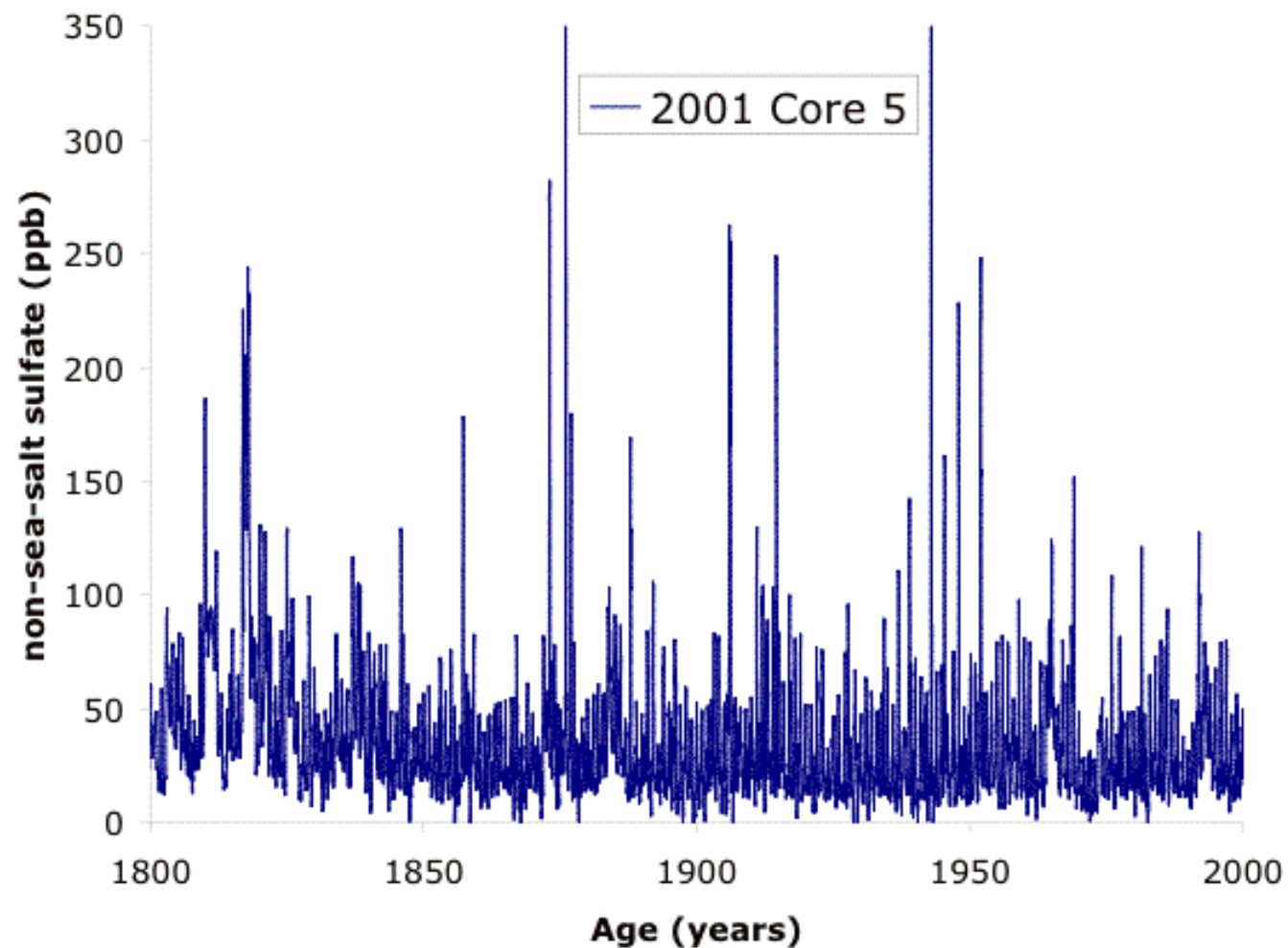
Spring plankton
bloom in the
Southern Ocean



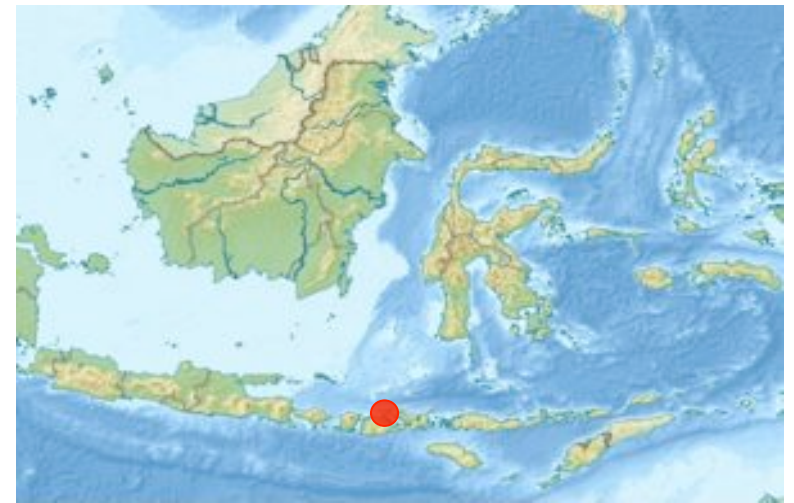
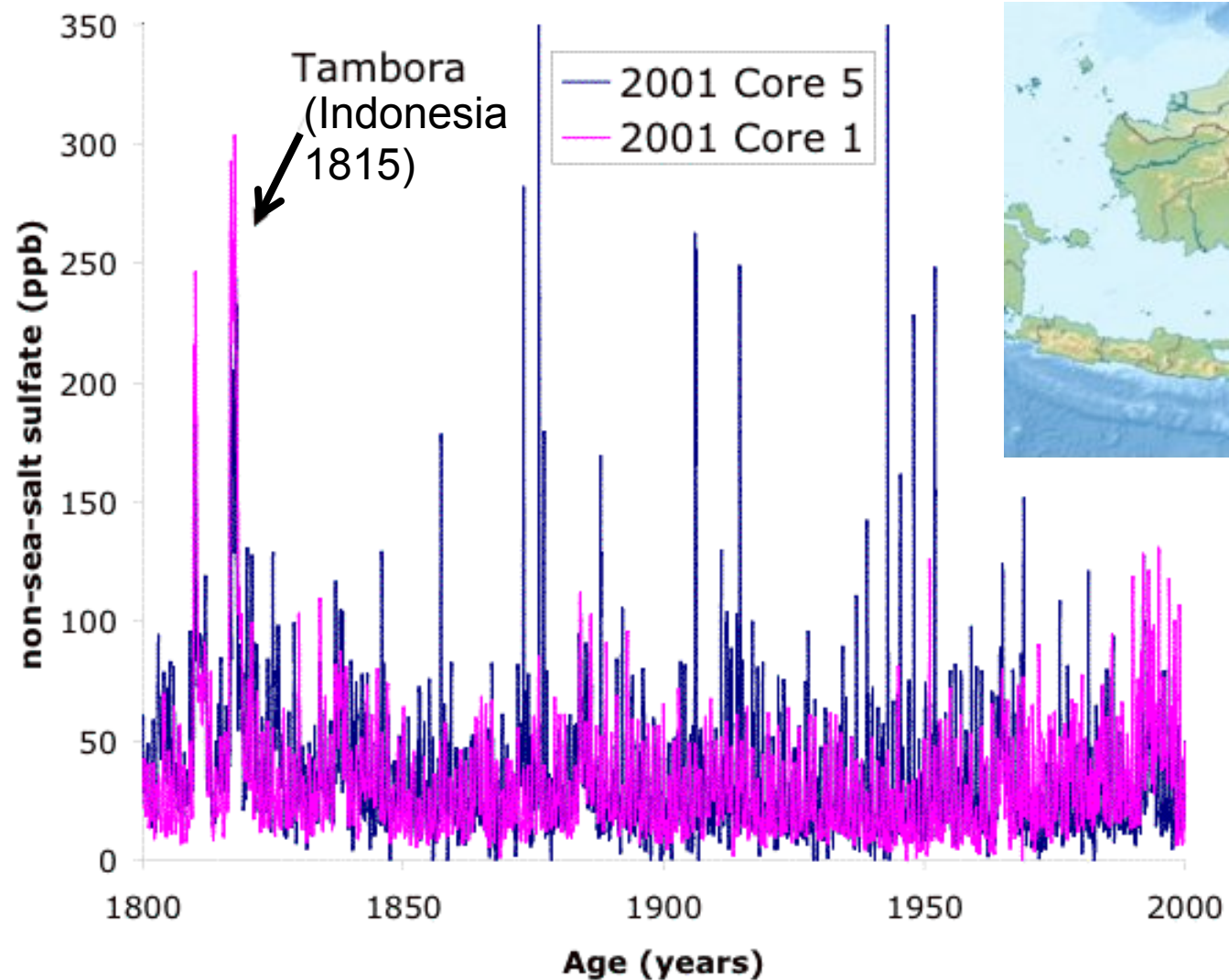
How high can *you* count?

- Annual layers in GISP2 ice core were counted back to ~40 ka
- accuracy estimated to be ~1-2%
- This was an amazing achievement.
- Other Greenland cores have also been layer-counted well back into the ice age.
- WAIS Divide ice core (West Antarctica) layer-counted to more than 30 ka, giving bipolar perspective.

West Antarctic Ice Cores



West Antarctic Ice Cores



What can we learn from ice cores besides
past temperatures?

Ice-Core Stories

Temperature

- stable isotopes $\delta^{18}\text{O}$ and δD ; ^{15}N and ^{40}Ar
- borehole temperatures

Precipitation

- annual layer thicknesses,
- ^{10}Be - constant fallout diluted by snowfall

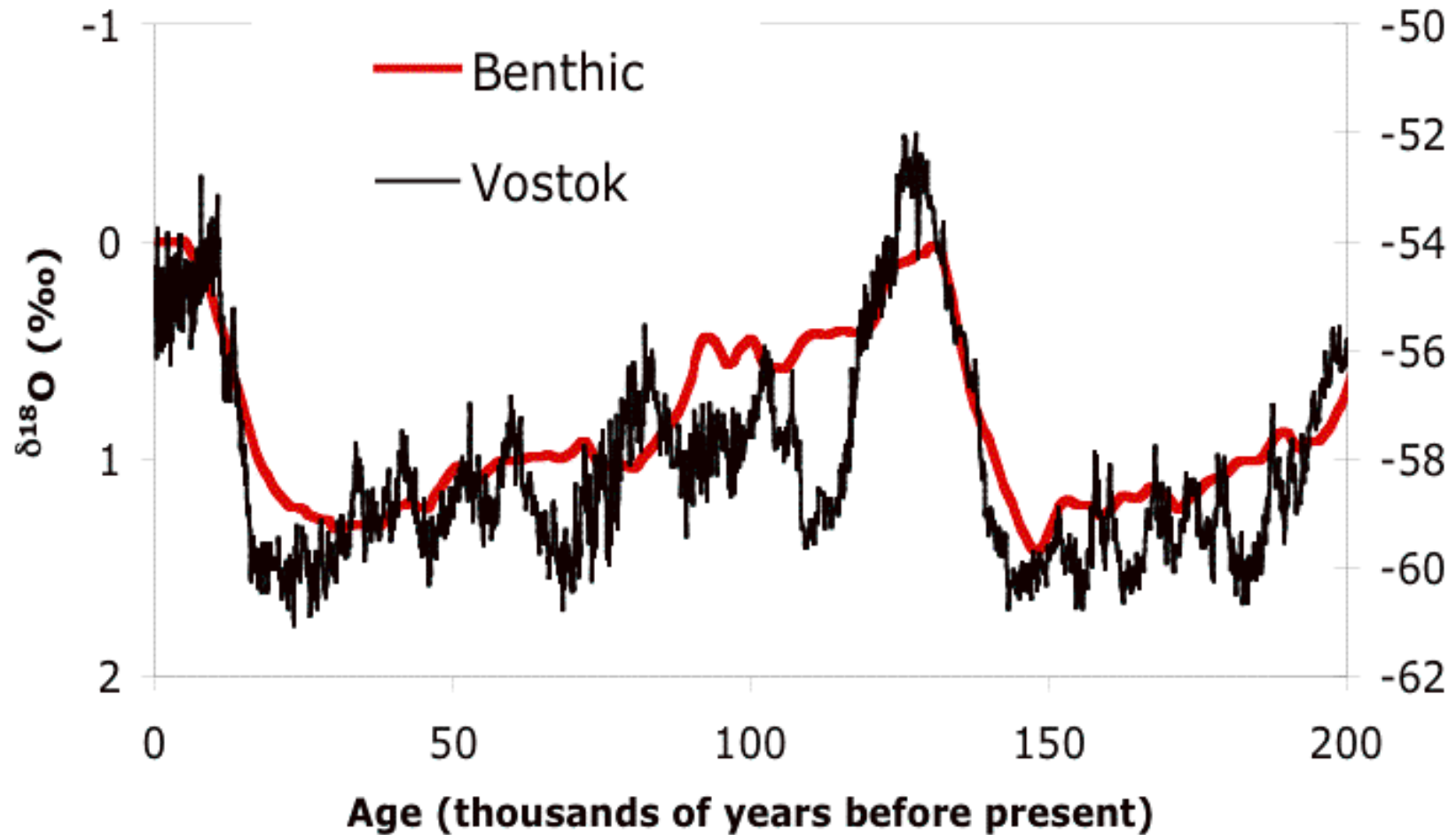
Synoptic systems and Wind

- dust – amount and provenance

Greenhouse gases

- bubbles

Temperature and Ice Volume



Modes of Deposition

Dry fallout

- SO_4^{2-} , ^{10}Be , dust

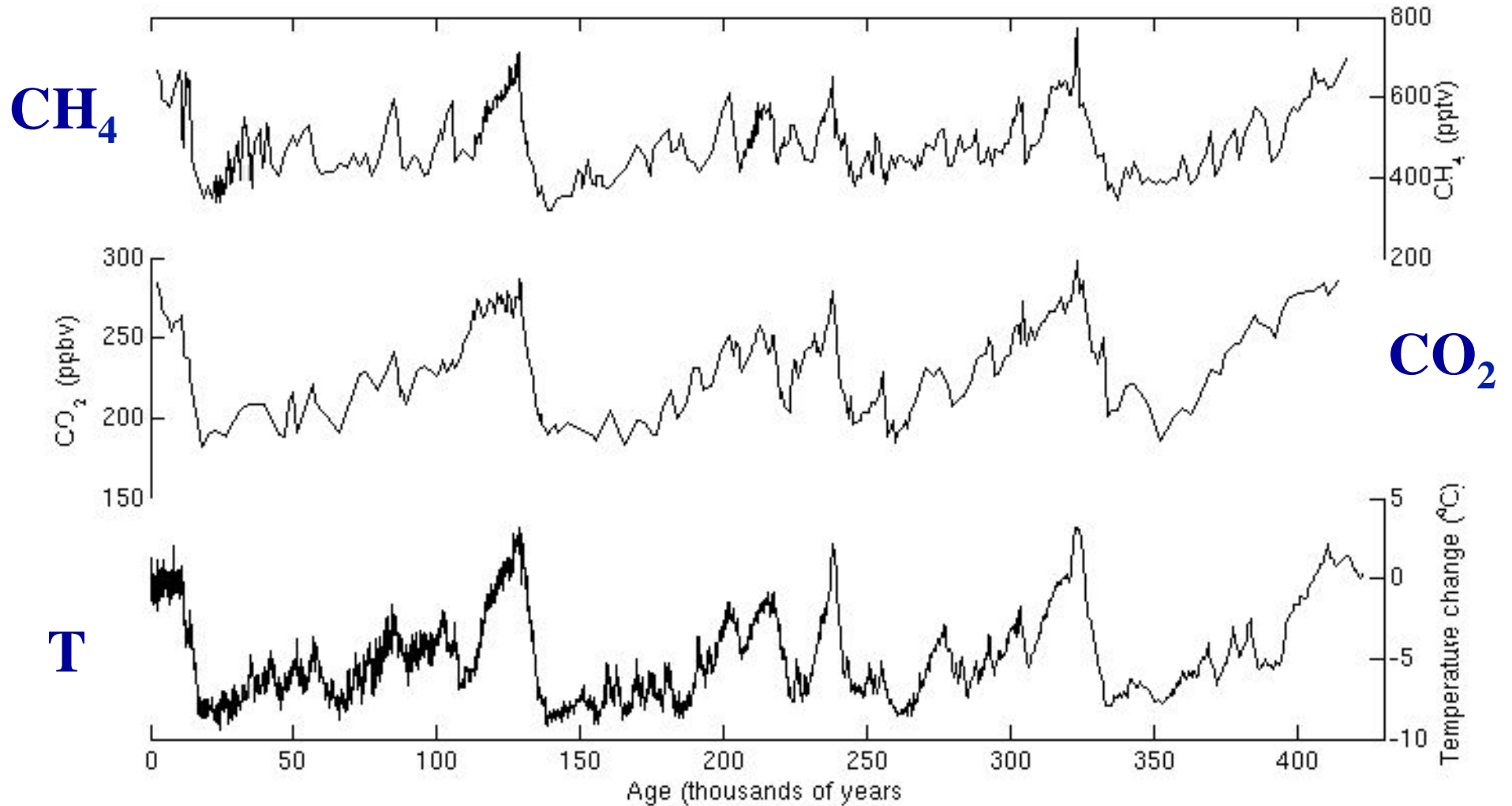
Wet deposition

- Na^+ , Cl^- , SO_4^{2-}

Gas occlusion in bubbles

- CO_2 , CH_4

Greenhouse Gases and Ice-Age Temperature

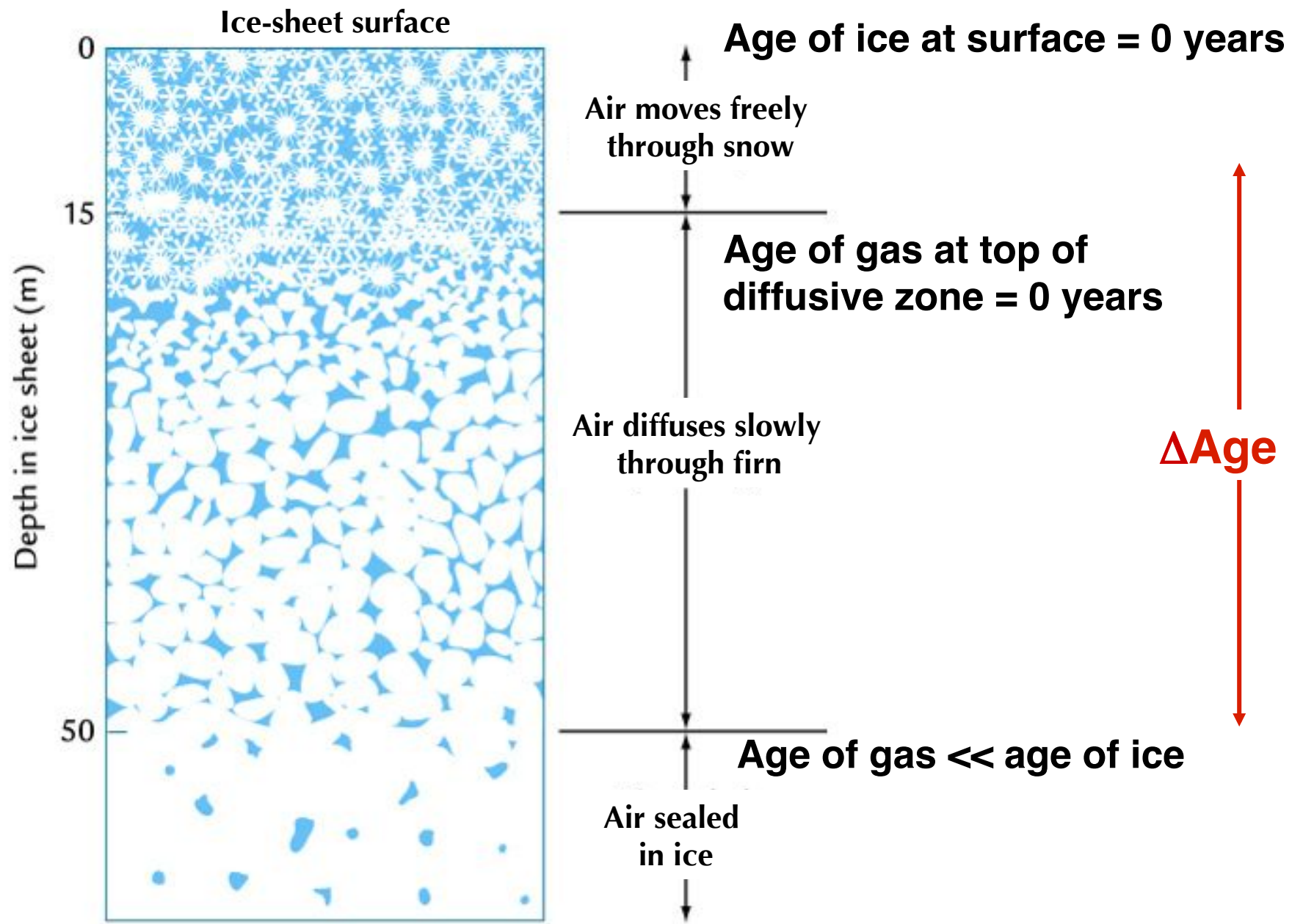


Ice holds samples of our past atmosphere



It's in the
bubbles ...

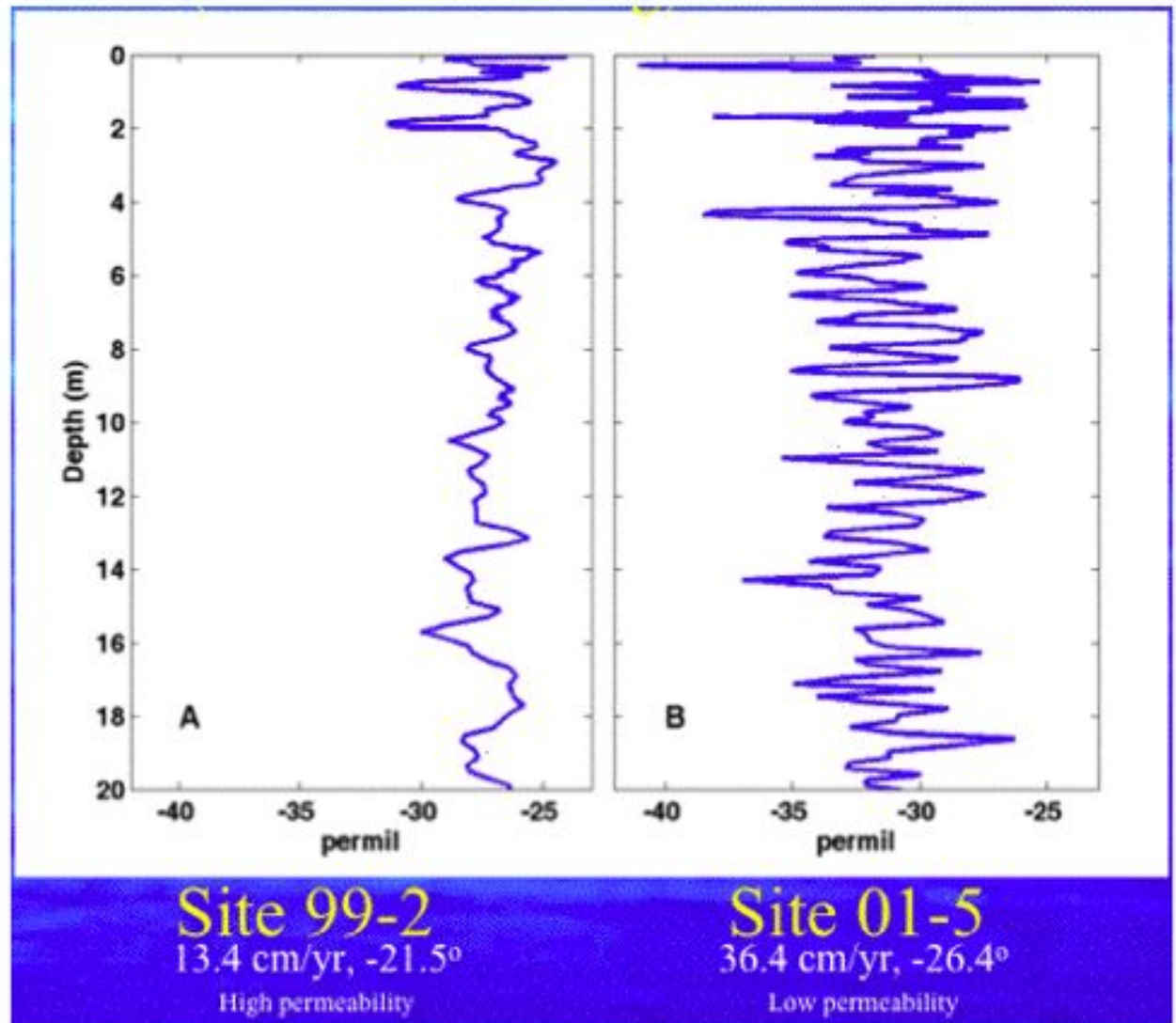




Evidence for Gas Mobility in Firn

Seasonal gradients in $\delta^{18}\text{O}$ are steeper where layers are thinner i.e. at low-snowfall sites.

So seasonal $\delta^{18}\text{O}$ signal diffuses away faster and is lost as water vapor diffuses in the firn.



Calculating Δ age

- Δ age is the age difference between the gas bubbles and the ice surrounding them.
- Δ age depends on the processes converting snow to firn and eventually ice, sealing off air bubbles
- These processes are dependent on **temperature** and **snow accumulation** rate; wind and other meteorological factors may also play an important role.

Uncertainties in Δ age

Item	How determined	How well known for sites with	
		low accumulation	high accumulation
Bubble close-off process	Empirical and theoretical models of firn densification (conversion of snow to ice)	poorly	well
Temperature history	Stable isotope profiles, borehole thermometry, gas isotopes (for selected time periods only)	moderately well, but variable	
Accumulation history	Inferred from geochemistry or isotopes	well	poorly

Rare isotopes in Air

Air contains N_2 , O_2 , and Ar

- These gases contain atoms with rare but stable isotopes ^{15}N (vs ^{14}N), ^{36}Ar (vs ^{40}Ar), and ^{18}O (vs ^{16}O)
- Content of ^{15}N and ^{40}Ar can be expressed in δ notation $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$, just like $\delta^{18}\text{O}$
- Gas with these rare isotopes behaves slightly differently to normal gas when temperature changes.

In still air in pore spaces, gas with a heavy isotope tends to:

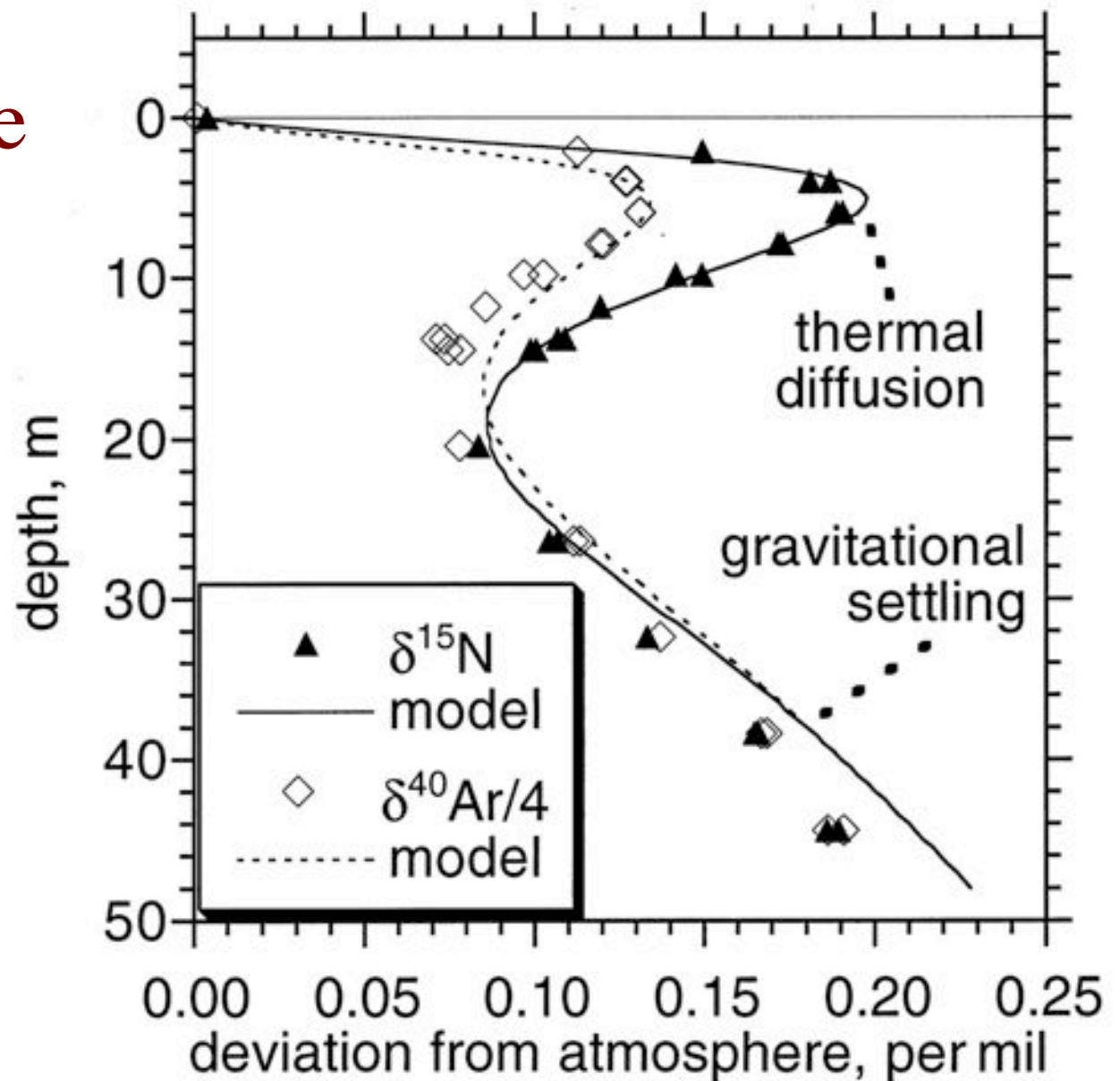
- Settle to bottom
- Move toward colder places

$\delta^{15}\text{N}$ and fast climate change

N_2 gas is largest component of atmosphere.

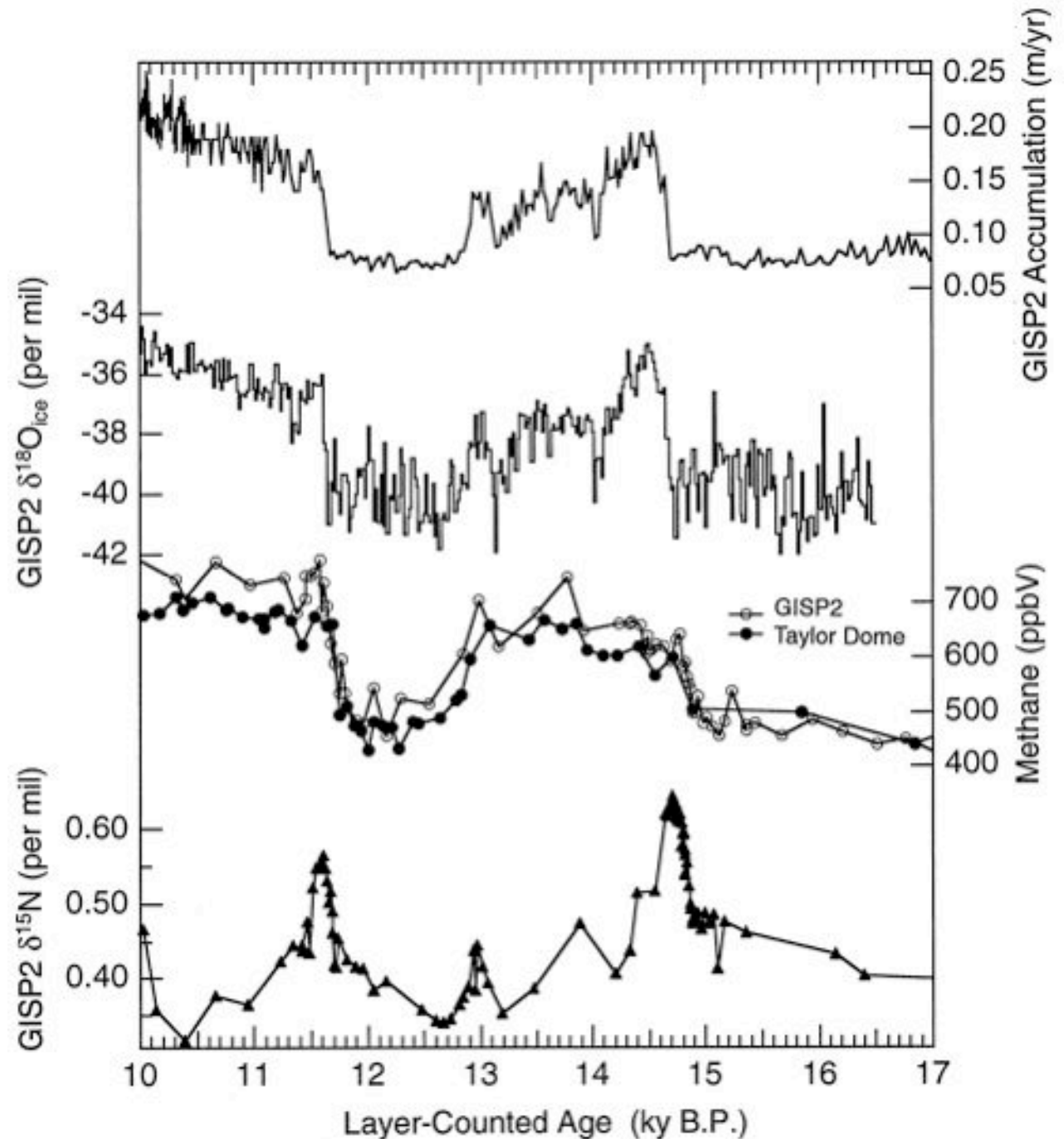
In still air in pore spaces, gas with heavy isotope e.g. ^{15}N or ^{40}Ar tends to

- Settle to bottom
- Move toward cold
- Why are $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$ so positive at 8 meters depth?

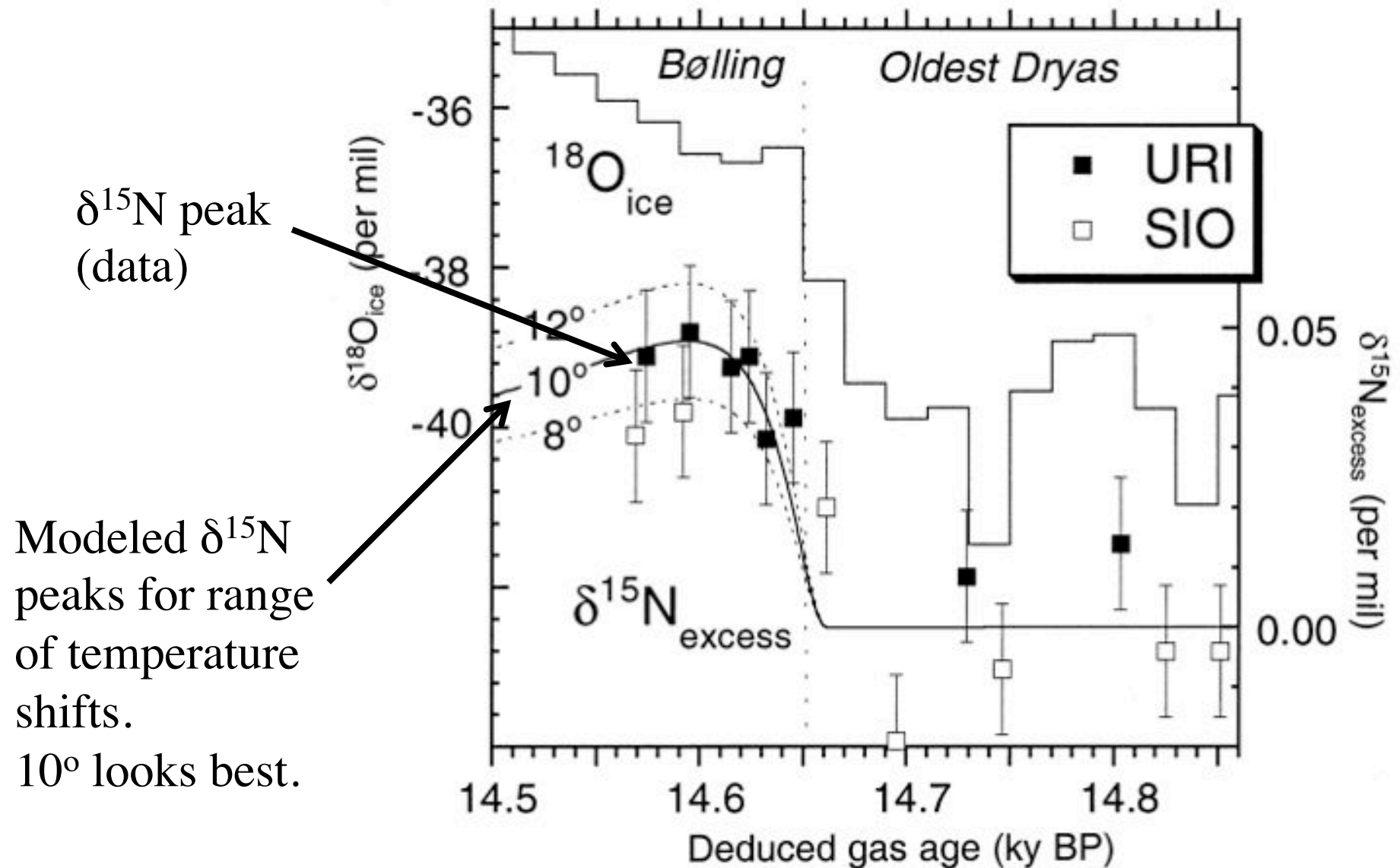


How large
were fast
temperature
changes?

Size of the $\delta^{15}\text{N}$
spikes is related
to the size of
the fast shift
in temperature

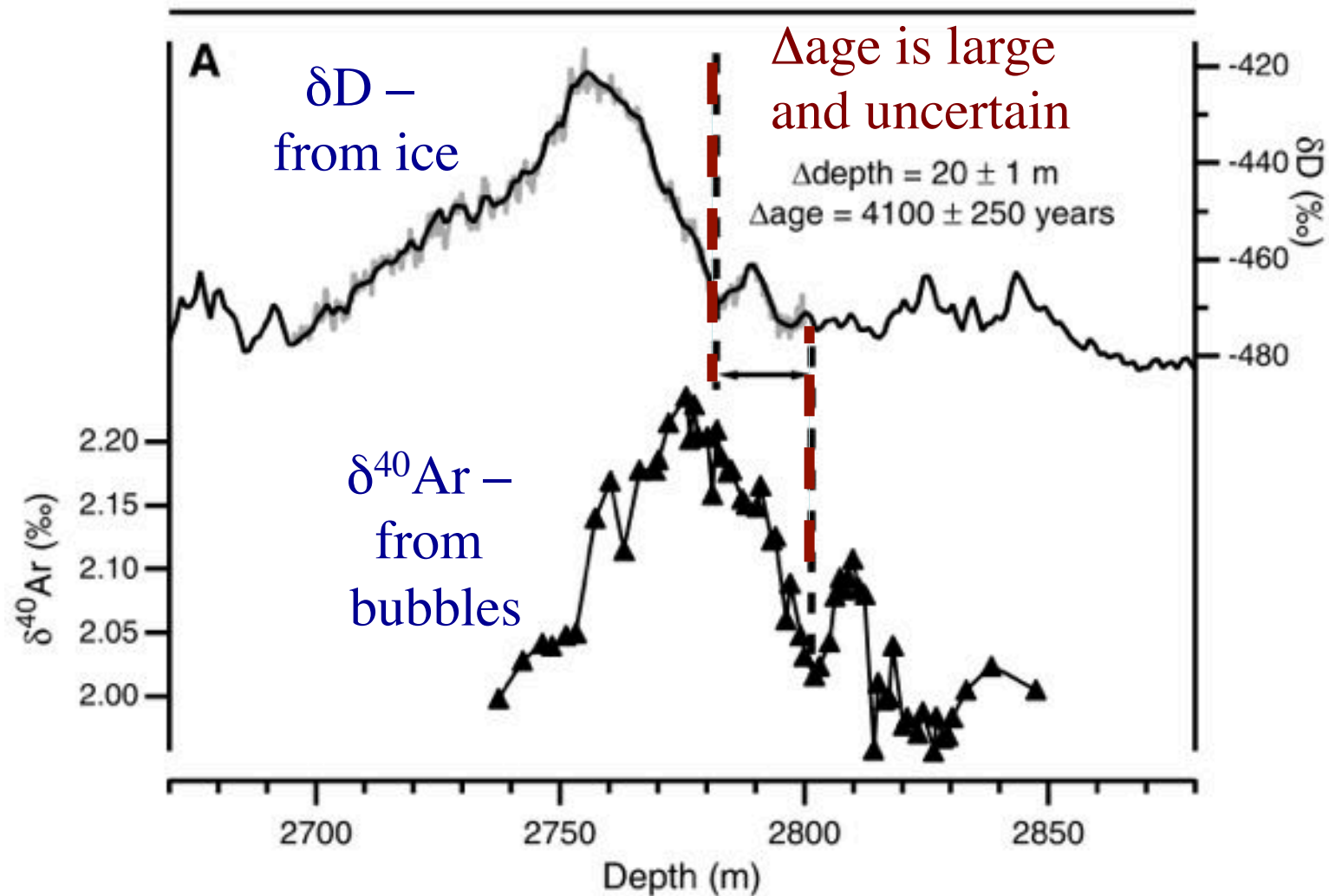


How large was this Temperature Change?



How to explore leads and lags between
Temperature and CO₂ in the distant past?

Vostok - Termination III - ~240 ka

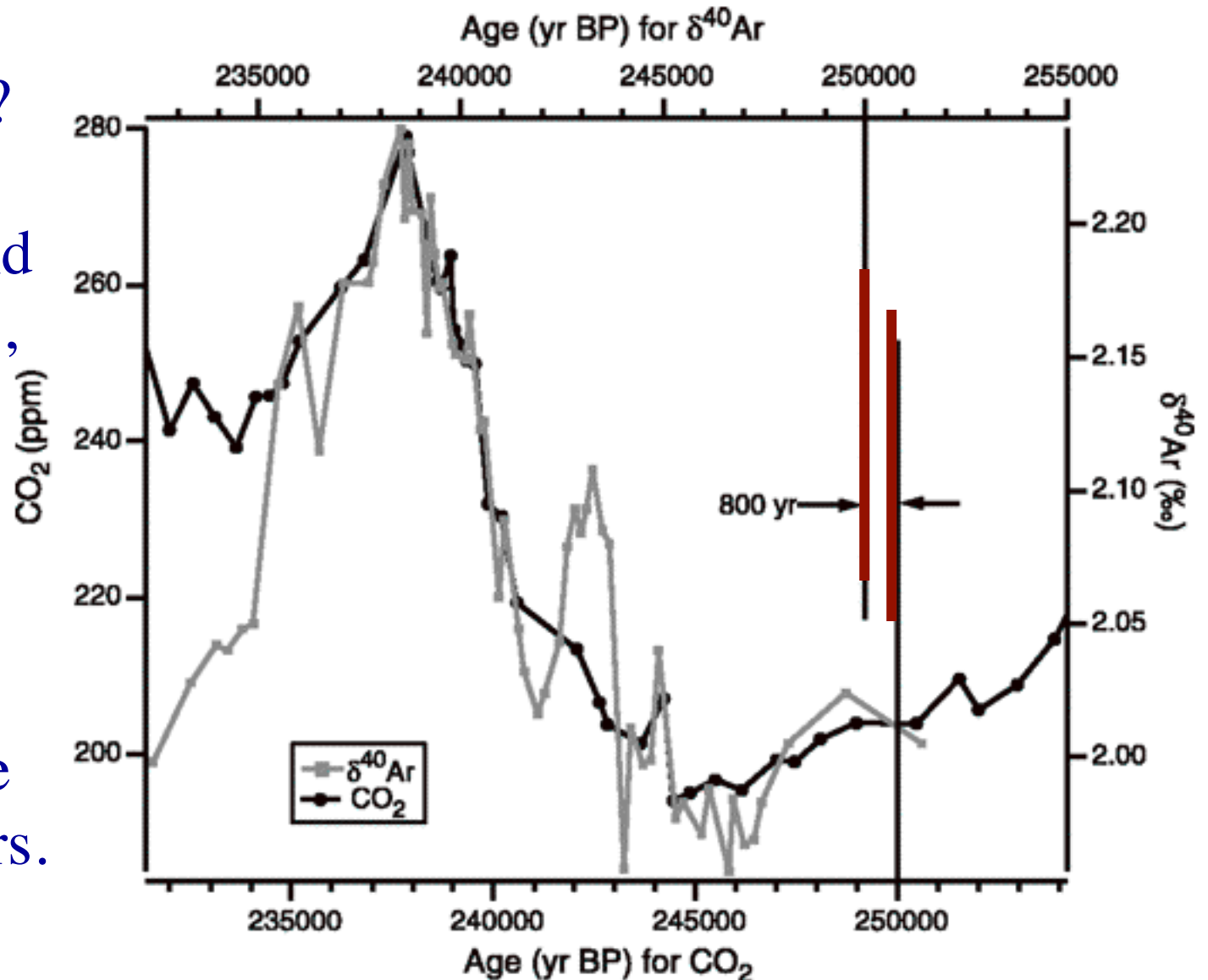


Caillon et al., 2003, *Science* 299, 1728.

CO₂ and Temperature shift from ⁴⁰Ar

A better way?

- both CO₂ and Ar are gases, so no Δ age problem.
- At Vostok, CO₂ led temperature by 800 years.

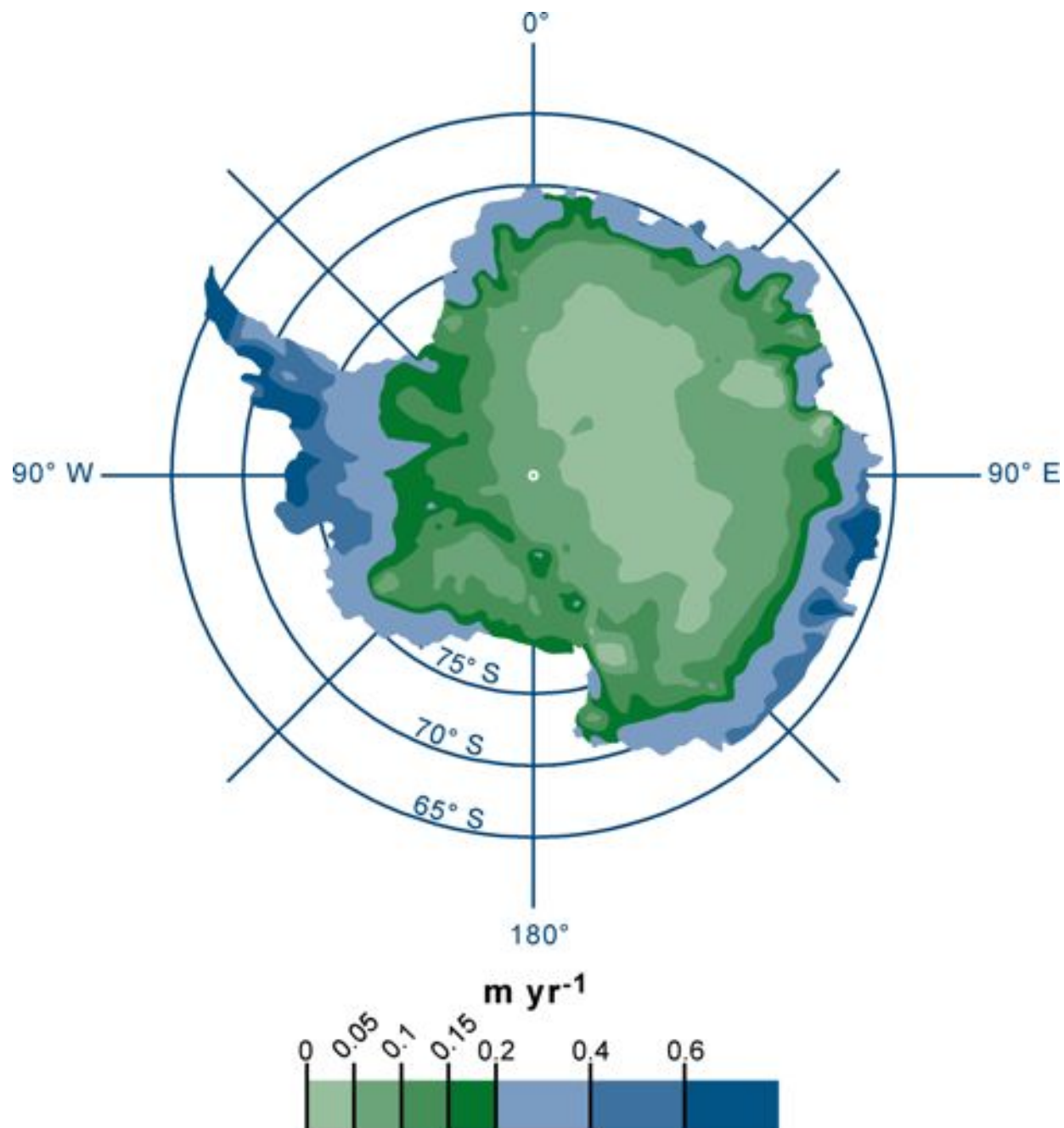


Caillon et al., 2003, *Science* 299, 1728.

What if we cannot count annual layers?

Where might this be a problem?

Antarctic Accumulation Rate



Cuffey and Paterson (2010)
The physics of glaciers.
FIGURE 4.16

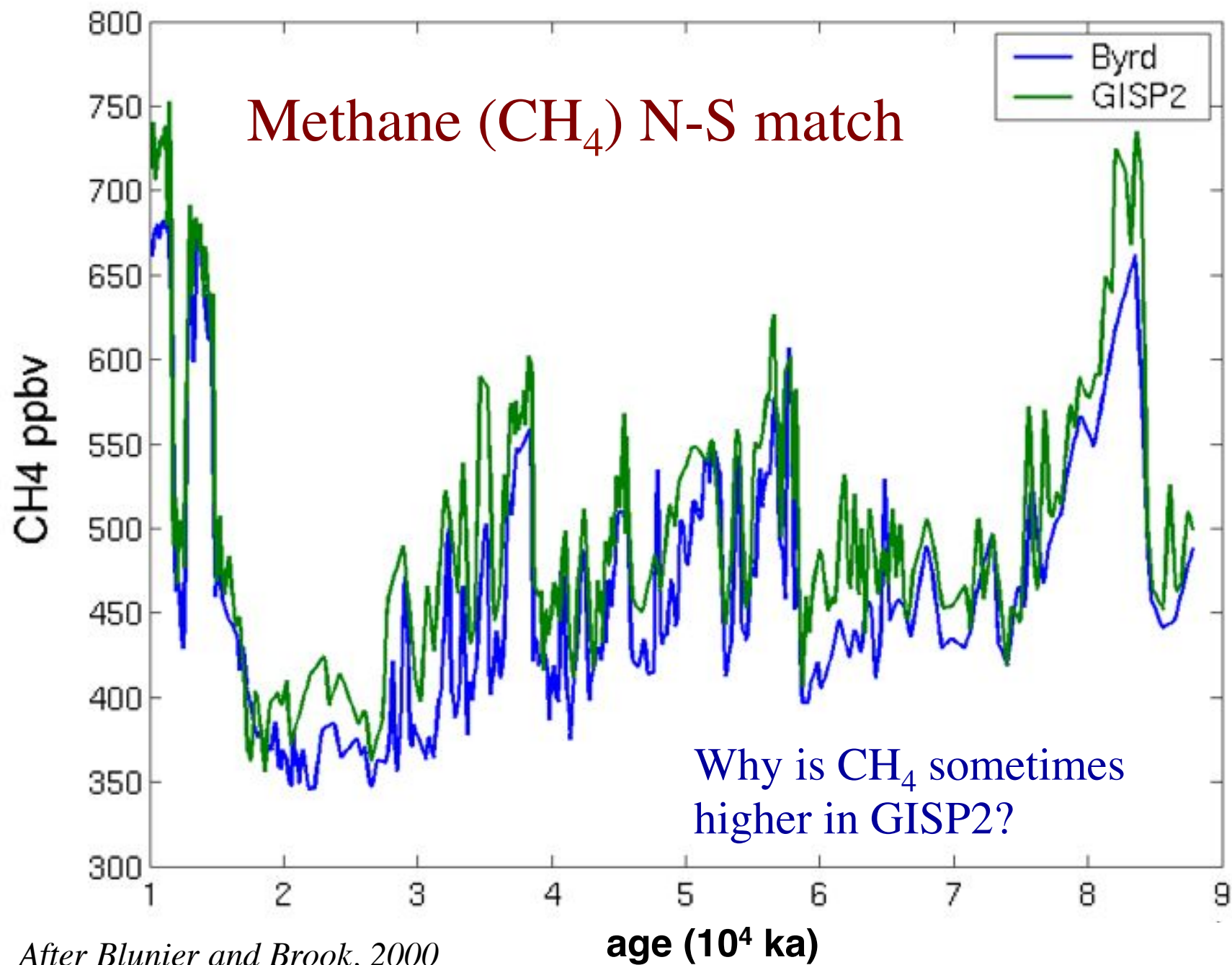
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Colorplate.2

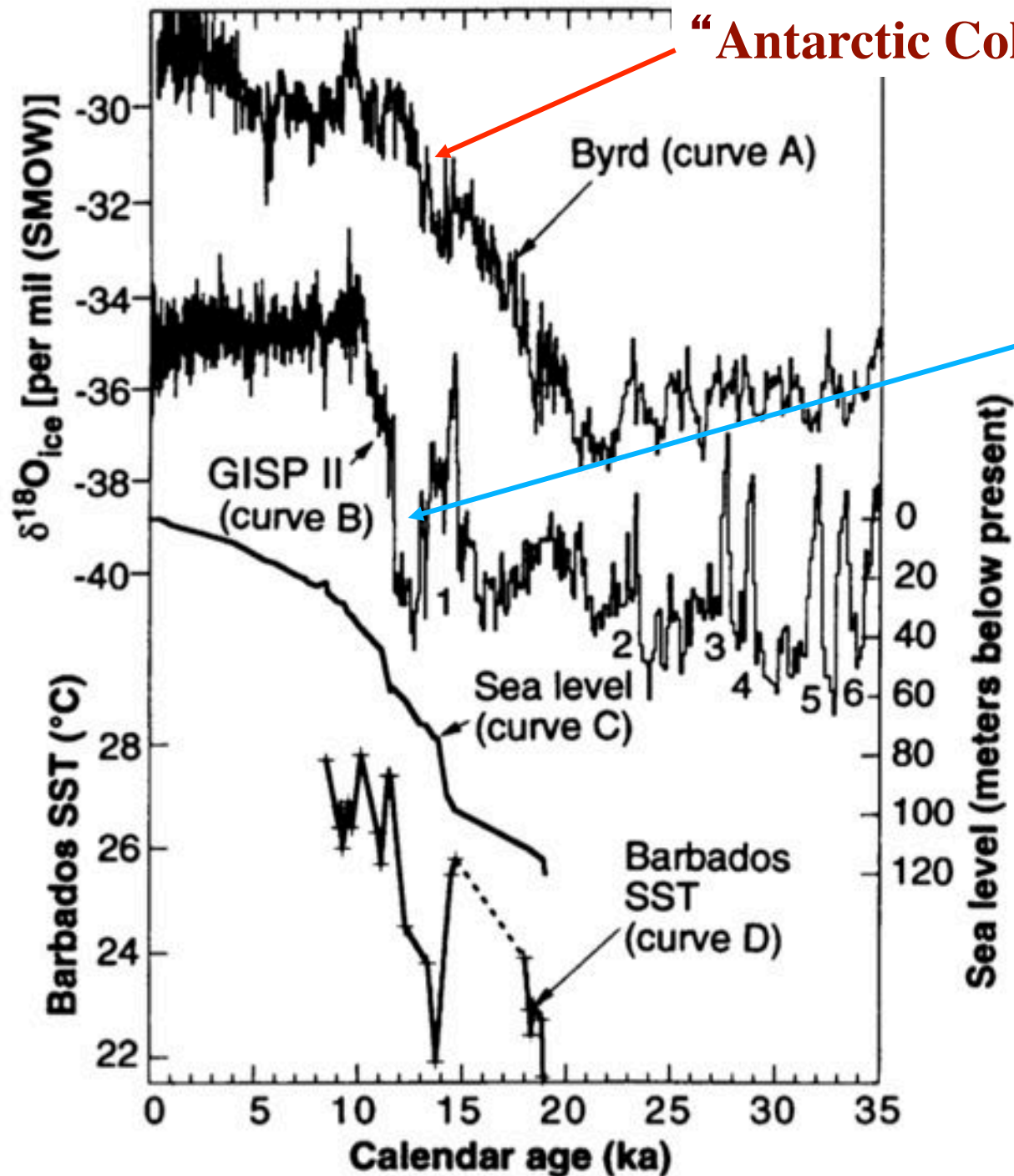
Steps in gas-correlation dating

- From layer-counted ice core (core A), calculate age of gas in the ice
- Match time series of globally mixed gases (CH_4 , $\delta^{18}\text{O}$ of O_2 , CO_2) between cores A and B
- Determine age of ice in core B

Note that we must know Δage in both cores ...



After Blunier and Brook, 2000

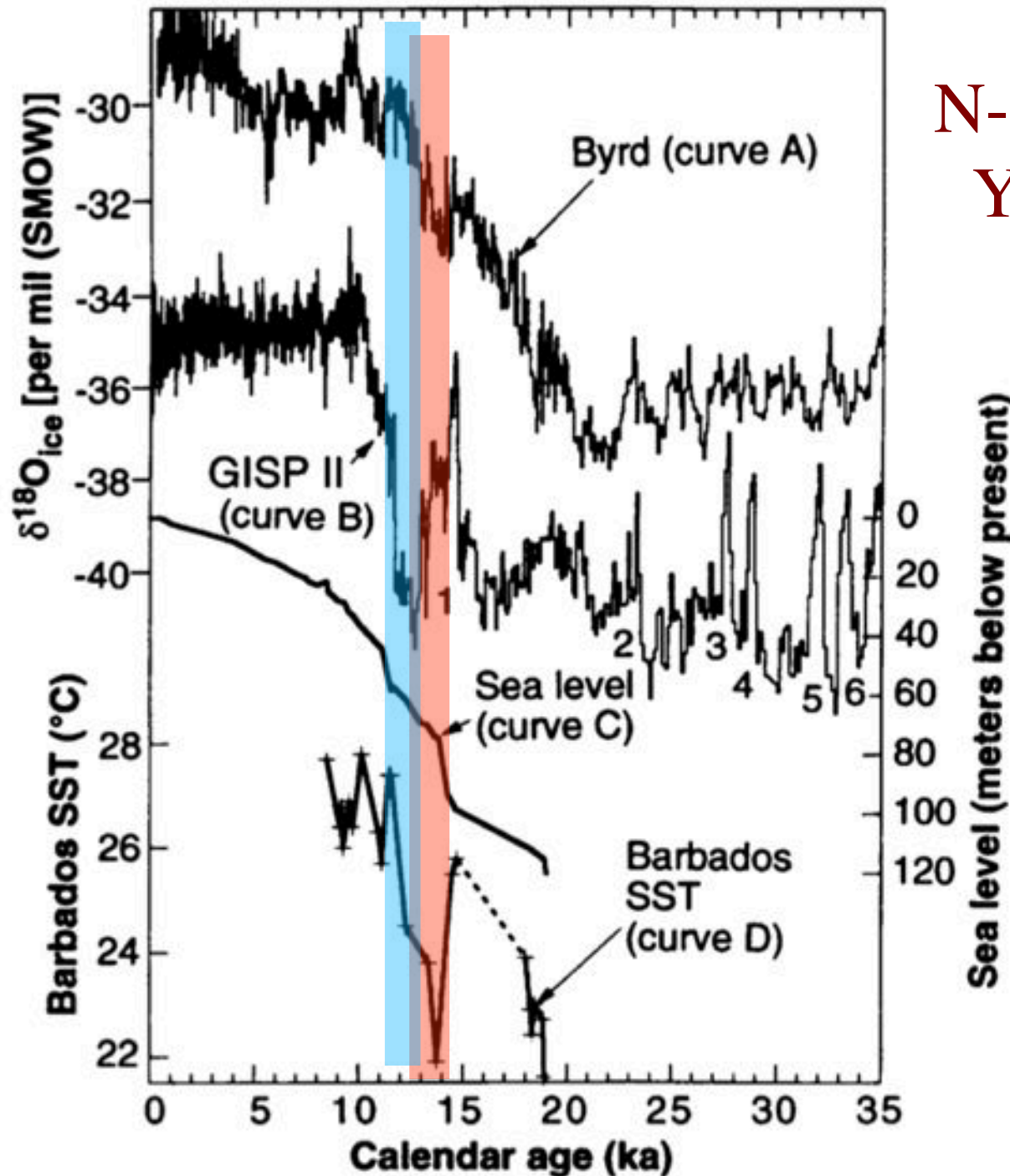


“Antarctic Cold Reversal”

Younger Dryas

**North-South
Comparisons:
Ice-Age
Termination**

After Sowers and Bender, 1995

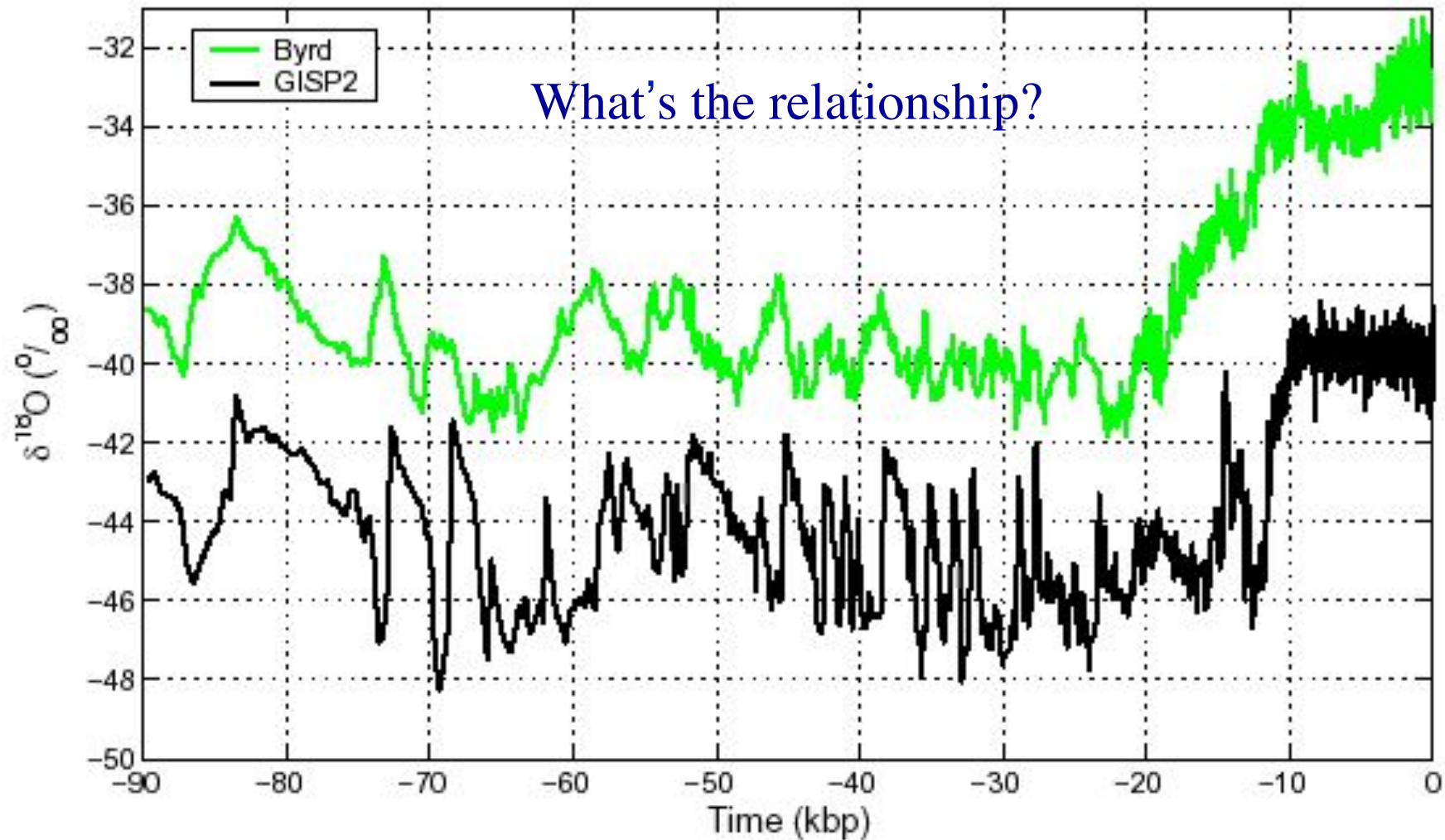


N-S comparisons: Younger Dryas Results

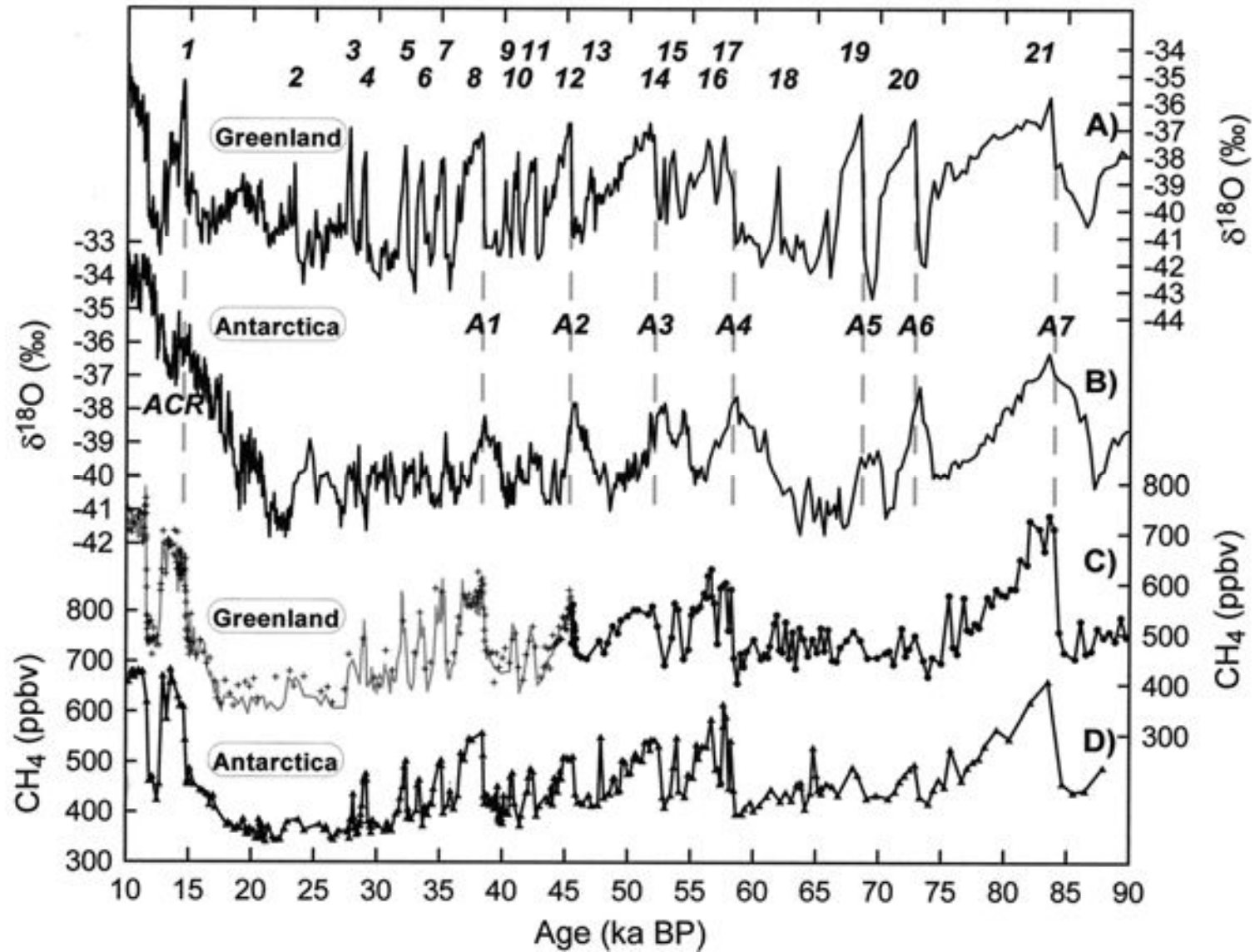
Cold ACR in
Antarctica was
simultaneous
with warm
Bolling-Allerod
interval in
Greenland

After Sowers and Bender, 1995

N-S Comparison on Common time Scale from $\delta^{18}\text{O}$ of O_2



Gas-based correlation



Anthropogenic Impacts

- CO₂
- N₂O
- CH₄
- CFC
- Pb

Nature 484, 5 April 2012

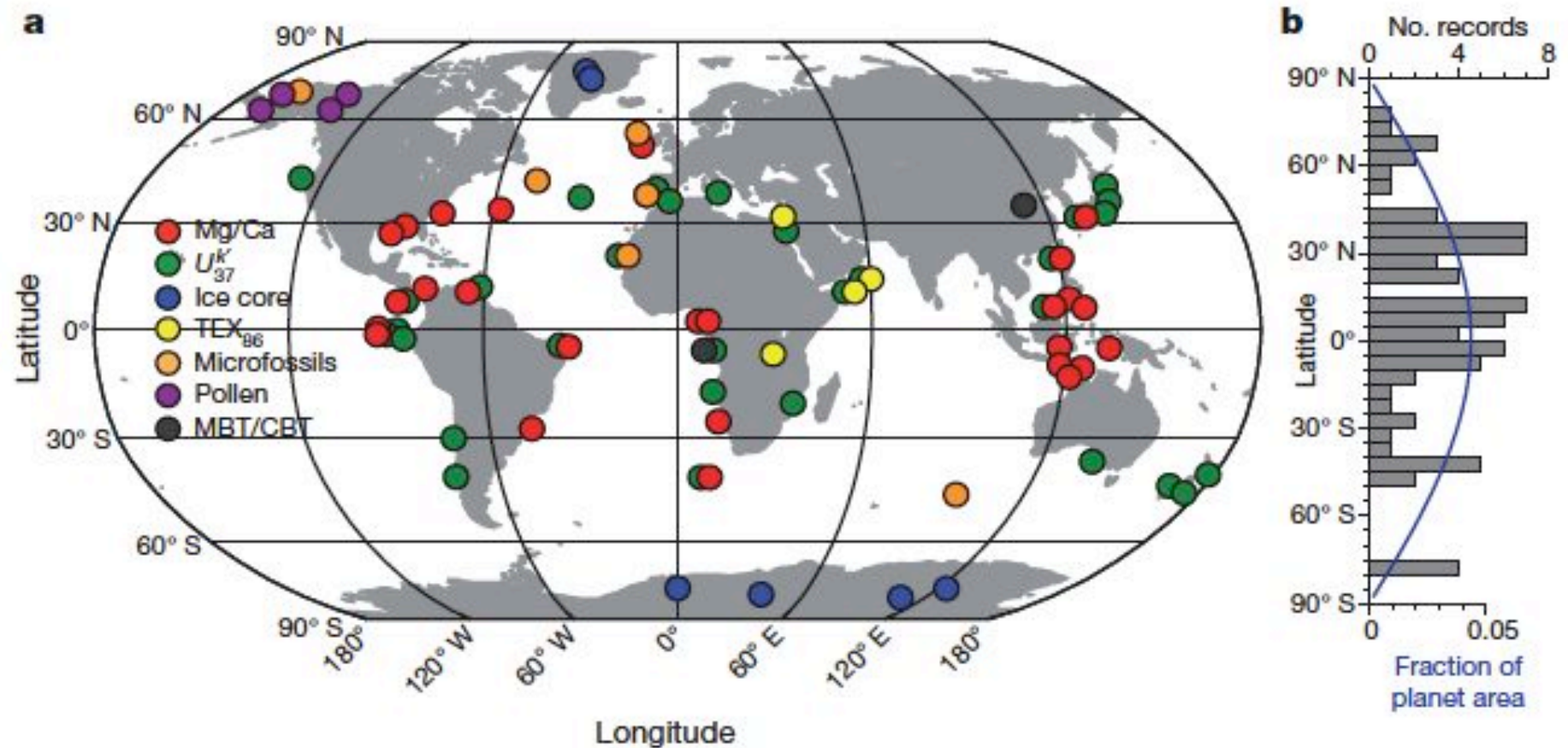
ARTICLE

doi:10.1038/nature10915

Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation

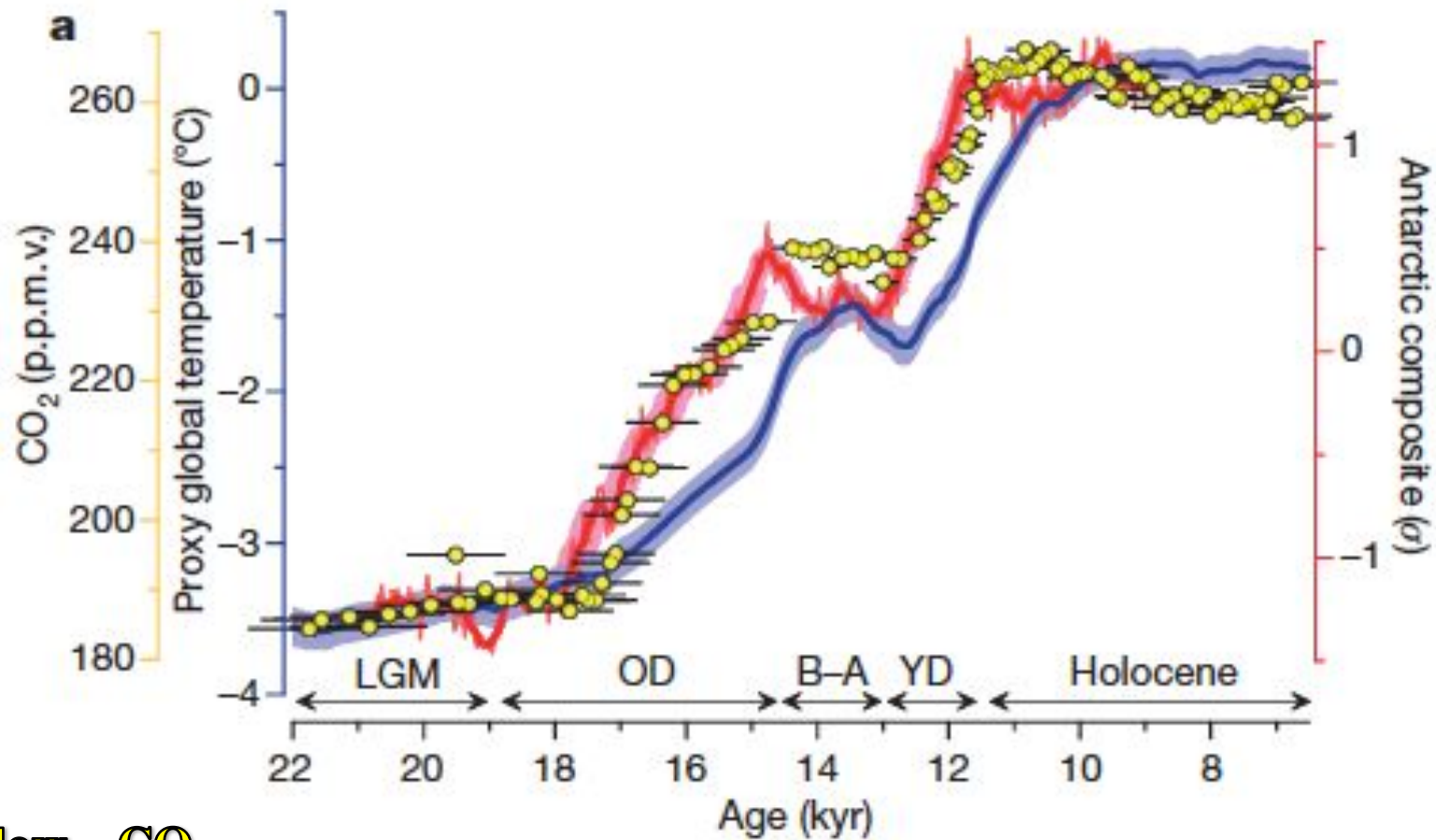
Jeremy D. Shakun^{1,2}, Peter U. Clark³, Feng He⁴, Shaun A. Marcott³, Alan C. Mix³, Zhengyu Liu^{4,5,6}, Bette Otto-Bliesner⁷, Andreas Schmittner³ & Edouard Bard⁸

Sites with climate records – (temperature)



Shakun et al. *Nature* 484 5 April 2012.

CO₂ and Temperature



Yellow – CO₂

Blue – Global proxy-temperature stack

Red – Antarctic ice cores

Shakun et al. *Nature* 484 5 April 2012.

CO₂ and Temperature

- Meltwater in North alters ocean currents
- South warms first
- Southern Ocean releases CO₂
- CO₂ contributes to global warming
- North warms

In (a-d)

Yellow – CO₂

Blue – Northern hemisphere T proxy stack

Red – Antarctic ice cores

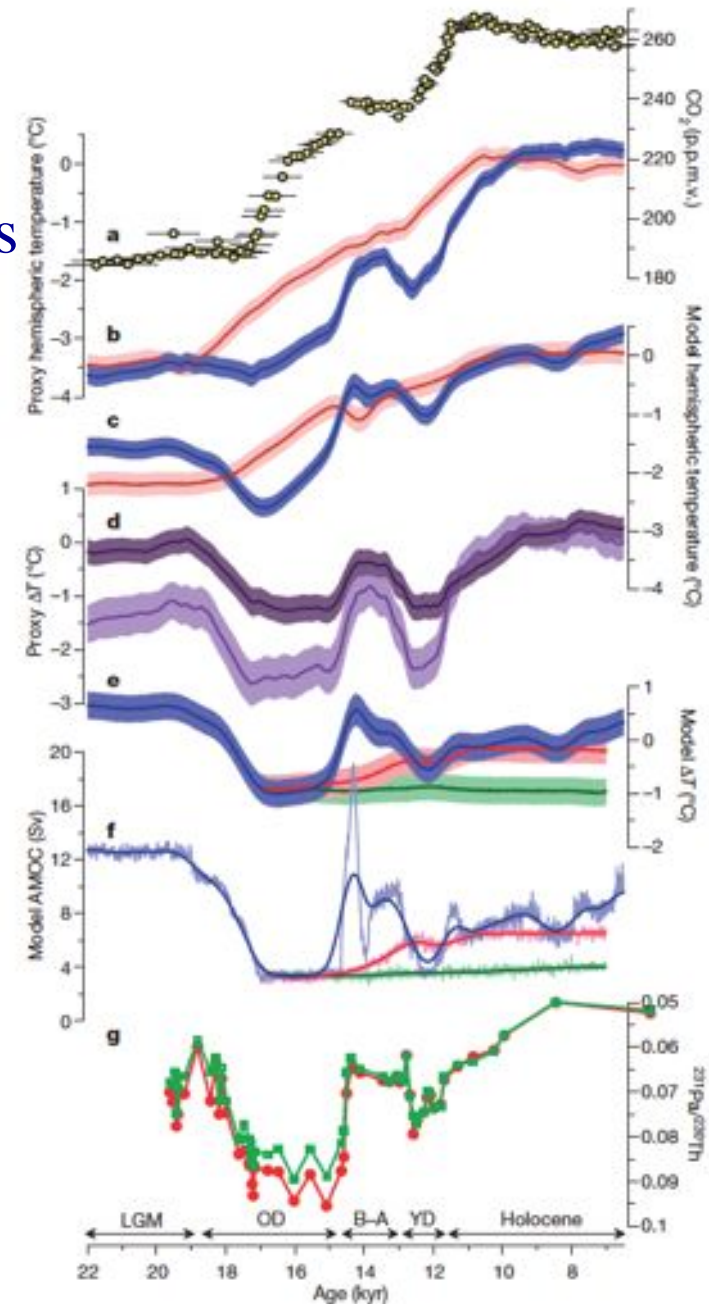
Purple – North minus South

In (e)

Blue – full coupled climate model

Red – CO₂ forcing only

Green – orbital forcing only



Ice-core Questions

1. Why is it so difficult to figure out leads and lags between temperature and CO₂ in the past? Both are measured in the same ice cores, for gosh sakes!
2. What might happen to the ice-age/gas-age difference in central Antarctica when the climate cools by 10°C in an ice age?
3. Detecting annual layers is a way to date an ice core absolutely, in calendar years. How well would you expect to be able to date a core using dust, in Greenland, and in East Antarctica? Using δD ? Explain your reasoning.
4. After experiencing a summer of near-continuous sunlight, the Greenland ice sheet undergoes strong daily cycles during autumn. Where and when would you expect to see hoar layers forming? Why?
5. Suppose a layer of surface hoar formed every autumn on an ice sheet. Could you use this to date the core? Would this work for ice older than the pore-closeoff age?
6. Using bubbles in ice cores, how well do you think you could resolve (or detect) changes in atmospheric gases on a seasonal scale? Annual scale? Decadal scale? Centennial scale? Why?