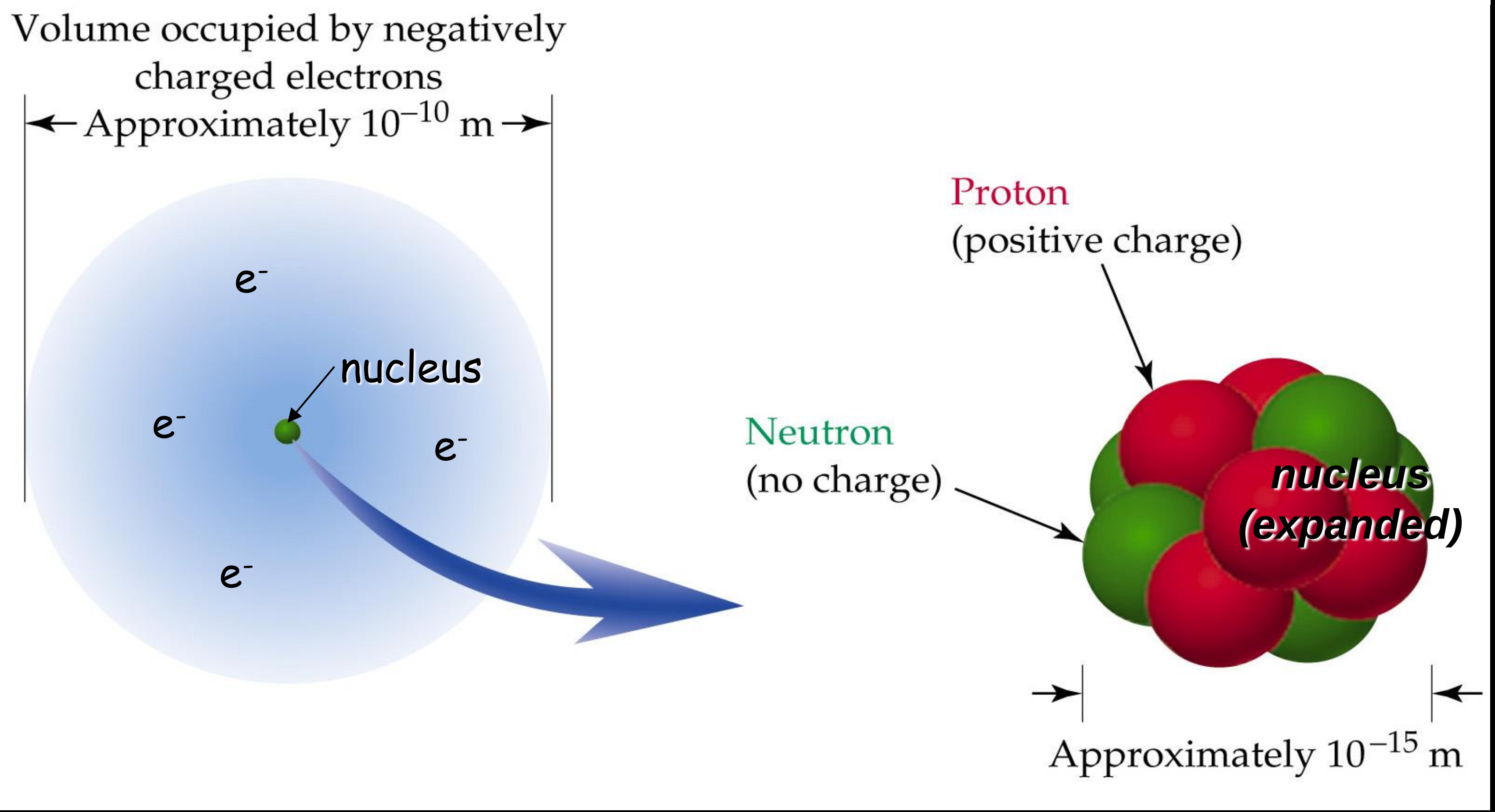
EARTH SYSTEM AND CLIMATE

Week 2: Oxygen Isotope Systematics and Proxy Records

Review: Isotopes

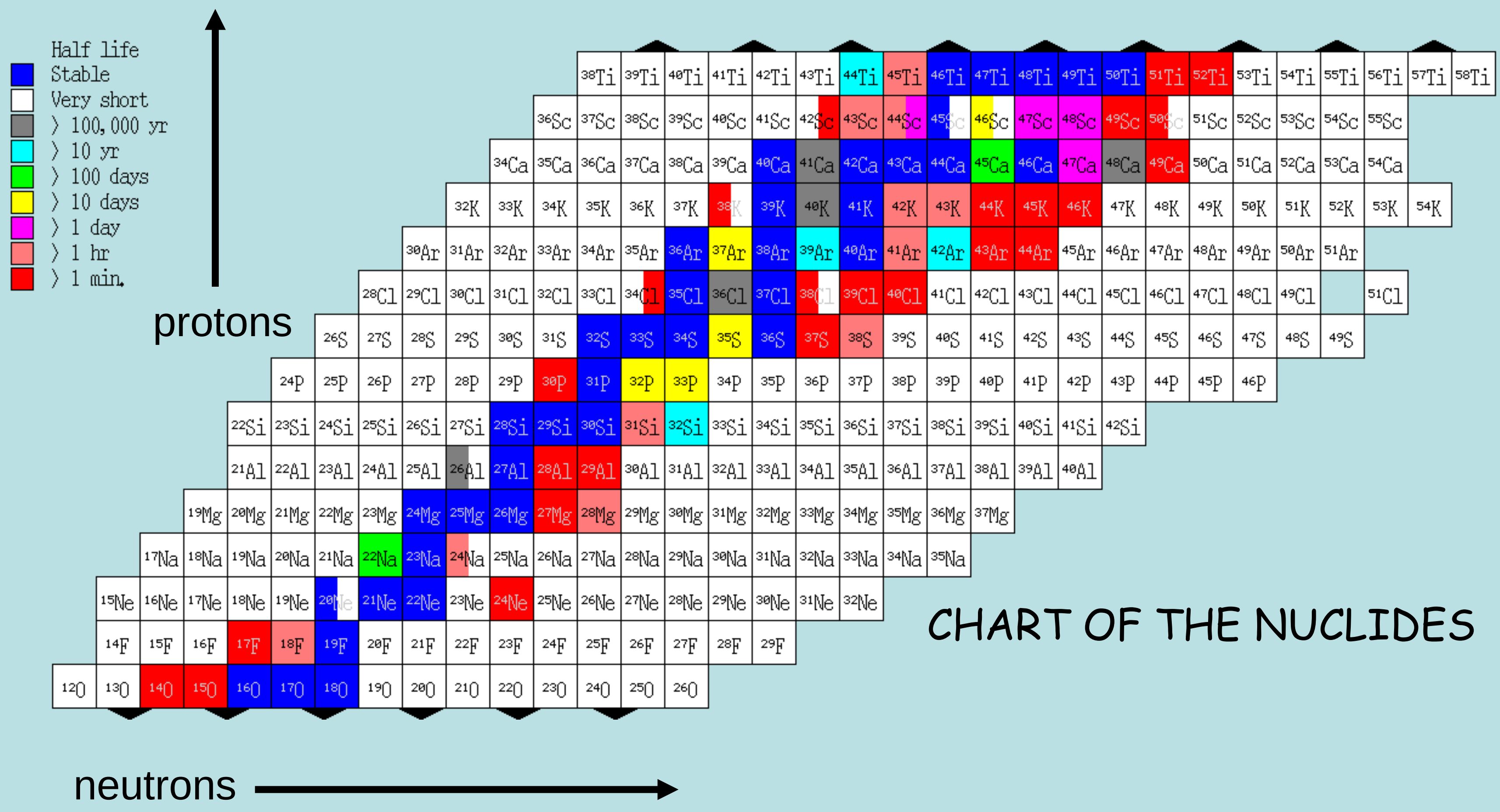
Atomic Structure



Atomic Mass:

- Neutron = 1 gram/mole no charge
- Proton = 1 gram/mole (+) charge
- Electron = 0 grams/mole (-) charge

number of protons determines what the atom **"<u>is</u>"**


Half life
Stable
Very short
> 100,000 yr
> 10 yr
> 100 days
> 10 days
> 1 day
> 1 hr
> 1 min.
protons
neutrons
38Ti 39Ti 40Ti 41Ti 42Ti 43Ti 44Ti 45Ti 46Ti 47Ti 48Ti 49Ti 50Ti 51Ti 52Ti 53Ti 54Ti 55Ti 56Ti 57Ti 58Ti
36Sc 37Sc 38Sc 39Sc 40Sc 41Sc 42Sc 43Sc 44Sc 45Sc 46Sc 47Sc 48Sc 49Sc 50Sc 51Sc 52Sc 53Sc 54Sc 55Sc
34Ca 35Ca 36Ca 37Ca 38Ca 39Ca 40Ca 41Ca 42Ca 43Ca 44Ca 45Ca 46Ca 47Ca 48Ca 49Ca 50Ca 51Ca 52Ca 53Ca 54Ca
32K 33K 34K 35K 36K 37K 38K 39K 40K 41K 42K 43K 44K 45K 46K 47K 48K 49K 50K 51K 52K 53K 54K
30Ar 31Ar 32Ar 33Ar 34Ar 35Ar 36Ar 37Ar 38Ar 39Ar 40Ar 41Ar 42Ar 43Ar 44Ar 45Ar 46Ar 47Ar 48Ar 49Ar 50Ar 51Ar
28Cl 29Cl 30Cl 31Cl 32Cl 33Cl 34Cl 35Cl 36Cl 37Cl 38Cl 39Cl 40Cl 41Cl 42Cl 43Cl 44Cl 45Cl 46Cl 47Cl 48Cl 49Cl 51Cl
26S 27S 28S 29S 30S 31S 32S 33S 34S 35S 36S 37S 38S 39S 40S 41S 42S 43S 44S 45S 46S 47S 48S 49S
24P 25P 26P 27P 28P 29P 30P 31P 32P 33P 34P 35P 36P 37P 38P 39P 40P 41P 42P 43P 44P 45P 46P
22Si 23Si 24Si 25Si 26Si 27Si 28Si 29Si 30Si 31Si 32Si 33Si 34Si 35Si 36Si 37Si 38Si 39Si 40Si 41Si 42Si
21Al 22Al 23Al 24Al 25Al 26Al 27Al 28Al 29Al 30Al 31Al 32Al 33Al 34Al 35Al 36Al 37Al 38Al 39Al 40Al
19Mg 20Mg 21Mg 22Mg 23Mg 24Mg 25Mg 26Mg 27Mg 28Mg 29Mg 30Mg 31Mg 32Mg 33Mg 34Mg 35Mg 36Mg 37Mg
17Na 18Na 19Na 20Na 21Na 22Na 23Na 24Na 25Na 26Na 27Na 28Na 29Na 30Na 31Na 32Na 33Na 34Na 35Na
15Ne 16Ne 17Ne 18Ne 19Ne 20Ne 21Ne 22Ne 23Ne 24Ne 25Ne 26Ne 27Ne 28Ne 29Ne 30Ne 31Ne 32Ne
14F 15F 16F 17F 18F 19F 20F 21F 22F 23F 24F 25F 26F 27F 28F 29F
12O 13O 14O 15O 16O 17O 18O 19O 20O 21O 22O 23O 24O 25O 26O
CHART OF THE NUCLIDES

Changing the number of protons (p) changes the atomic number (Z) producing a distinctly different element

Different Elements:

	Carbon	Nitrogen	Oxygen
	$^{12}_{6}C$	$^{14}_{7}N$	$^{16}_{8}O$

Atomic mass (A)

Atomic number (Z)

A = 12	A = 14	A = 16
Z = 6	Z = 7	Z = 8
p = 6	p = 7	p = 8
n = 6	n = 7	n = 8
e = 6	e = 7	e = 8

Changing the number of neutrons (n) keeps the same atomic number (*Z*) but changes the atomic mass (*A*) producing an ISOTOPE of the same element

Isotopes of Oxygen:

Atomic mass (A)

Atomic number (Z)

$^{16}_{8}O$	$^{17}_{8}O$	$^{18}_{8}O$
A = 16	A = 17	A = 18
Z = 8	Z = 8	Z = 8
p = 8	p = 8	p = 8
n = 8	n = 9	n = 10

So why do these very small changes in mass matter?

Isotopic fractionation leading to Raleigh Distillation

So why do these very small changes in mass matter?

- *isotopic fractionation: organisation of isotopes of a given element through various physical reactions that result in the 'organisation' of the isotopes into distinct groups.*

- The heavier isotopes (^{18}O, ^{2}H) prefer to be in the least energetic state
- Therefore, the heavier isotopes are included preferentially in rain rather than water vapour, and snow rather than water, and certainly snow rather than water vapour
- The degree of fractionation is dependent on temperature. The colder it is the more the isotopes as fractionated according to mass
- The further the moisture mass (clouds) have moved the more fractionated they become

Standard Mean Ocean Water (SMOW) has 1 ^{18}O for every 499 ^{16}O

Or

2005 ppm

So: $^{18}O/^{16}O$ for SMOW = 1/499 = 0.002005

$$\frac{[^{18}O/^{16}O_{sample} - {}^{18}O/^{16}O_{SMOW}] \times 1000}{[^{18}O/^{16}O_{SMOW}]} = \delta^{18}O$$

For our example with rain isotopic fractionation
(18/16 ratios changed to reflect reality!!)

day	$^{18}O/^{16}O$	$\delta^{18}O$ (‰)
0	0.002002	-1.49
1	0.002000	-2.49
2	0.001997	-3.99
3	0.001992	-6.48

Fractionation Factors

- At isotopic equilibrium, we can define equilibrium constant or fractionation factor:

$$\alpha_{(water\text{-}gas)} = (\delta^{18}O_{water} + 1000) / (\delta^{18}O_{gas} + 1000)$$

α(water-gas) = 1.002 fractionates less strongly than a(water-gas) = 1.004

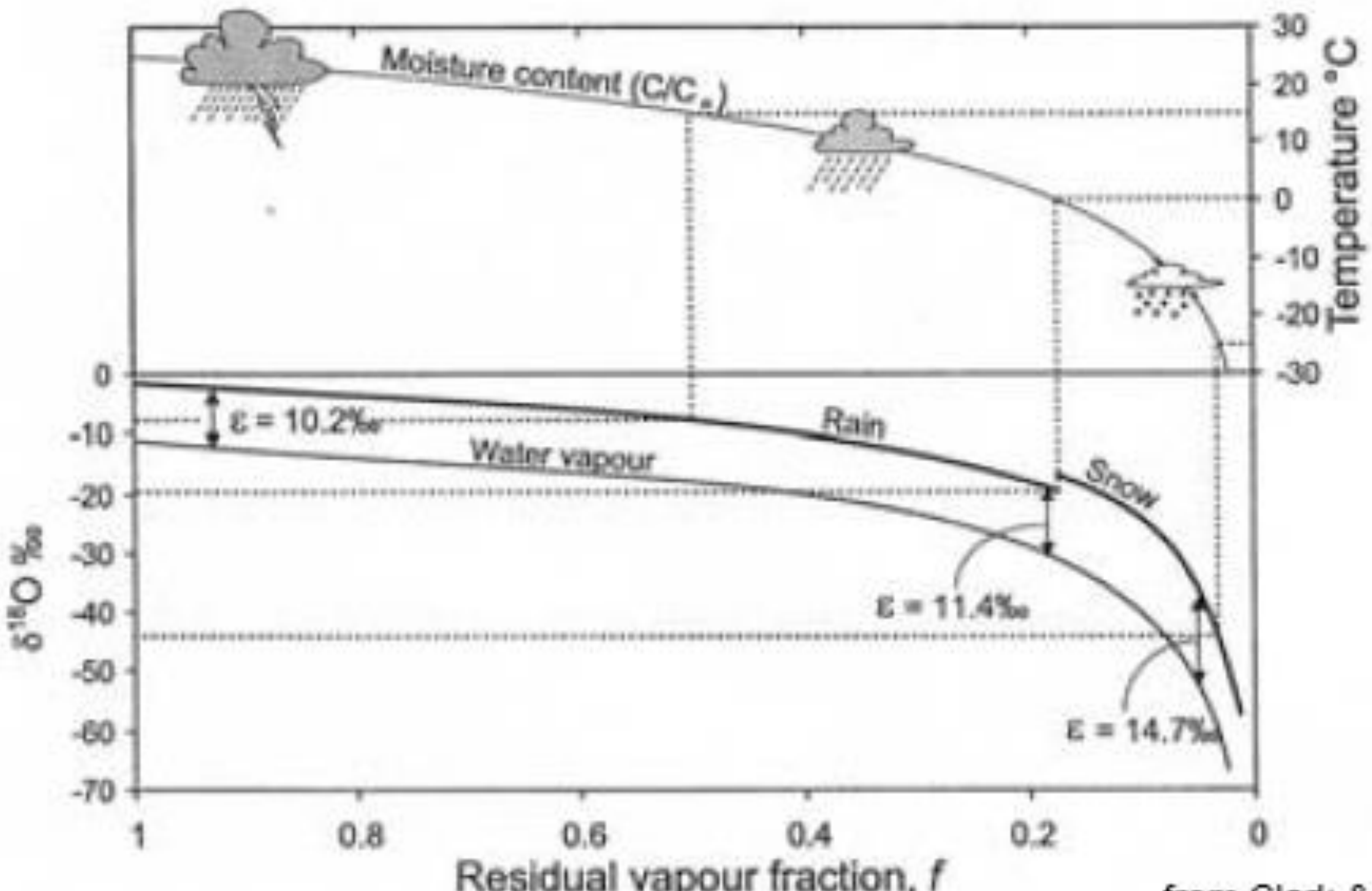
Fractionation factors determine how strongly stable isotopes are separated according to mass by natural processes

Temperature – $\delta^{18}O$ relationships vary

In general, stable isotopes in rainwater are affected by:

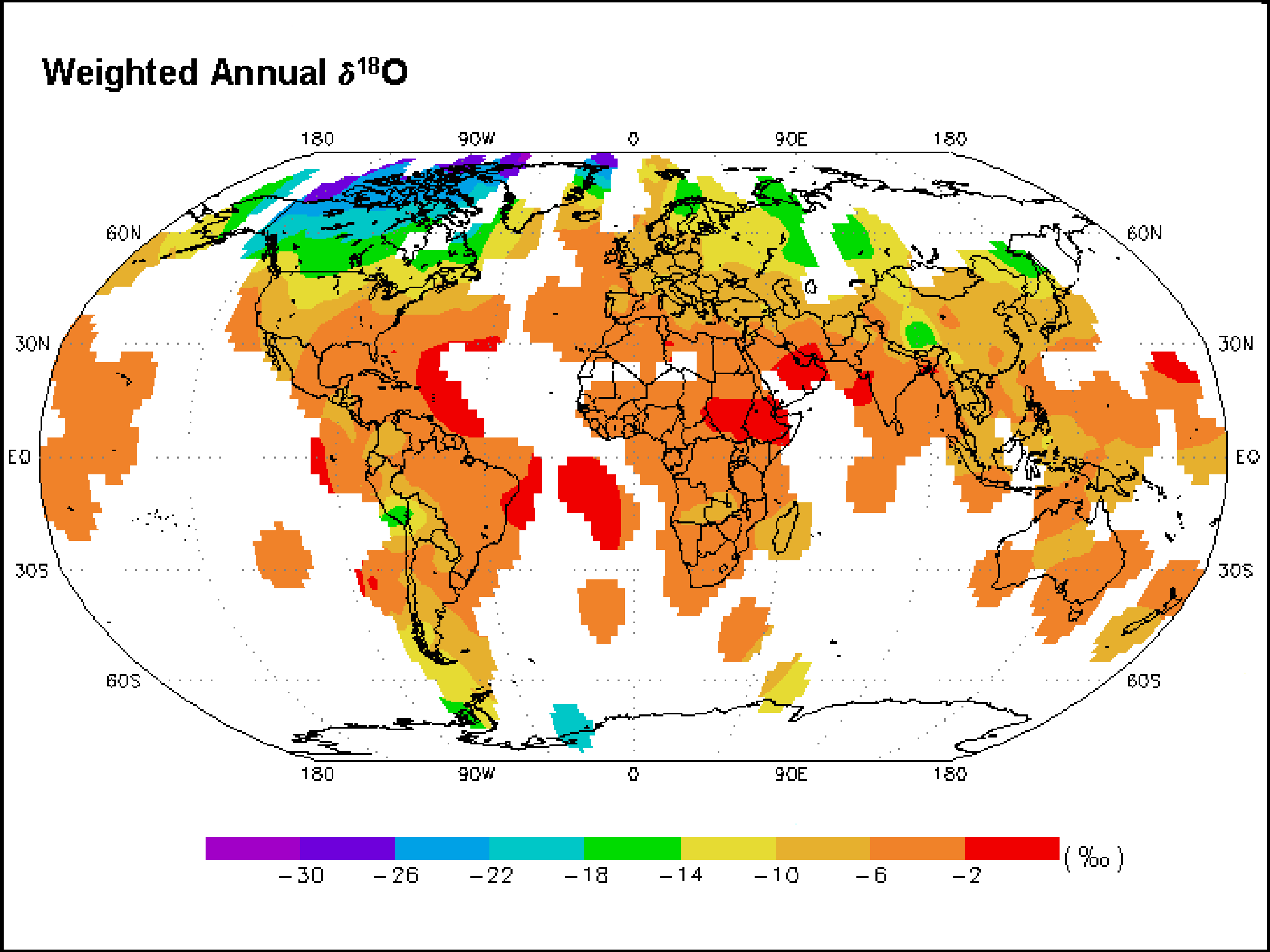
- Isotope ratio of source moisture
- Temperature
- 'Rainout effect'
- 'Amount effect'

Rayleigh distillation in clouds and moisture masses. This leads to increasingly lower oxygen isotope ratios

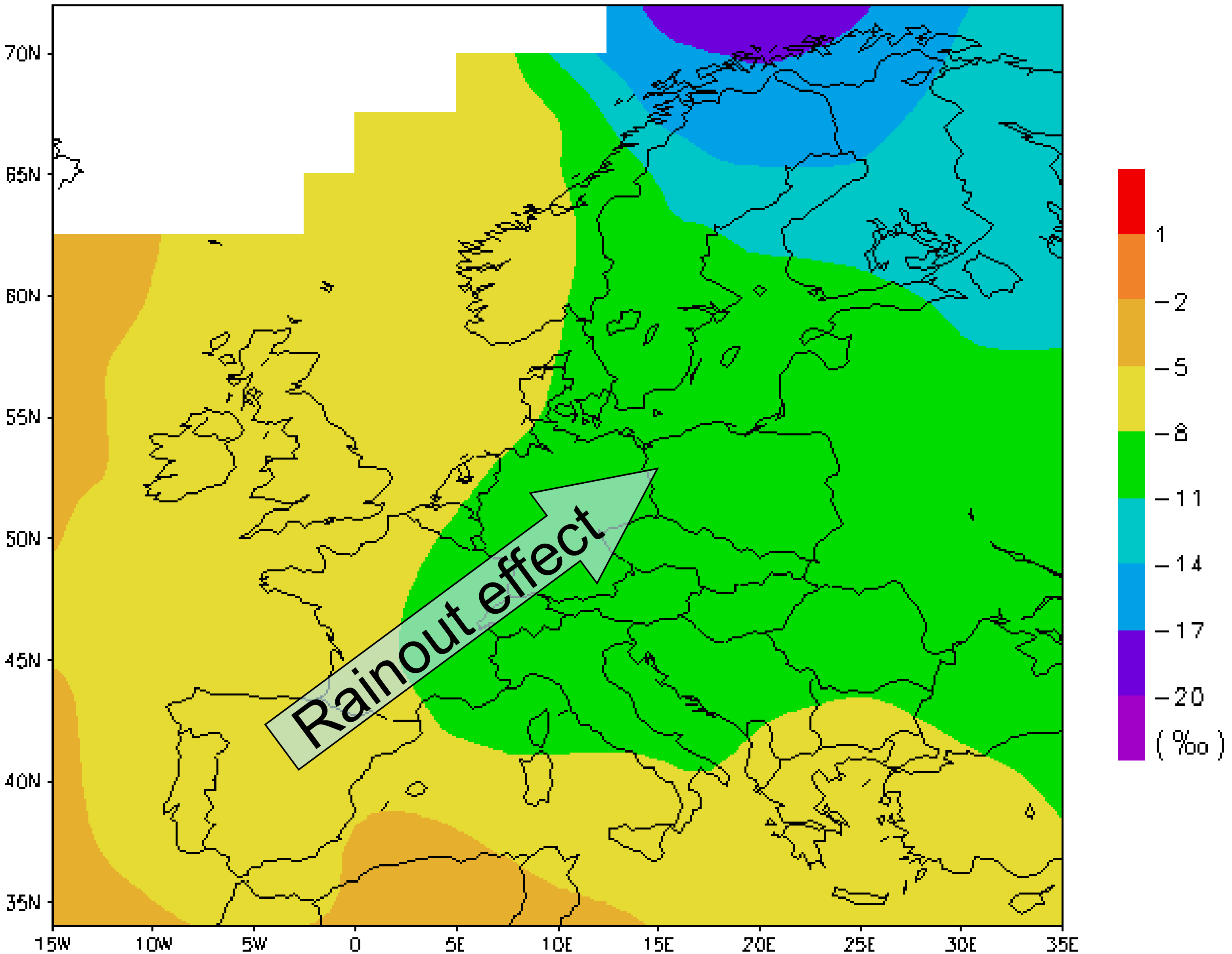


from Clark & Fritz, 1997 9

Dansgaard, 1964: $\delta^{18}O‰ = 0.69\ Temp - 13.6$



Weighted Annual $\delta^{18}O$



'Temperature Effect' controls fractionation factor

- lower T = greater fractionation

'Rainout Effect' controls the amount of ^{18}O left

- more rainout, less ^{18}O and more ratios
- Raleigh Distillation

The Amount Effect:

- During very strong rain events, $d^{18}O$ is observed to be anticorrelated with rainfall amount
- The reason is intense and rapid fractionation
- Low temperatures related to the height of the cloud mass
- Abundant rain means abundant fractionation

Commonly Measured Stable Isotopes

• Hydrogen	D	99.9852%	Ratio Reported
	H	0.0148%	D/H
• Carbon	^{12}C	98.89%	
	^{13}C	1.11%	$^{13}C/^{12}C$
• Oxygen	^{16}O	99.63%	
	^{17}O	0.0375%	
	^{18}O	0.1995%	$^{18}O/^{16}O$
• Sulphur	^{32}S	95.02%	
	^{33}S	0.75%	
	^{34}S	4.21%	$^{34}S/^{32}S$
	^{36}S	0.02%	

Reference Materials

Hydrogen------------Standard Mean Ocean Water

(V) SMOW

Oxygen-------------- Standard Mean Ocean Water

(V) SMOW

Reference Materials

Carbon--------------Pee Dee Belemnite

(V) PDB

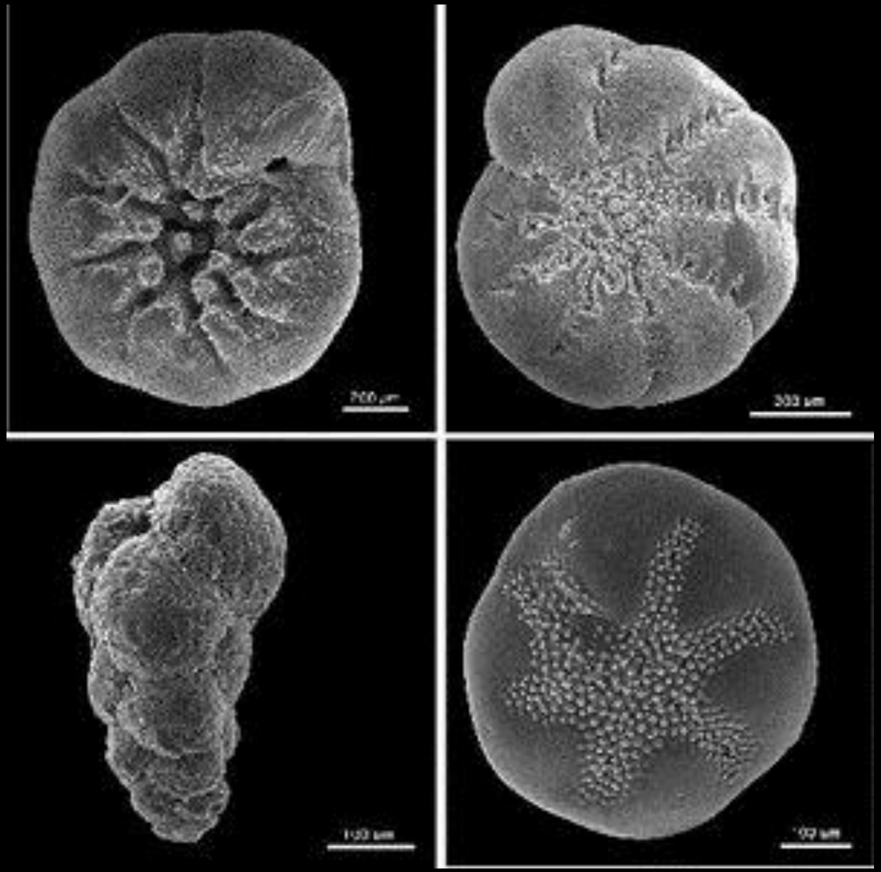
PeeDee Formation, South Carolina

The first real geochemical proxy records to show the effects of multiple glaciations were deep sea sediment cores

First deep sea sediment cores used in palaeoclimatology were obtained by the Swedish Deep Sea Expedition on board the research ship *Albatross* in 1947-1949

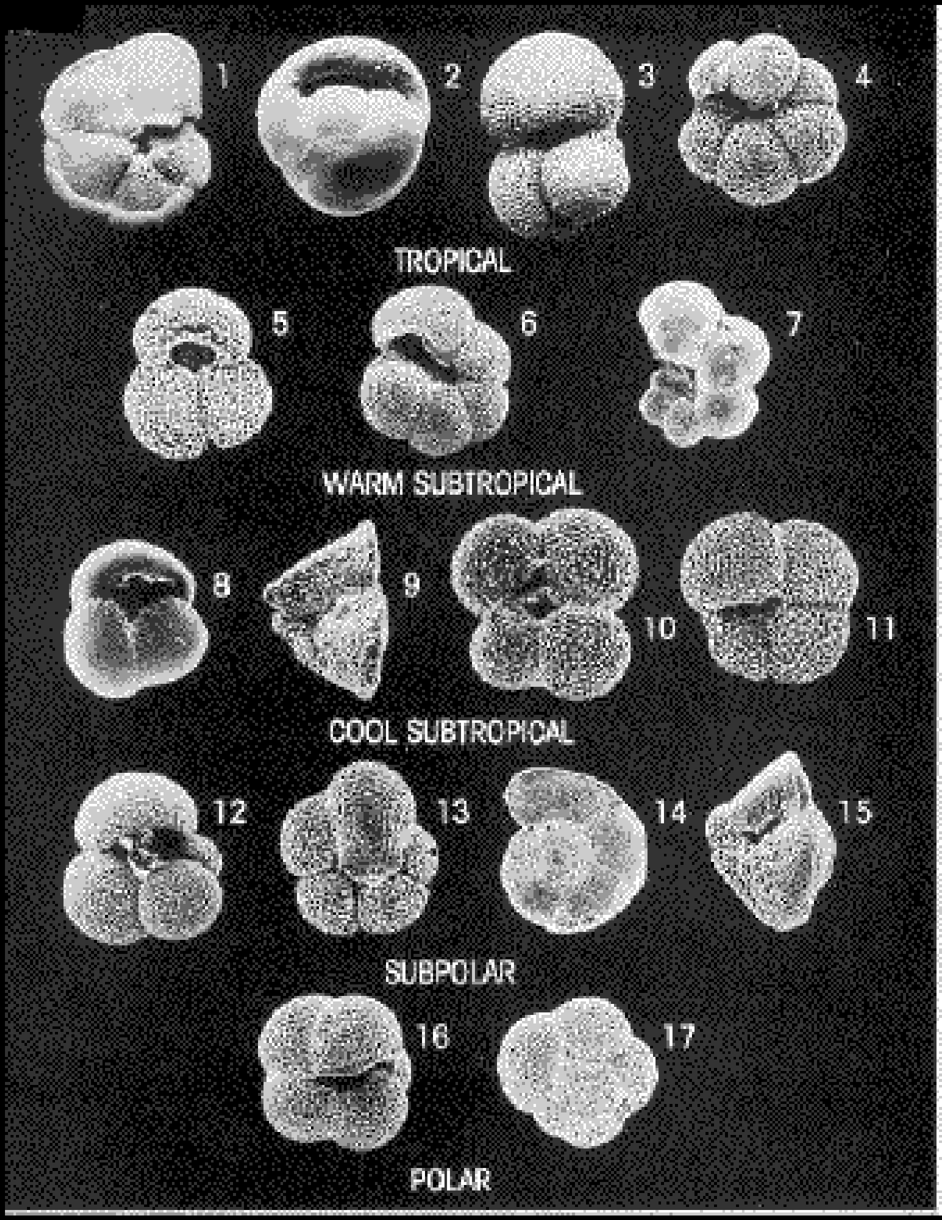
Chronology established by estimating sedimentation rates, by palaeomagnetism, and by looking for ash beds

- Common proxies measured include $\delta^{18}O$, $\delta^{13}C$, and Sr/Ca
- Measurements are generally not taken on whole core, but on individual *foraminifera*



Ocean sediment cores

- 250,000 varieties of forams known
- Amoeboid protists that develop a calcite test, or shell.
- Forams that live near the surface are called *pelagic (or planktic)*
- Forams living near the ocean floor are called *benthic*
- *Local water conditions recorded in shell*



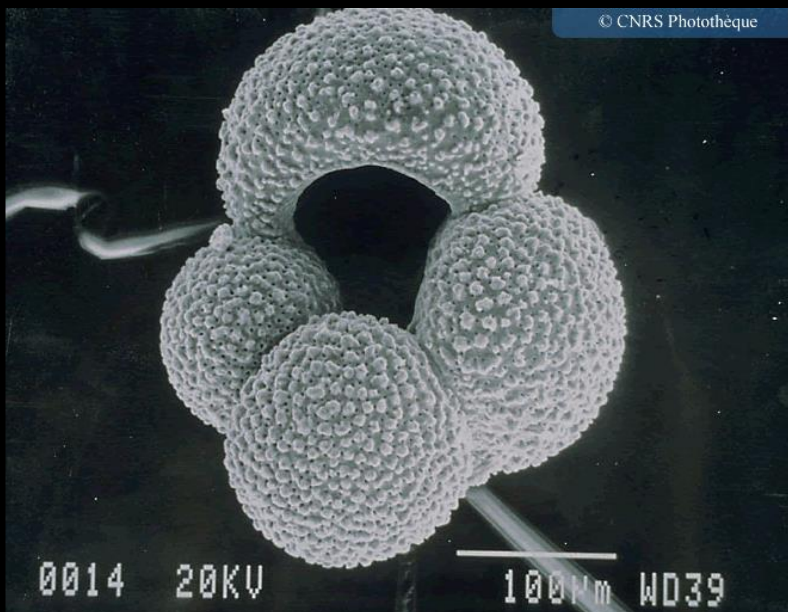
Foraminiferal oxygen isotope composition

- Isotopic composition of the water from which the carbonate was extracted
- Water emperature
- Sali
- Deg on
- Degree of bioturbation
- Vital effects

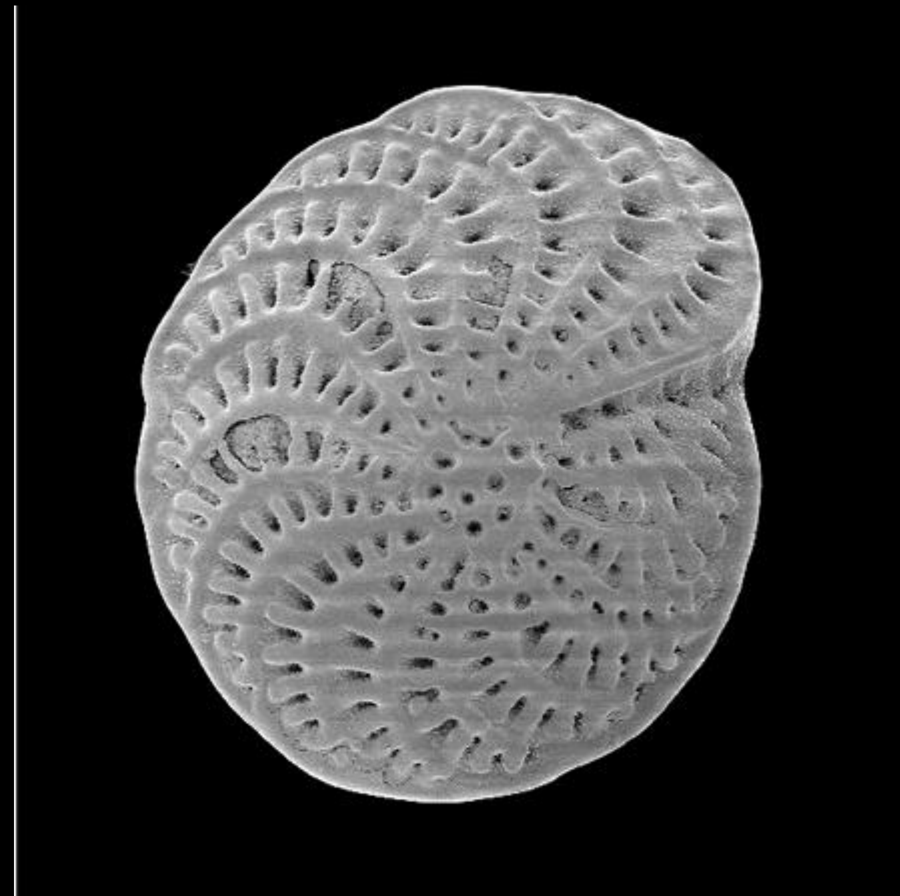
Isotopic composition of water reflects global ice volume

Majority of oxygen isotope signature due to the composition of the water

How Can We Measure $\delta^{18}O$ of Ancient Ocean Water?



Globigerina bulloides (planktic species)



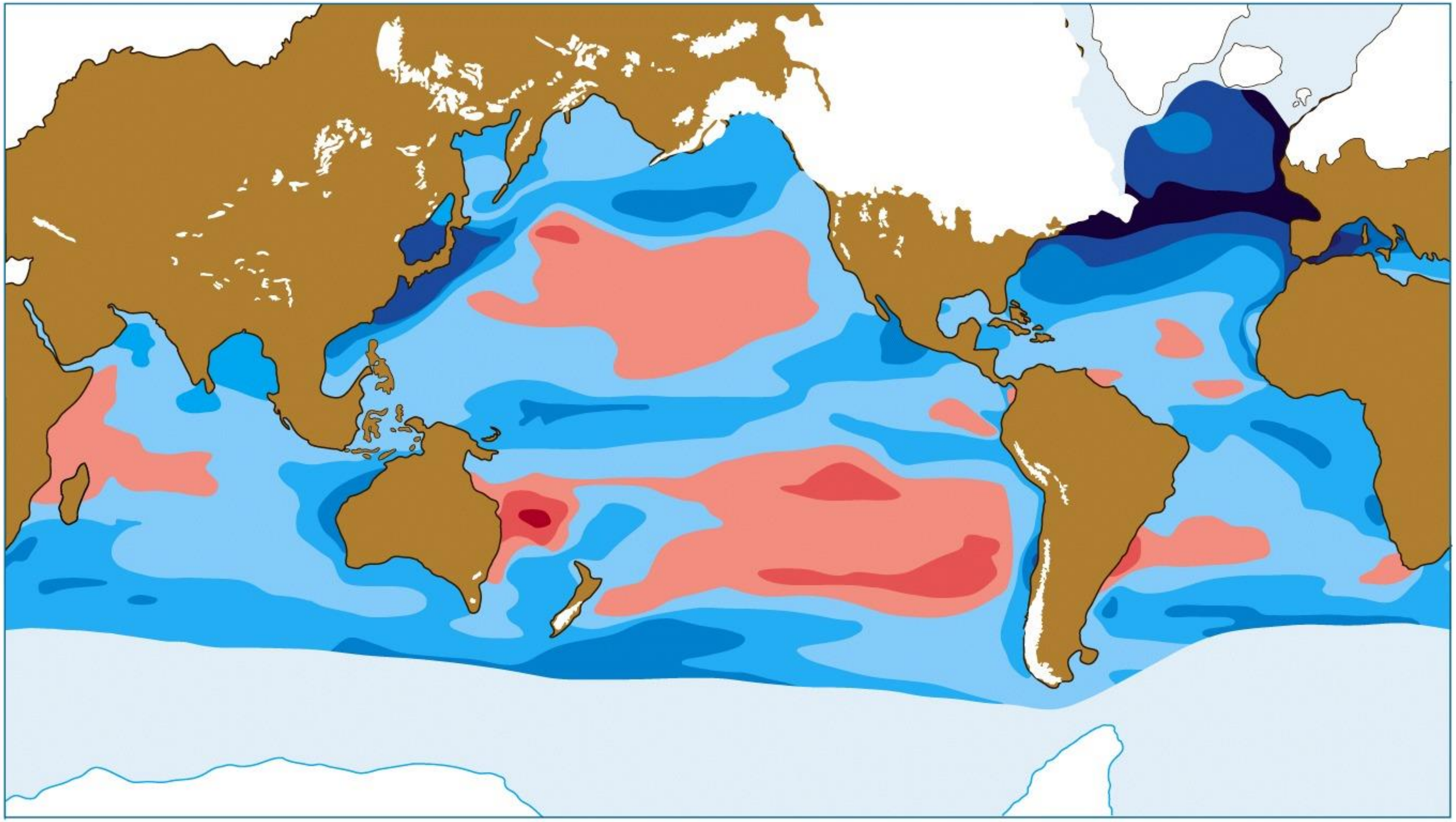
Elphidium macellum (benthic species)

http://www.ucl.ac.uk/GeolSci/micropal/foram.html

The General Idea

- The calcite ($CaCO_3$) shells grown by foraminifera can be used to measure $\delta^{18}O$ of ocean water.
- When these organisms secrete their shells, the del-18-O in the calcite reflects (mainly): (1) the del-18-O of the sea water they live in, and (2) the temperature of the water.
- Initial studies focused on estimating changes in ocean temperature from fossil forams found in deep ocean sediment cores.
- However, it was soon discovered that past changes in ice volume are also a primary control on the measured del-18-O variation.

Changes in Ocean Temperatures Largest Near Surface - LGM



B August ocean temperature change (°C) Cooling > 8 6 – 8 4 – 6 2 – 4 0 – 2
Warming 0 – 2 > 2

Marine Del-18-O Results From Planktonic and Benthonic Forams

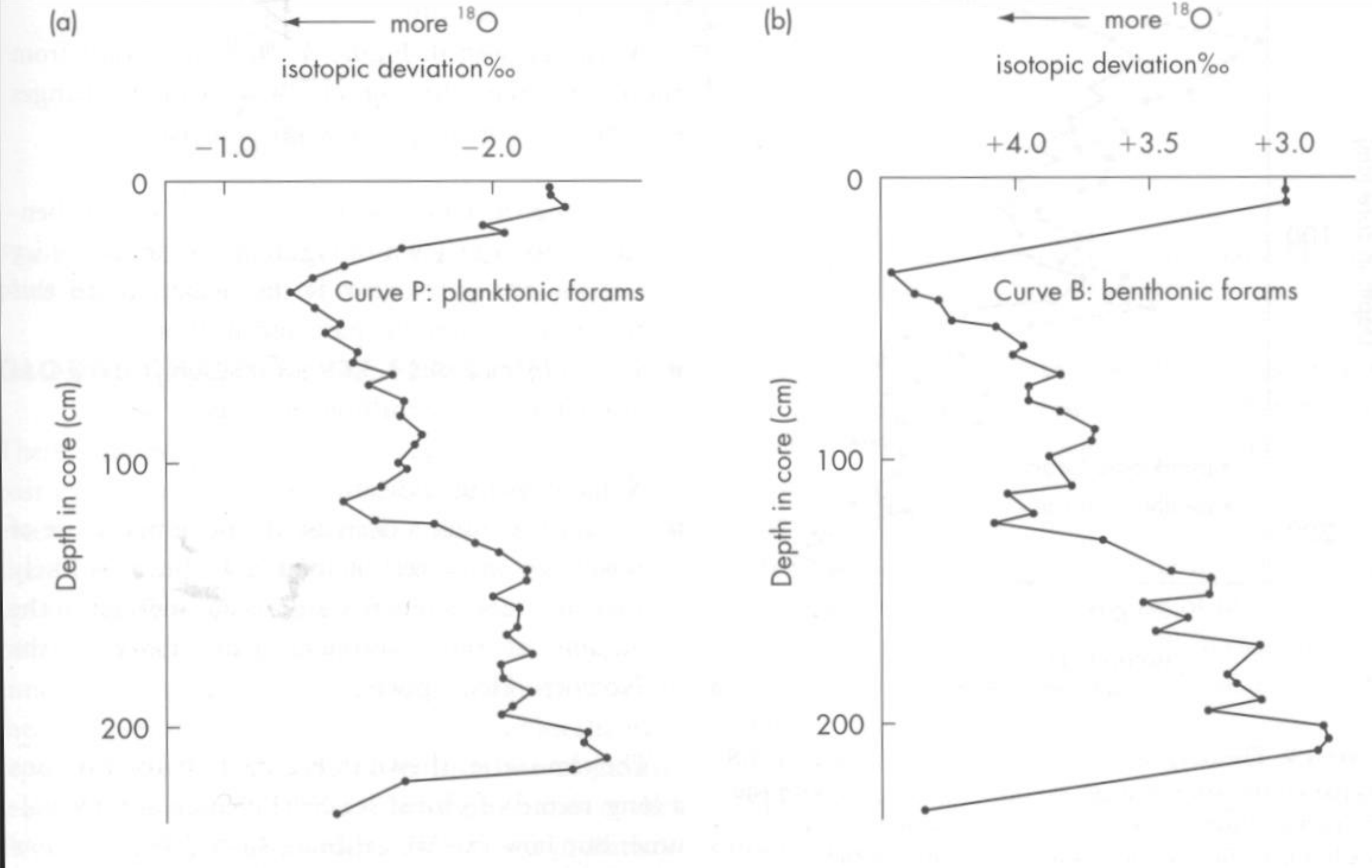


Figure 4.8 Oxygen isotope compositions of (a) planktonic and (b) benthonic forams obtained from a core of ocean floor sediments taken in the western equatorial Pacific Ocean.

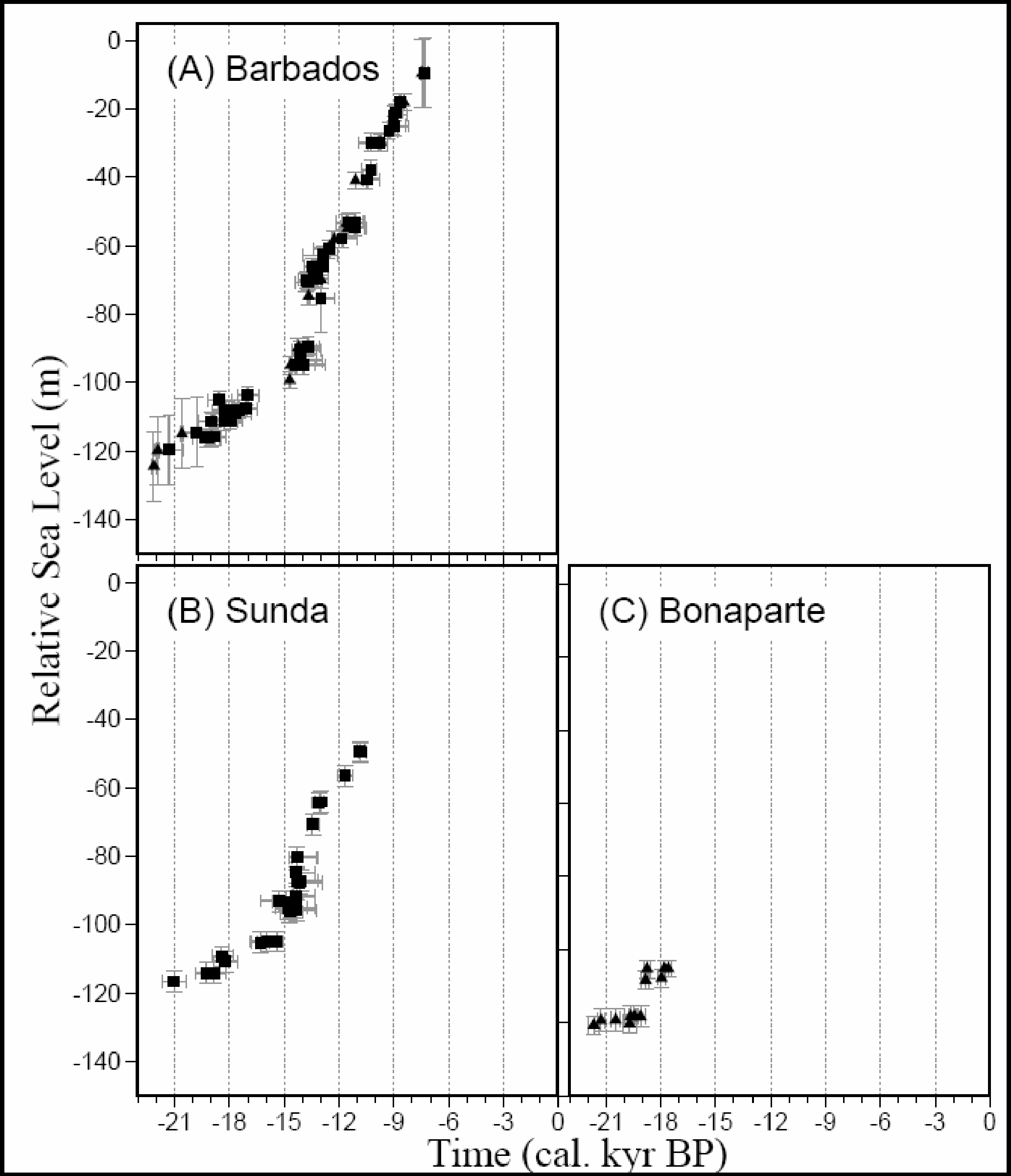
Wilson et al., 2000.

The Approximate Magnitudes of the Temperature and Ice Volume Signals in Marine Del-18-O

- Temperature effect: lab experiments show that a ~5°C increase causes a ~1‰ decrease in del-18-O of foram shell (note: species dependent)

- Both effects are significant – are there ways to separate these components of the measured signal?

Some Important “Far-Field” Sea-Level Curves



- Sea levels reconstructed from fossil fauna and flora.
- LGM sea levels were around -120 m.

Sea-Level Measurements From Low Latitudes <u>Approximate</u> the Eustatic Change

- Measurements of LGM sea levels give a value of ~120 m.

- You can use this value and the $\delta^{18}O$ signal from benthic forams to relate $\delta^{18}O$ changes to eustatic sea level changes (see Practical).

$\delta^{18}O$ as a Proxy for Ice Volume

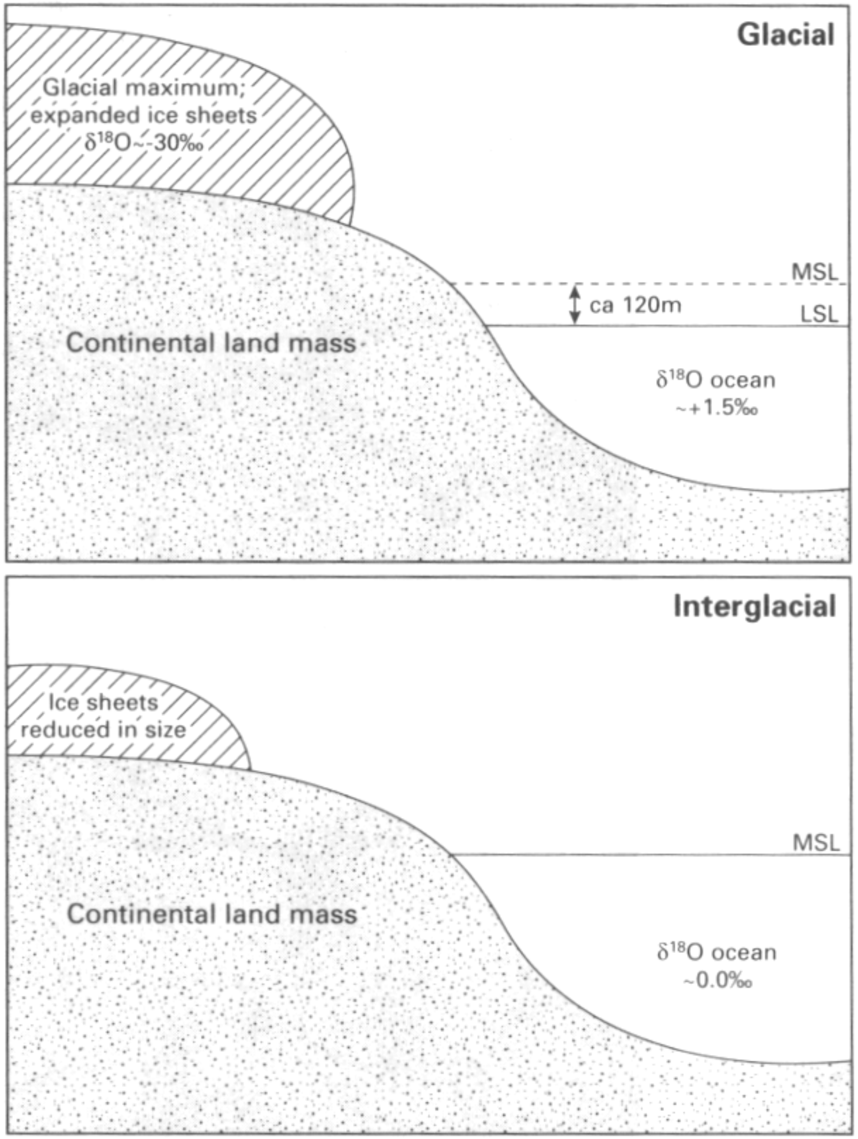


Figure 3.44 Variations in surface water oxygen isotope ratios during times of glacial maxima and interglacial high sea-level stands (minimal ice cover).

From Lowe and Walker, *Reconstructing Quaternary Environments,* 1997 (2nd edition). See Sections 3.10.2-3.10.4.

Marine Isotope Stages

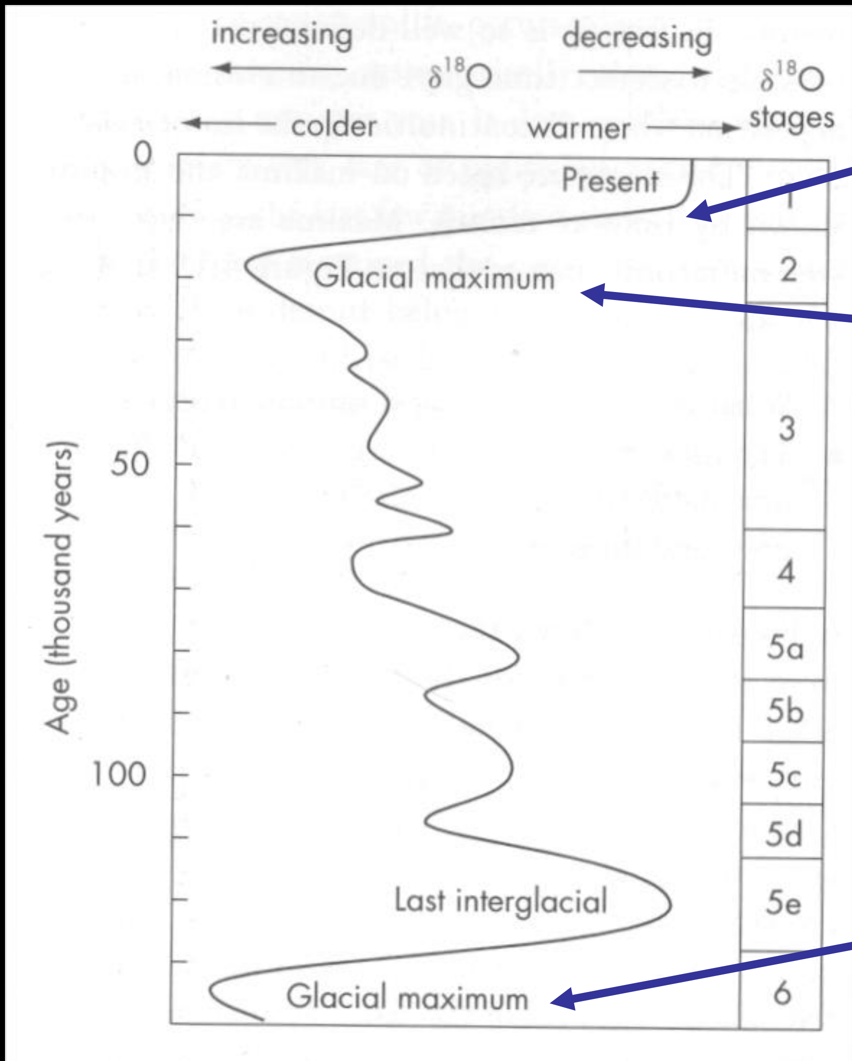


Figure 4.13 Oxygen Isotope Stages for the past 150 thousand years. Odd numbered stages indicate warm periods, and even numbers indicate cold periods.

Stadial (Younger Dryas)

glacial

glacial

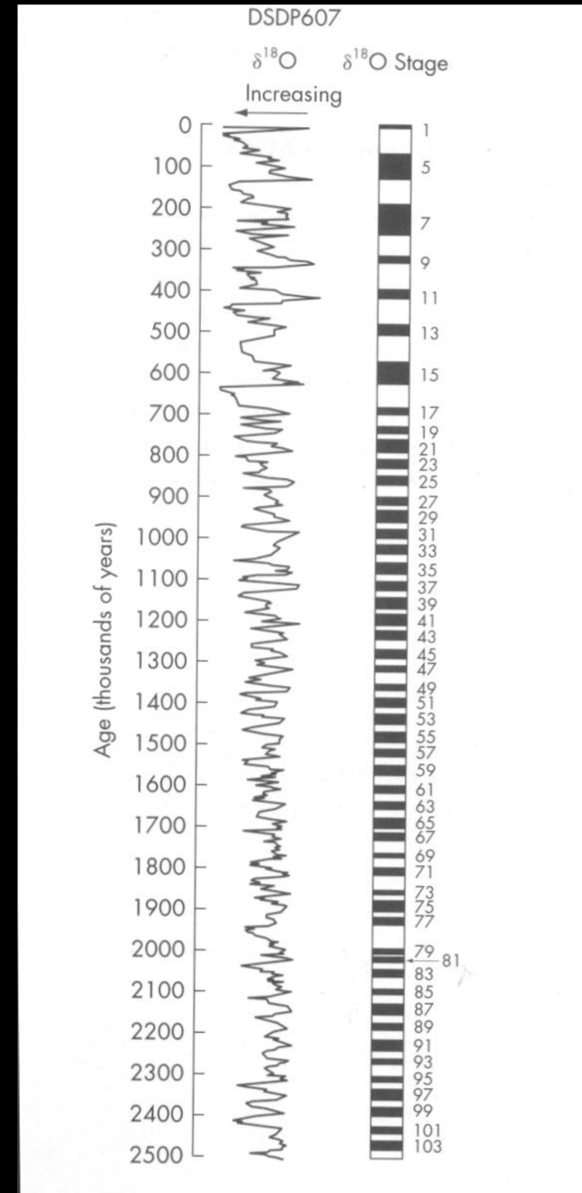


Figure 4.14 The $\delta^{18}O$ record from cores taken at Deep Sea Drilling Program Site 607 in the Pacific, showing isotope stages recognised since 2.5 Ma. The black bars indicate interglacials.

Both figures from Wilson et al.

Summary

- Stable isotope ratios in rainfall (and snowfall) controlled by fractionation
- Because most water vapour originates in low-latitudes, $\delta^{18}O$ in low latitudes tends to be high
- Because water vapour has travelled a great distance to reach poles, and because of low temperatures, $d^{18}O$ in high latitudes is low (negative)
- The $\delta^{18}O$ of ocean water is dependent on a number of different factors
- But can largely be linked to ice volume
- And is recorded in biogenic marine calcites
- …but this record is also affected by T

Some Key References

Shackleton, N.J., 1967. Oxygen isotope analysis and Pleistocene temperature reassessed, *Nature* **215** (1967), pp. 15–17.

Lambeck, K., T.M. Esat and E.-K. Potter, Links between climate and sea levels for the past three million years, *Nature* **419** (2002), pp. 199–206.

Quaternary Science Reviews, **25**, December 2006 (dedicated to Nick Shackleton).