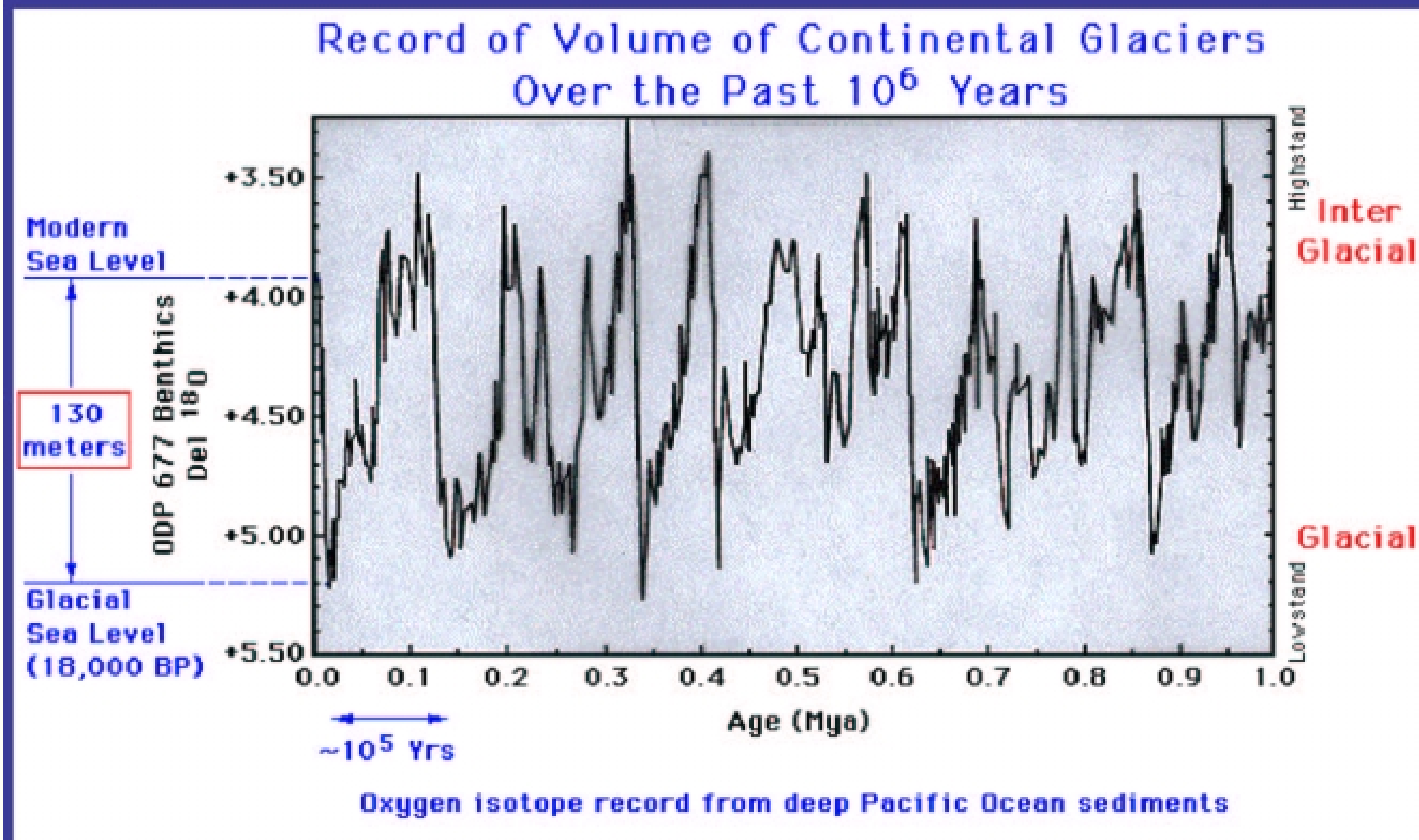
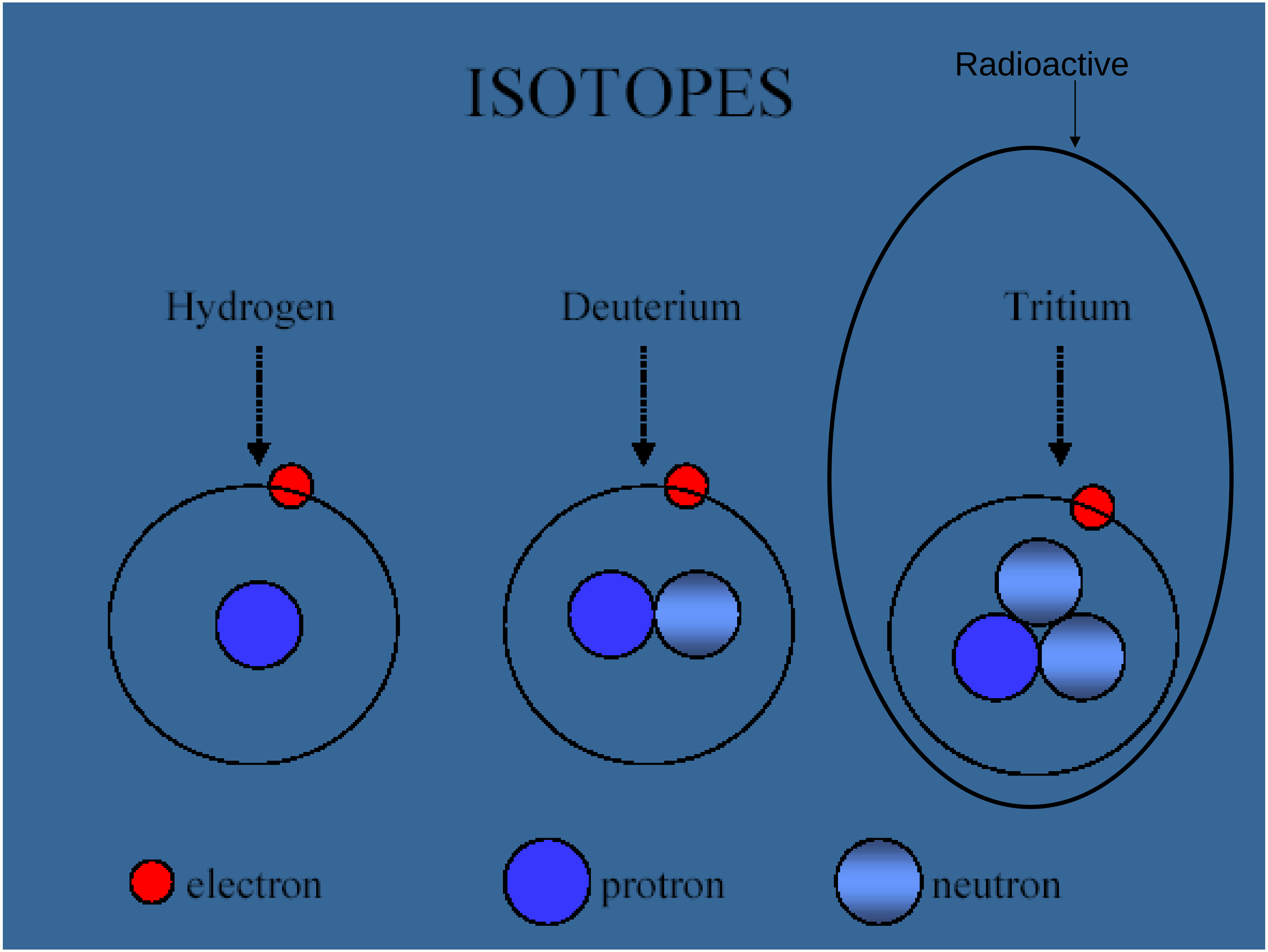
Stable Isotopes & Marine Geochemistry

- Do not decay (not radioactive)
- Used for purposeful tracer experiments in the laboratory and the field
- Small, **natural variations** in isotopic abundance use to study geochemical processes on large temporal/spatial scales (up to global spatial scale/as long as origin of earth temporal scale)


Record of Volume of Continental Glaciers
Over the Past 10^6 Years
Modern
Sea Level
130
meters
Glacial
Sea Level
(18,000 BP)
ODP 677 Benthics
Del 18O
+3.50
+4.00
+4.50
+5.00
+5.50
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Age (Mya)
~10^5 Yrs
Highstand
Lowstand
Inter
Glacial
Glacial
Oxygen isotope record from deep Pacific Ocean sediments


ISOTOPES
Radioactive
Hydrogen
Deuterium
Tritium
electron
protron
neutron

Stable isotope valley

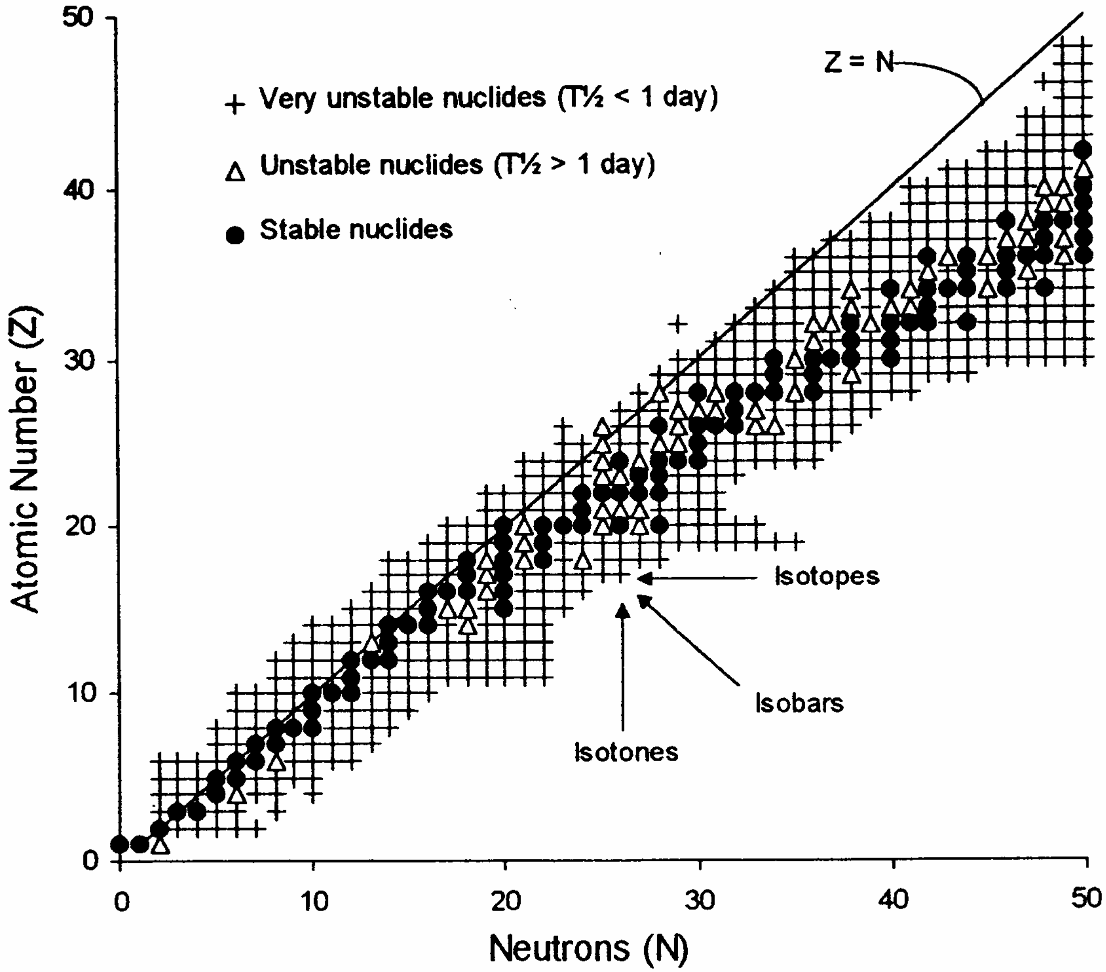


Fig. 1-1 Plot of Z vs. N for nuclides up to tin (Z=50) showing the "stable" valley of the nuclides. The Z : N ratio is 1 for the light nuclides and increases towards 1.5 for the heavier nuclides. Increases or decreases in N for given element produces increasingly unstable isotopes (decreasing T½).

Stable isotope abundance

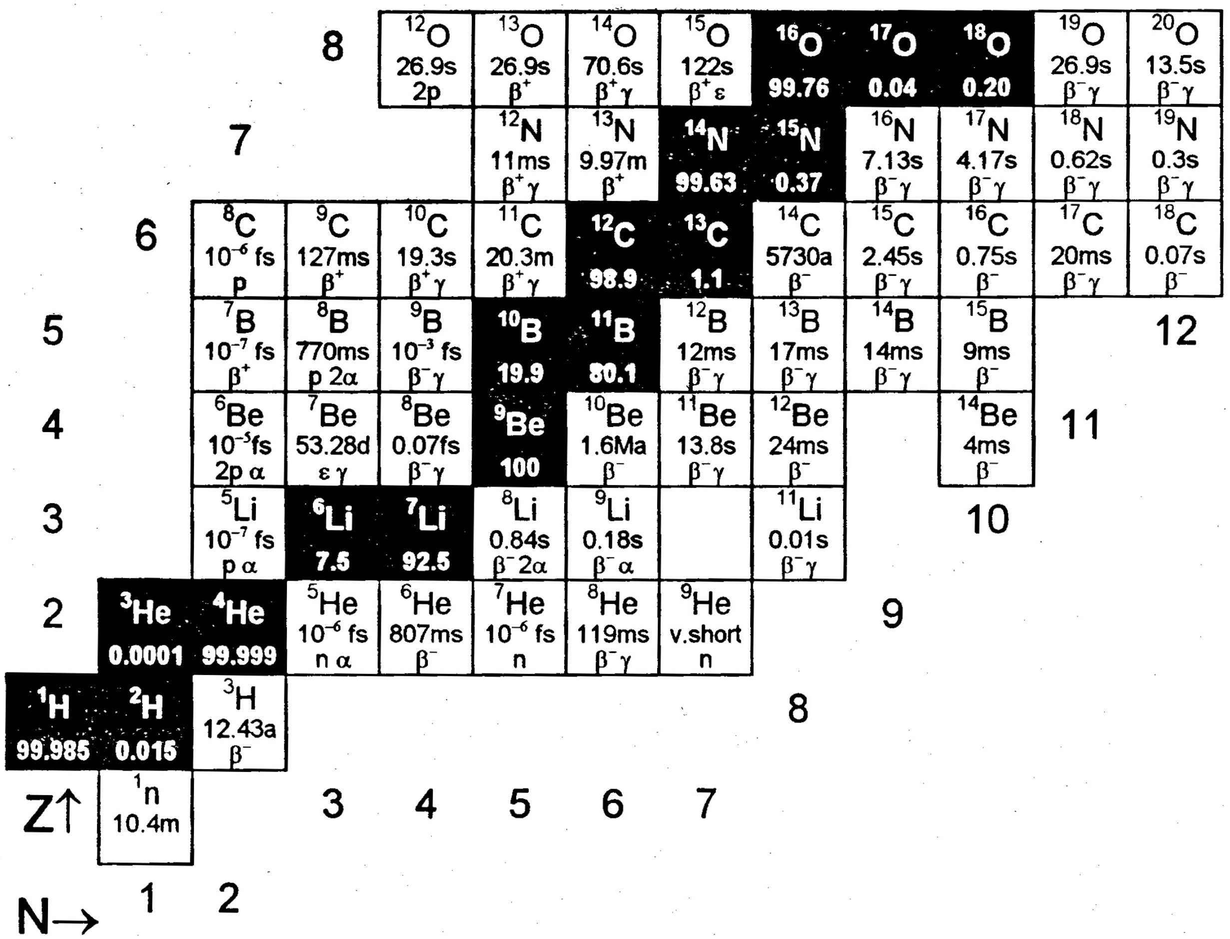


Fig. 1-2 Chart of the light element isotopes showing percent abundances of the stable isotopes (shaded black) and half-lives of radioisotopes (s = second, m = minute, d = day, a = year) with their principal and secondary decay modes, where α = alpha emission (2p and 2n), ε = electron capture, β^- = electron (beta) emission, β^+ = positron, γ = gamma emission, n = neutron emission, p = proton emission (after General Electric Ltd., 1989).

Some selected early publications in stable isotope geochemistry

(http://ees2.geo.rpi.edu/abrajanoCourses/Isotope/Isotope2001/ReferencesCited.html)

1932
A hydrogen isotope of mass 2 and its concentration.
Urey, H.C., Brickwedde, F.G. and Murphy, G.M., Phys. Rev. 40, 1.

1934
The natural separation of the isotopes of hydrogen.
Dole, M., J. Amer. Chem. Soc. 56, 999.

1935
Isotopic exchange equilibria. Urey, H.C. and Greiff, L.J., J.Am. Chem. Soc. 57, 321

1935
The relative atomic weight of oxygen in water and air.
Dole, M., J. Amer. Chem. Soc. 57. 2731.

1939
Isotopic composition of rain water.
Teis, R.V., Compt. Rend. Acad. Sci. U.R.S.S. 23, 674.

1947
The thermodynamic properties of isotopic substances.
Urey, H.C., J. Chem.Soc. (London), p.562-581.

Harold Clayton Urey *1893 — 1981*

Isotope Effects on Properties of Water Isotopomers

Property	$H_2{}^{16}O$	$D_2{}^{16}O$	$H_2{}^{18}O$
Density (@20) (g/cc)	0.997	1.1051	1.1106
T of max. ρ (760torr) (°C)	3.98	11.24	4.30
Melting Point (760torr) (°C)	0.00	3.81	0.28
Boiling Point (760torr) (°C)	100.0	101.42	100.14
Vapor Pressure (@100°C)	760	721.6	-
Viscosity (@20°C) centipoise	1.002	1.247	1.056

The delta (δ) Notation

The per mil ($^{o}/_{oo}$) deviation of isotope ratio from a standard

For oxygen isotopes:

$$\delta^{18}O = [(^{18}O / ^{16}O_{sample}) / (^{18}O / ^{16}O_{std}) - 1] \times 10^3$$

Or

$$\left\{ \frac{(^{18}O / ^{16}O_{sample}) - (^{18}O / ^{16}O_{std})}{(^{18}O / ^{16}O_{std})} \right\} \times 10^3$$

Isotopic composition of primary standards

- Vienna Standard Mean Ocean Water (VSMOW) — $D/H = 155.76 \times 10^{-6}$
  Hagemann et al., 1970
- Vienna Standard Mean Ocean Water (VSMOW) — $^{18}O/^{16}O = 12005.2 \times 10^{-6}$
  Baertschi, 1976
- Pee Dee Belemnite (PDB) (original supply exhausted) — $^{18}O/^{16}O = 2067.2 \times 10^{-6}$
  calculated using $\delta^{18}O_{VSMOW} = 30.91$
- Pee Dee Belemnite (PDB) (original supply exhausted) — $^{13}C/^{12}C = 1123.75 \times 10^{-5}$
  Craig, 1957
- Air, NBS-14 — $^{15}N/^{14}N = 367.6 \times 10^{-5}$
  Junk and Svec, 1958
- Canon Diablo Troilite — $^{34}S/^{32}S = 449.94 \times 10^{-4}$
  Thode et al., 1961

How about $\delta^{13}C$ variations??

Element	Isotope	Abundance	Variation in ‰
Carbon	^{12}C	98.89%	$^{13}C/^{12}C$ = 100
	^{13}C	1.11%	

If a sample of Pee Dee Belemnite has an absolute $^{13}C/^{12}C$ ratio of 1123.75×10^{-5}, then it has a $\delta^{13}C$ value of 0 $^{o}/_{oo}$ (by definition)

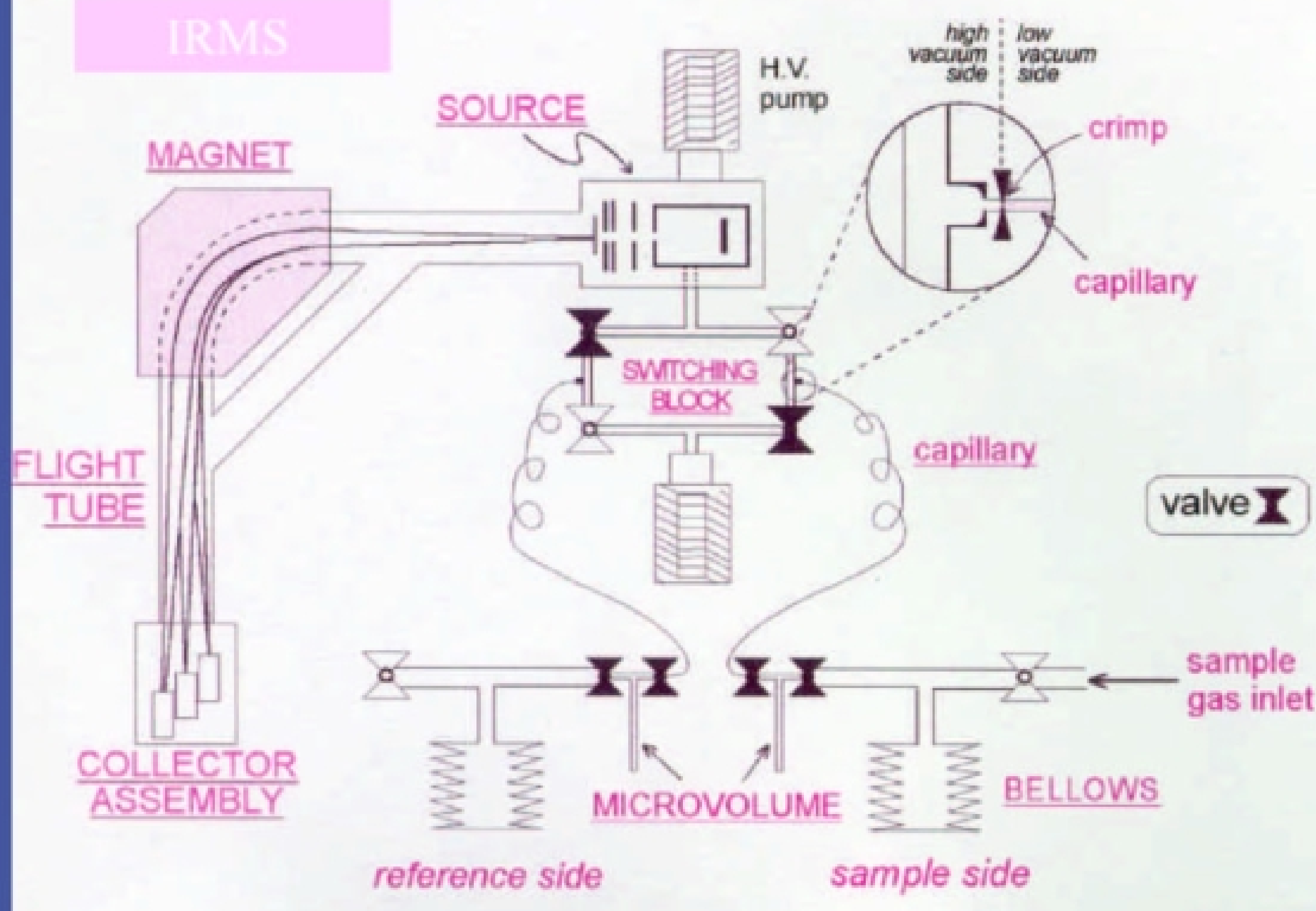
∴ A sample of bacterial mat with a $\delta^{13}C$ value of **-100 $^{o}/_{oo}$** will have a ratio of 1011.32×10^{-5}. That implies an absolute abundance of ^{13}C of 1.0012%Total change within the **1st** decimal place. Most variations within the 0.1-10 $^{o}/_{oo}$ range or **3rd - 4th** decimal place.

How well can we measure? To the **6**th decimal place (MS).
4th decimal place due to prep/CF

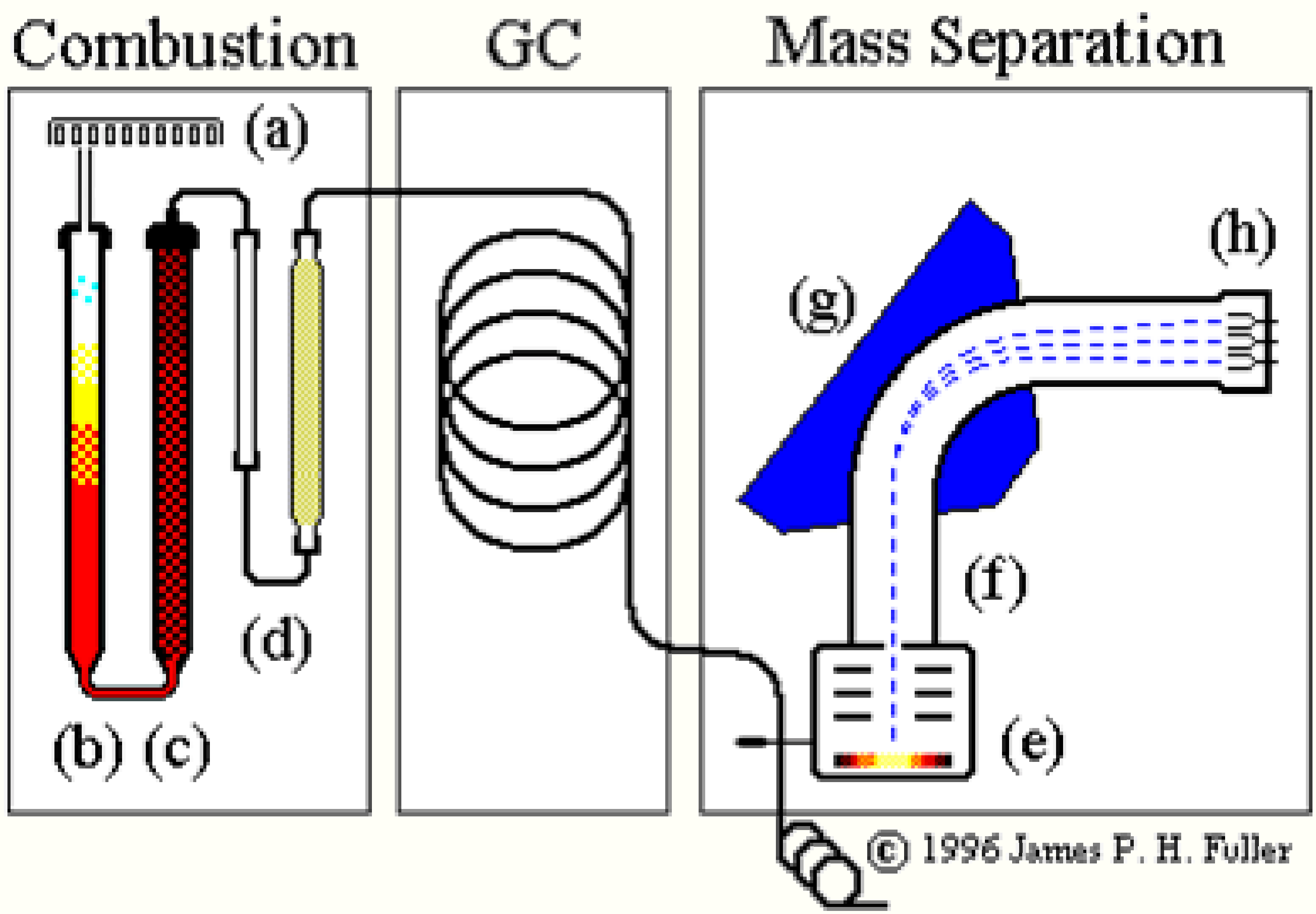
Isotope Ratio Mass Spectrometers: REQUIREMENTS

- Inlet
- Ion source (ionizing energy, ion optics) - ionization and acceleration
- Mass analyser (quad, ion trap config, magnetic sector, TOF) - isotopomer separation
- Detector (single, multiple; ion → electrical impulse → amplifier (head amp careful spec). Signal processing.

IRMS



SOURCE
H.V. pump
MAGNET
high vacuum side
low vacuum side
crimp
capillary
SWITCHING BLOCK
capillary
FLIGHT TUBE
valve
sample gas inlet
COLLECTOR ASSEMBLY
MICROVOLUME
BELLOWS
reference side
sample side



Combustion
GC
Mass Separation
(a)
(b) (c)
(d)
(e)
(f)
(g)
(h)
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Element Gas Isotopomers Measured

Hydrogen, H_2 (2 & 3) (interference from H_3^+)

Carbon, CO_2 (44, 45 and 46)

Nitrogen, N_2 (28, 29 and 30)

N_2O (44, 45, 46)

Oxygen

CO_2 (44, 45, 46)

O_2 (32, 33, 34)

CO by pyrolysis (28, 30)

Sulfur

SO_2 (64, 66)

SF6 (146, 147, 148, 150)

Relative Proportions of CO_2 Isotopomers

Composition	Mass	Percent of total CO2 in sample
12C 16O 16O	44	98.43
12C 16O 17O	45	0.04
12C 16O 18O	46	0.20
12C 17O 16O	45	0.04
12C 17O 17O	46	0.00
12C 17O 18O	47	0.00
12C 18O 16O	46	0.20
12C 18O 17O	47	0.00
12C 18O 18O	48	0.00
13C 16O 16O	45	1.09
13C 16O 17O	46	0.00
13C 16O 18O	47	0.00
13C 17O 16O	46	0.00
13C 17O 17O	47	0.00
13C 17O 18O	48	0.00
13C 18O 16O	47	0.00
13C 18O 17O	48	0.00
13C 18O 18O	49	0.00

Craig Correction

CO_2 Isotopomers

Mass	Isotopomer
44	$^{12}C^{16}O^{16}O$
45	$^{13}C^{16}O^{16}O$, $^{12}C^{17}O^{16}O$, $^{12}C^{16}O^{17}O$
46	$^{12}C^{18}O^{16}O$, $^{12}C^{16}O^{18}O$, $^{13}C^{17}O^{16}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{17}O^{17}O$

$$\delta^{13}C = 1.0676\ \delta^{45}C - 0.0338\ \delta^{18}O$$

$$\delta^{18}O = 1.0010\ \delta^{46}O - 0.0021\ \delta^{13}C$$

Caveat: Works best for samples close to PDB !!

Isotopic fractionation (discrimination):

Causes of isotopic variation

1) Physical processes (e.g. evaporation, condensation, diffusion dependent on physical properties of molecular species - H_2O example)
2) Chemical and biochemical processes (chemical bond making and breaking - heavier isotope almost always has a lower specific reaction rate
3) Kinetic isotope effects occur when 1 & 2 occur as net unidirectional processes
4) Equilibrium isotope effects occur when 1 & 2 take place in steady state.

- Fractionation factor:

$$B \Rightarrow A$$

$$\alpha_{A-B} = R_A / R_B = {}^2H/{}^1H_a / {}^2H/{}^1H_b$$

Kinetic Fractionation Factor

$$B \overset{k}{\Rightarrow} A$$

$$B^* \overset{k^*}{\Rightarrow} A^*$$ (* denotes heavier isotope)

$$A^*/A = B^*/B \times k^*/k$$ (instantaneous product)

$$\alpha = k^*/k$$ (usually < 1)

$$\alpha \times B^*/B = A^*/A$$

$$\varepsilon\ (‰) = -(\alpha - 1) \times 1000$$

Rayleigh Fractionation
(Closed System)

$\Delta\delta$(reactant) = $-\varepsilon$ x ln f

$\Delta\delta$(product) = ε x f/ (1-f) x ln f

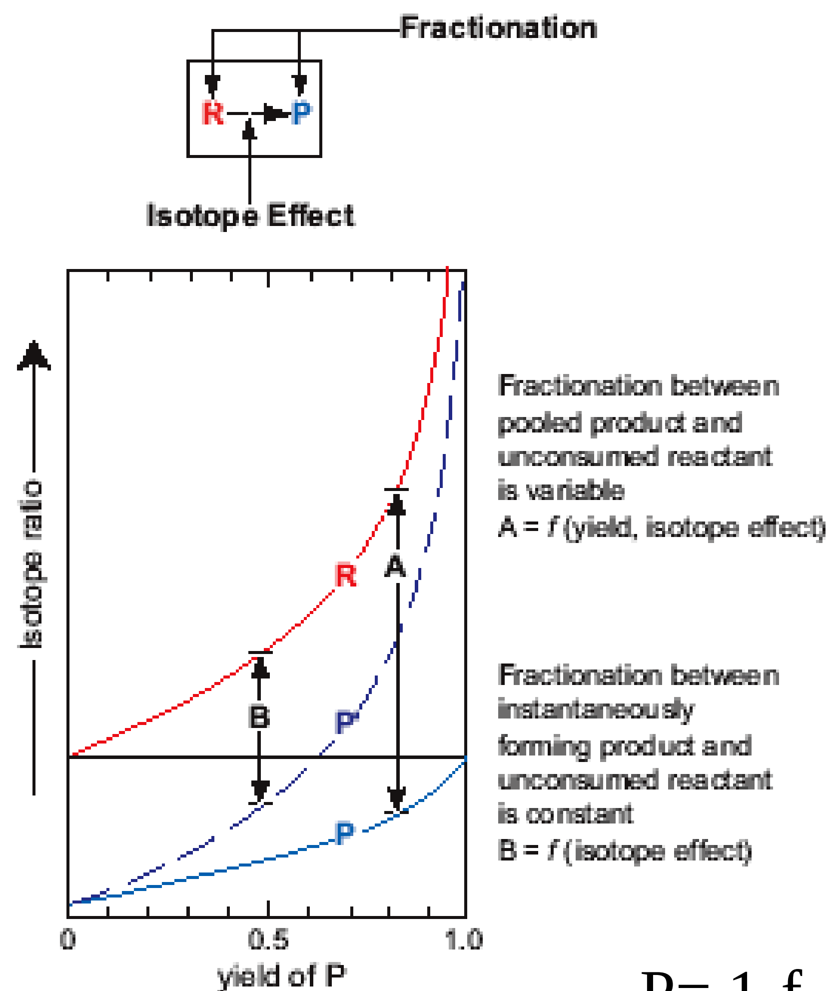
f = reactant(t)/reactant(i)

P= 1-f

Rayleigh Fractionation
(Open System)

$\Delta\delta$(reactant) = ε x (1-f)

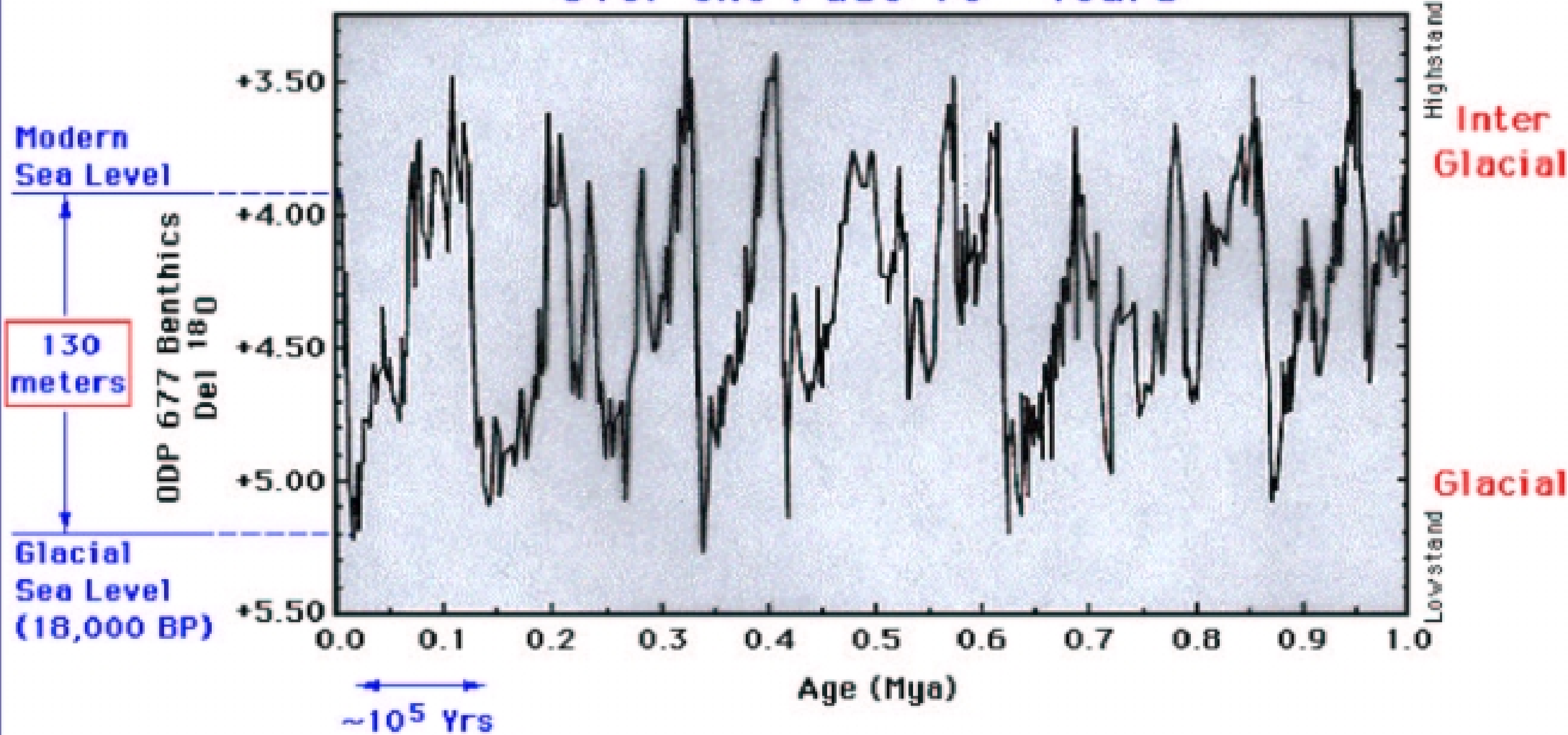
$\Delta\delta$(product) = - ε x f



P= 1-f

Figure 4. Schematic representation of a closed system and the isotopic fractionations occurring within it as a reaction proceeds to completion. Curve P' represents the isotopic composition of the instantaneously-forming product, and P represents the isotopic composition of the pooled product.

Record of Volume of Continental Glaciers Over the Past 10^6 Years



Oxygen isotope record from deep Pacific Ocean sediments

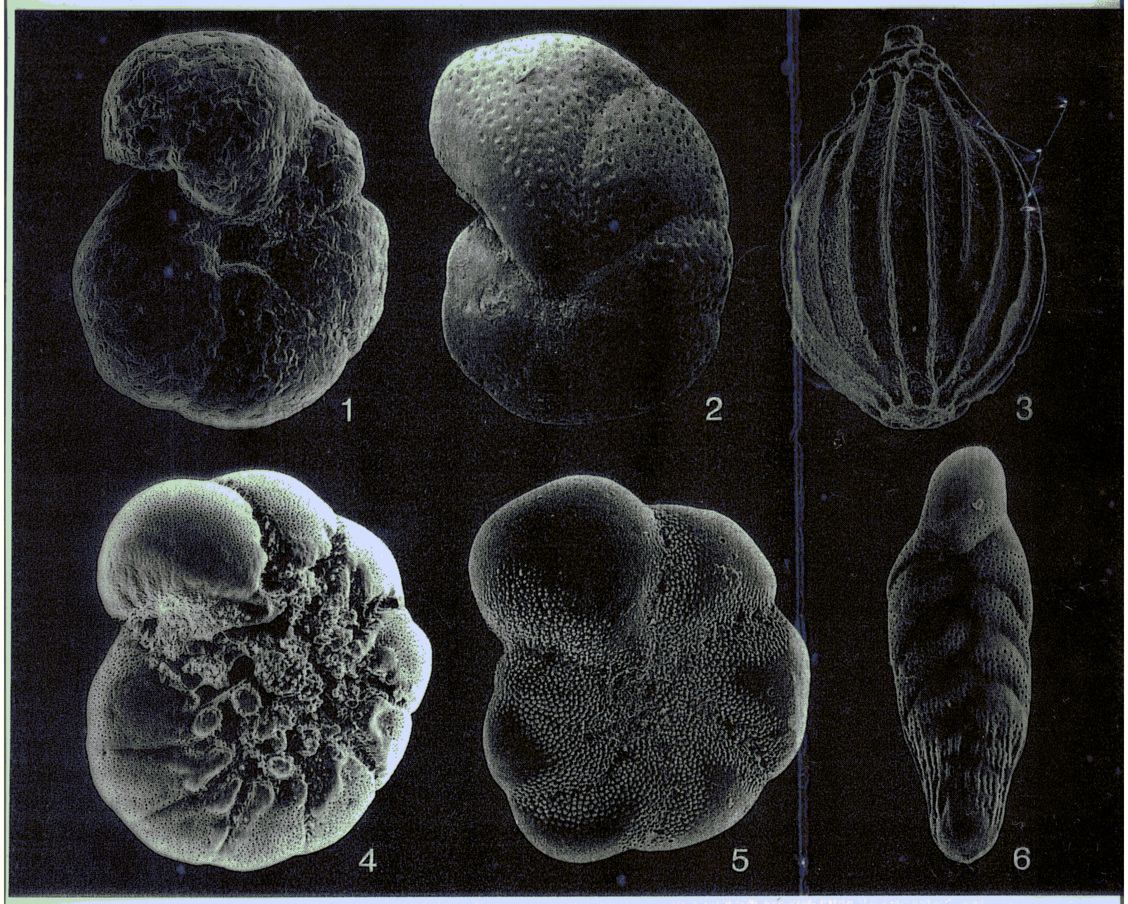


Figure 4.34 Modern benthic Foraminifera from a shallow marine setting (14 m) in Loch Creran on the west coast of Scotland (photo: Heather Anne Austin): 1. *Cribrostomoides jeffreysii* (Williamson) (oblique side view ×130); 2. *Cibicides lobatulus* (Walker and Jacob (side view ×102); 3. *Oolina williamsoni* (Alcock) (side view ×167); 4. *Ammonia beccarii* (Linné) (ventral view ×140); 5 *Elphidium albiumbilicatum* (Weiss) (side view ×137); 6. *Brizalina pseudopunctata* (Höglund) (side view ×183).

$$CO_2 + H_2O \overset{\varepsilon_1}{\Leftrightarrow} H_2CO_3$$

$$H_2CO_3 \overset{\varepsilon_2}{\Leftrightarrow} HCO_3^- + H^+$$

$$HCO_3^- \overset{\varepsilon_3}{\Leftrightarrow} CO_3^= + H^+$$

$$Ca^{+2} + CO_3^= \overset{\varepsilon_4}{\Rightarrow} CaCO_3$$

Through chemical equilibrium, biogenic $CaCO_3$ records the $\delta^{18}O$ of water and the $\delta^{13}C$ of DIC offset by the sum of the equilibrium fractionation factors. The magnitude of the latter is temperature dependent.

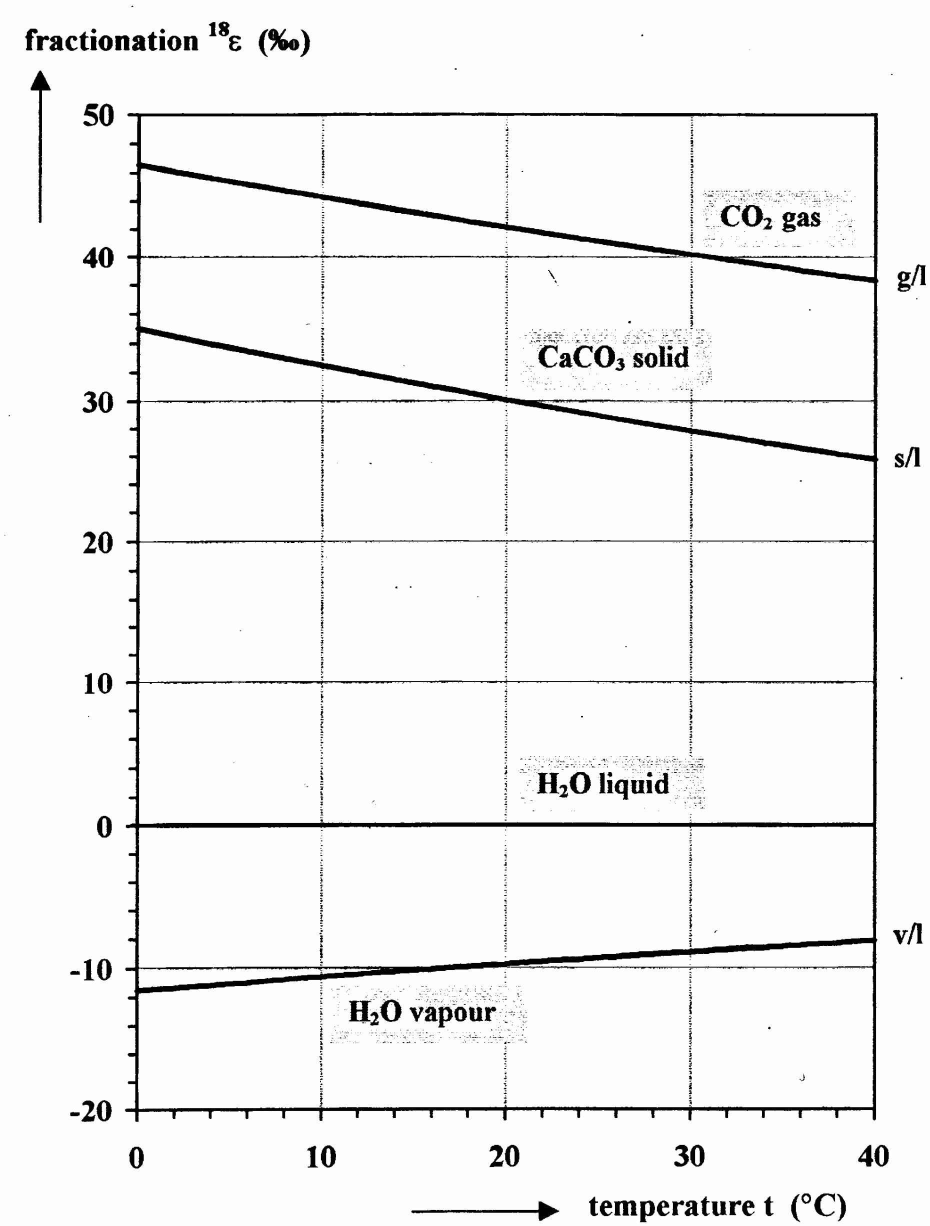
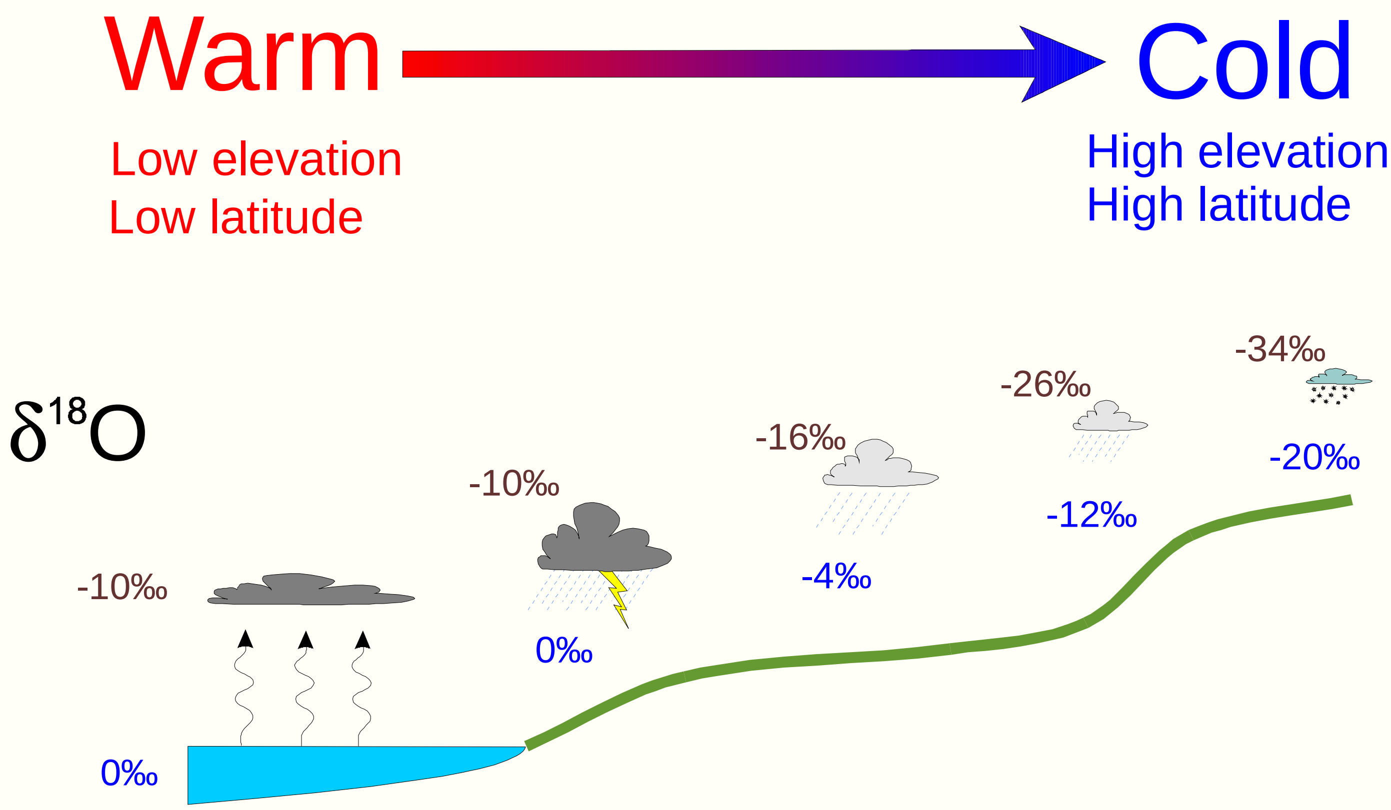
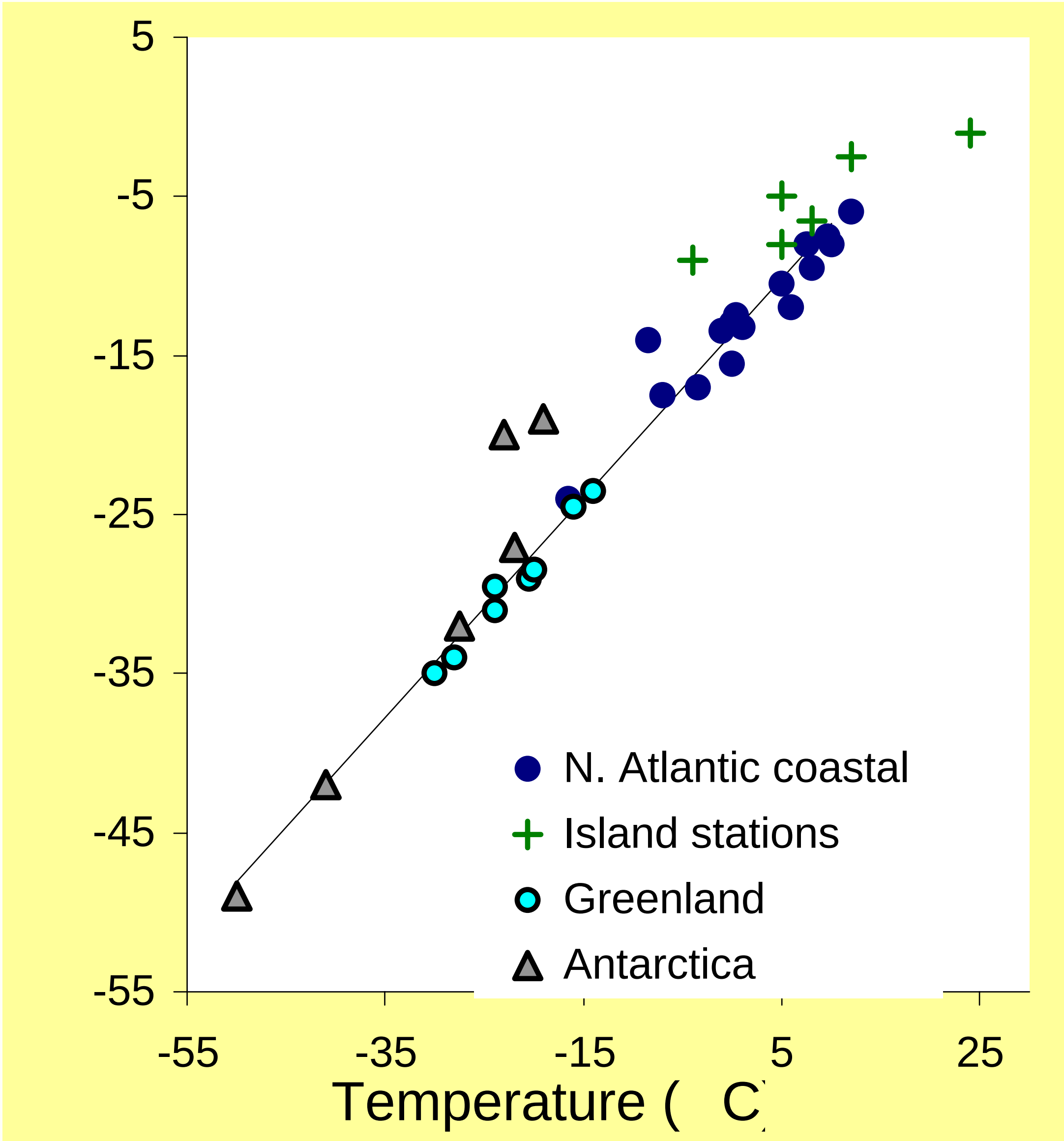


Fig.7.10 Temperature dependent equilibrium fractionations for oxygen isotopes of water vapour (v), gaseous CO_2 (g), and solid calcite (s) with respect to liquid water (l).

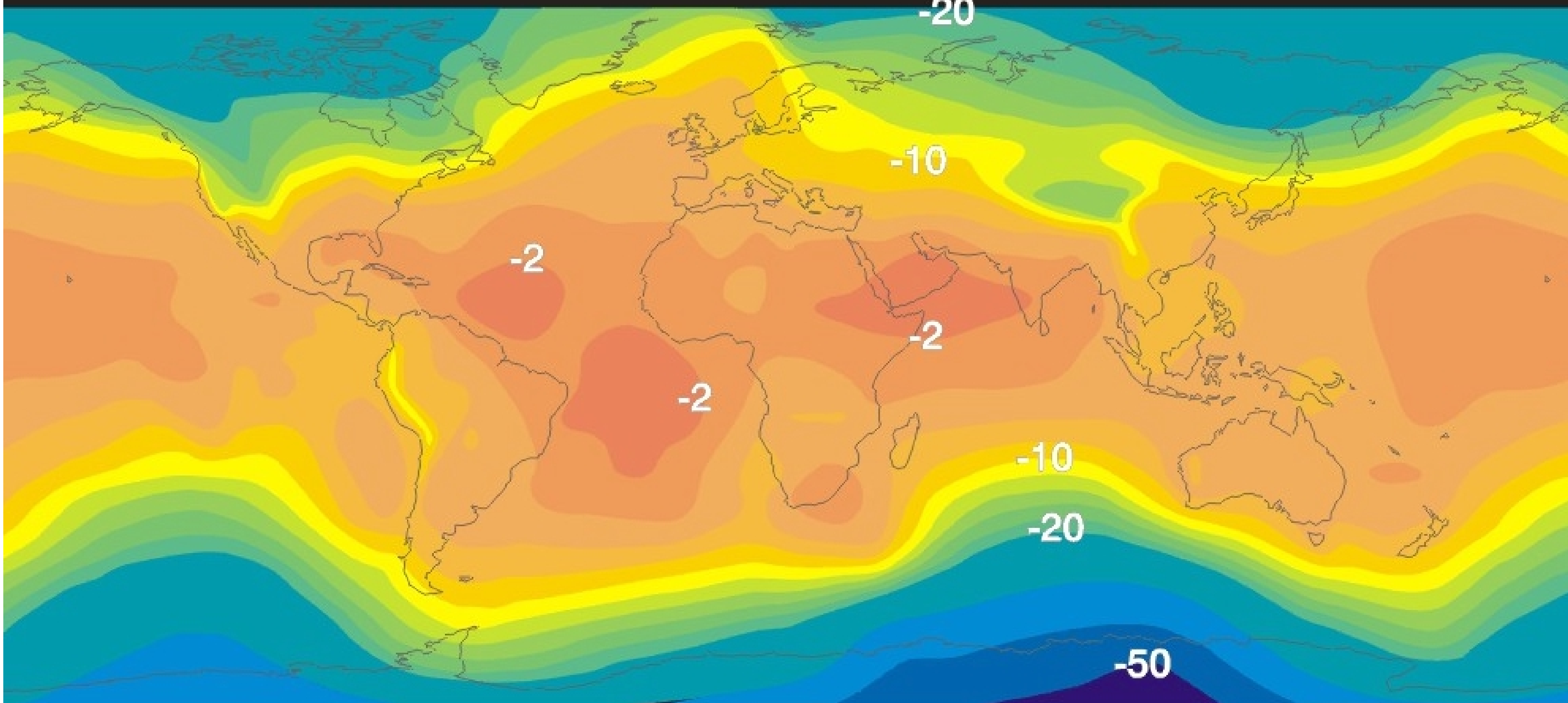
Rainout and Rayleigh Distillation

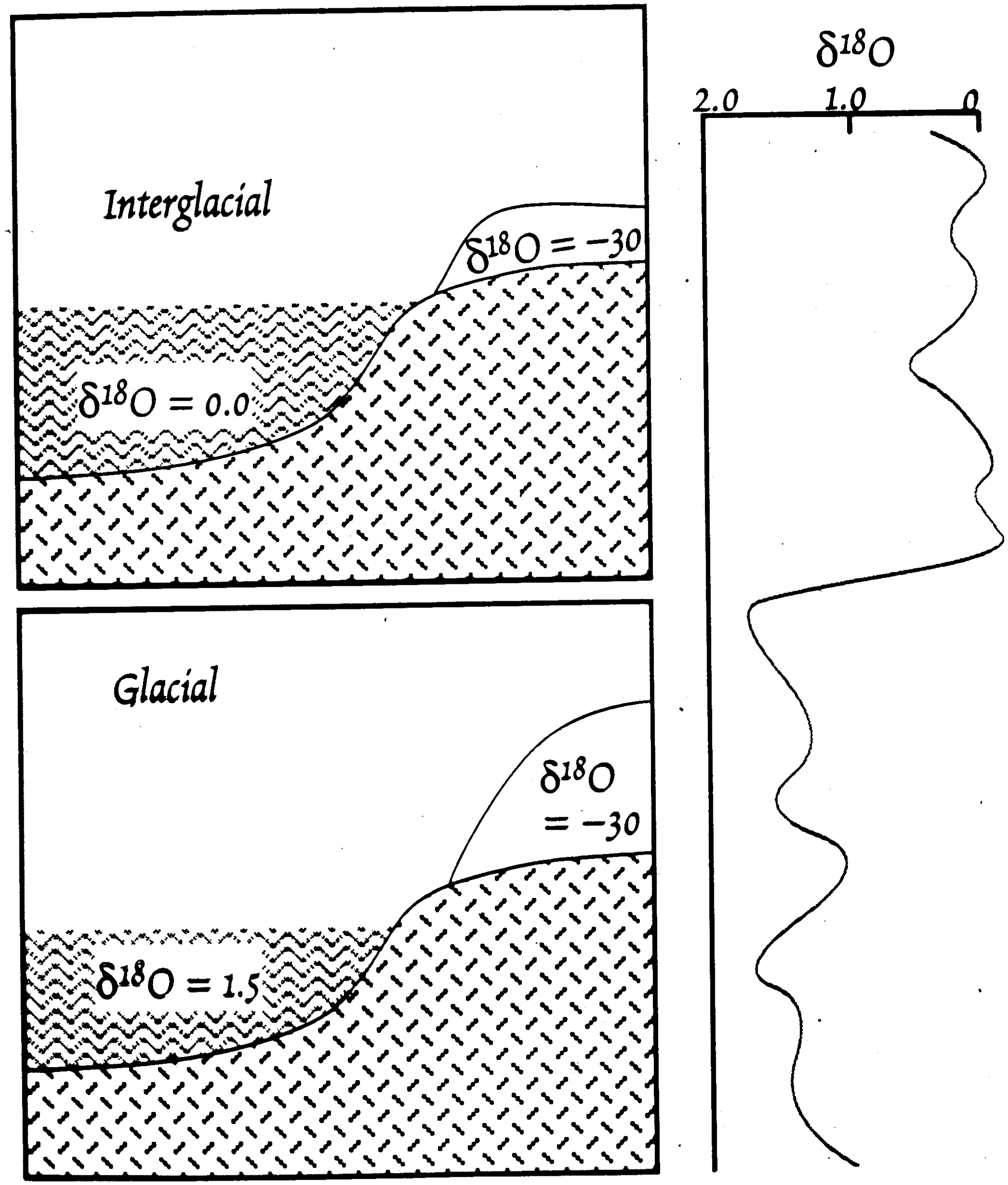


The $\delta^{18}O$ – T Correlation in Precipitation

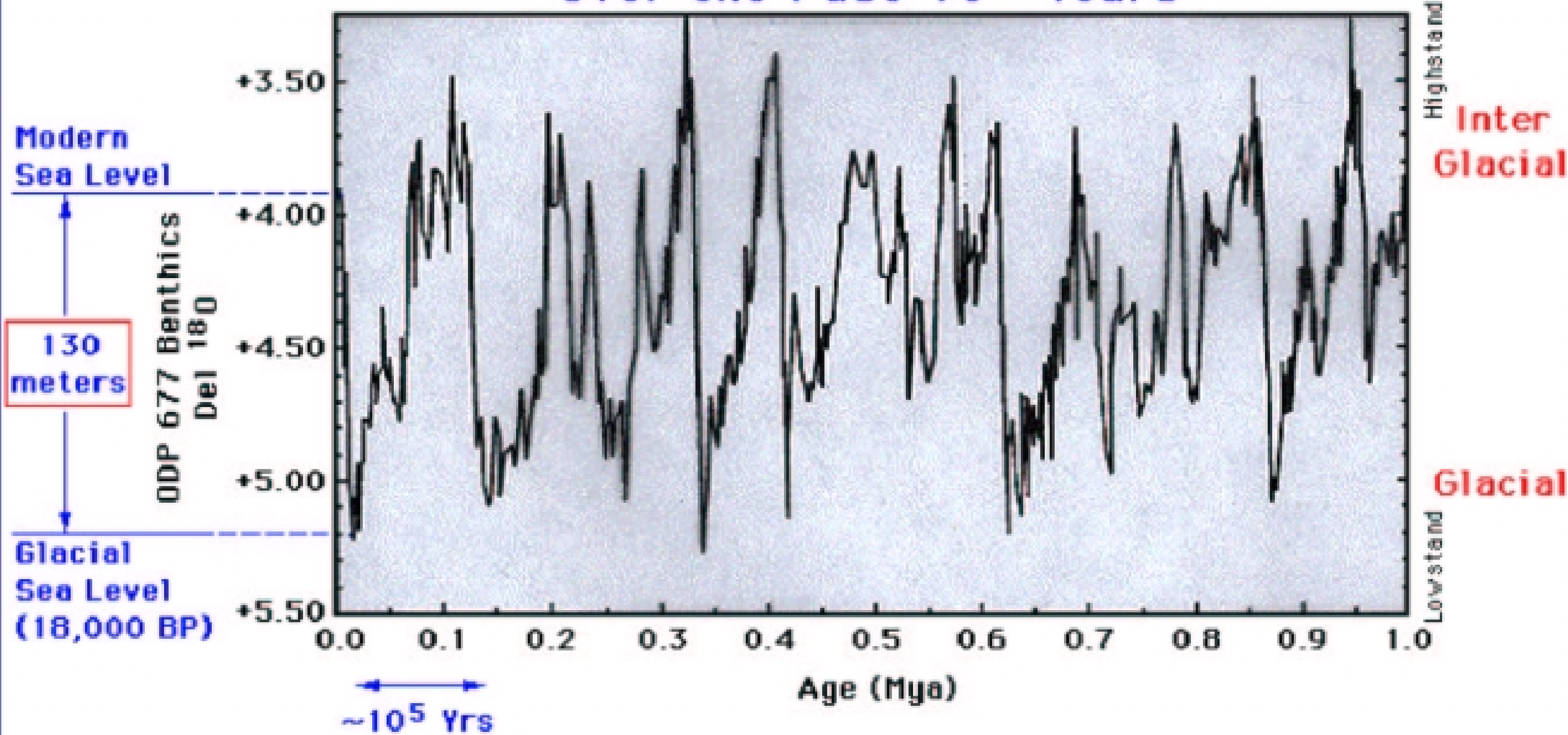


$\delta^{18}O$ in precipitation

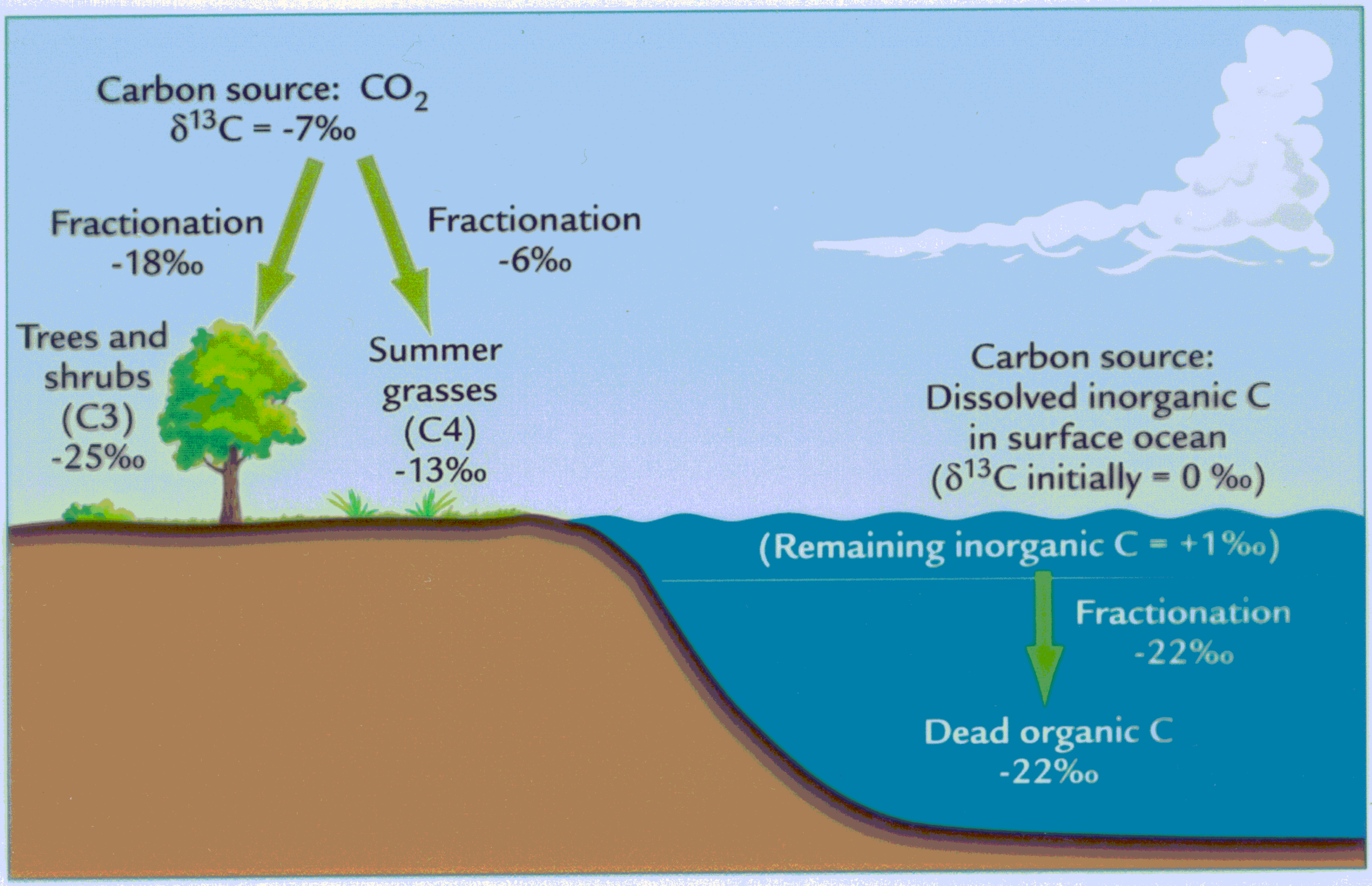



Interglacial
δ18O = −30
δ18O = 0.0
Glacial
δ18O
= −30
δ18O = 1.5
δ18O
2.0
1.0
0

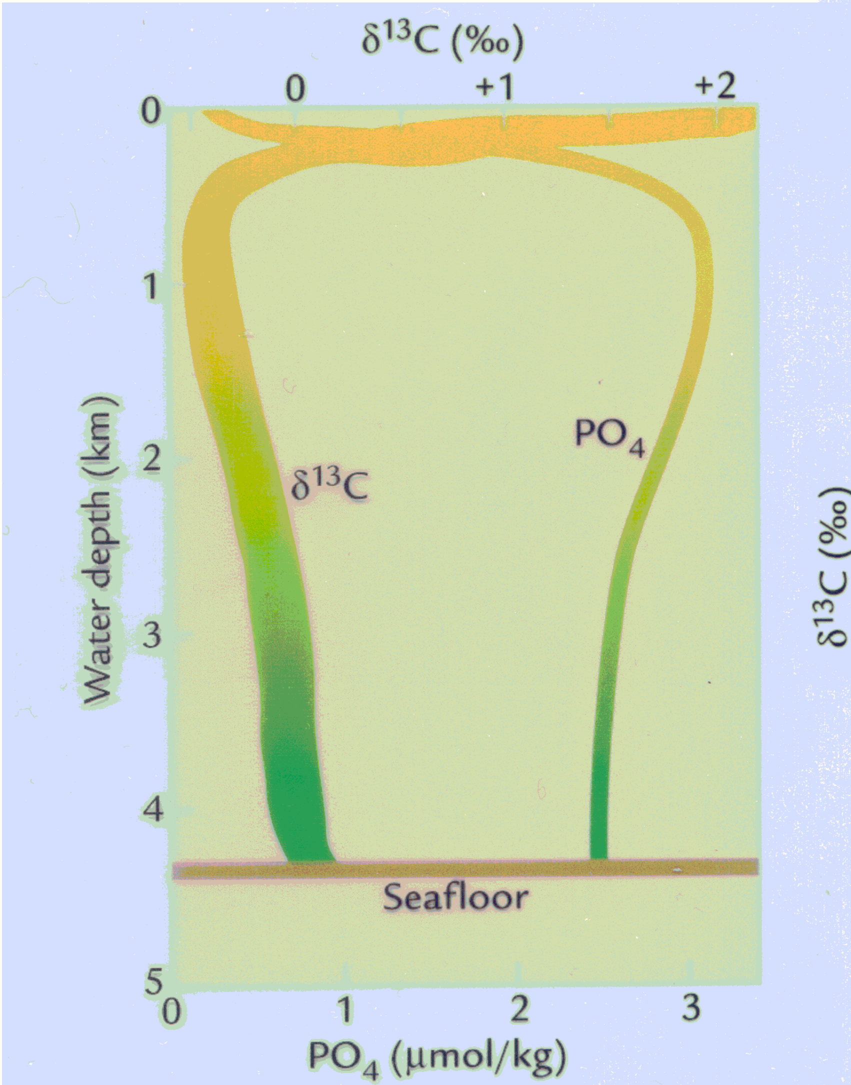
Record of Volume of Continental Glaciers Over the Past 10^6 Years

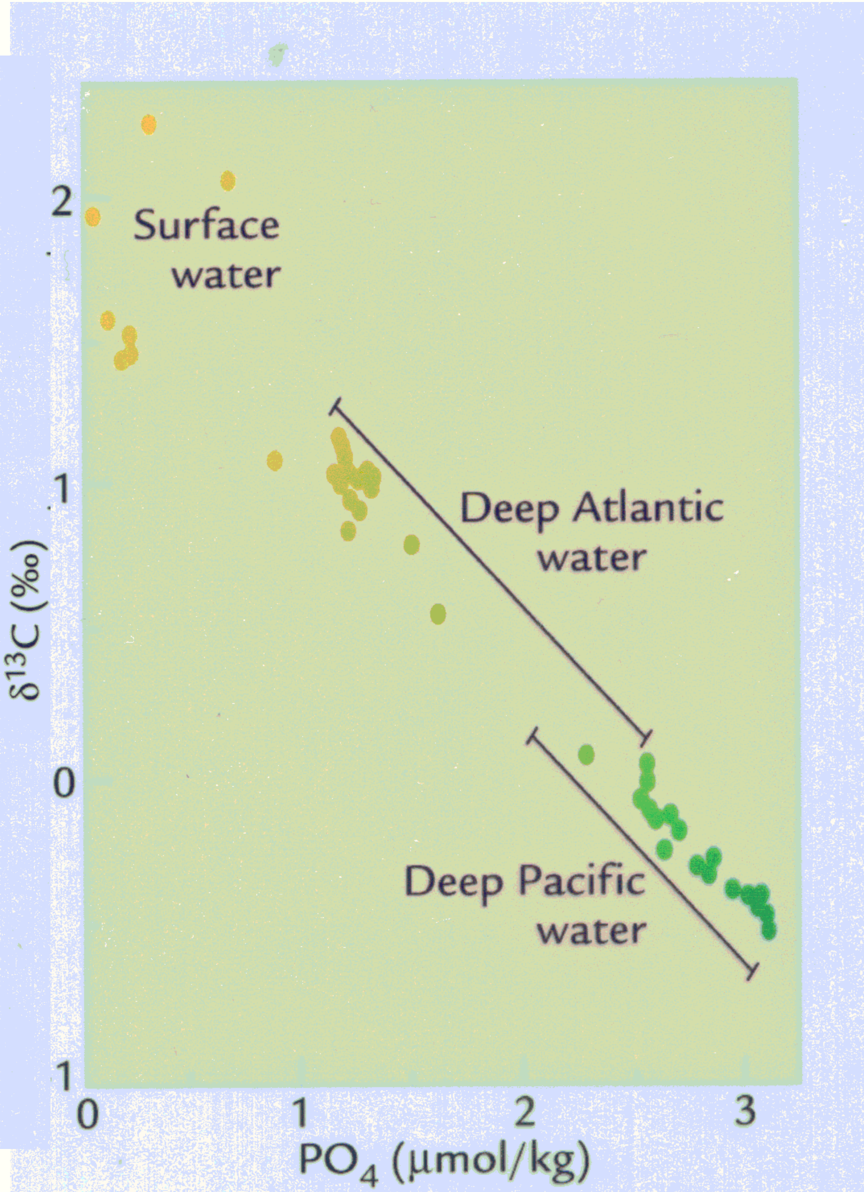


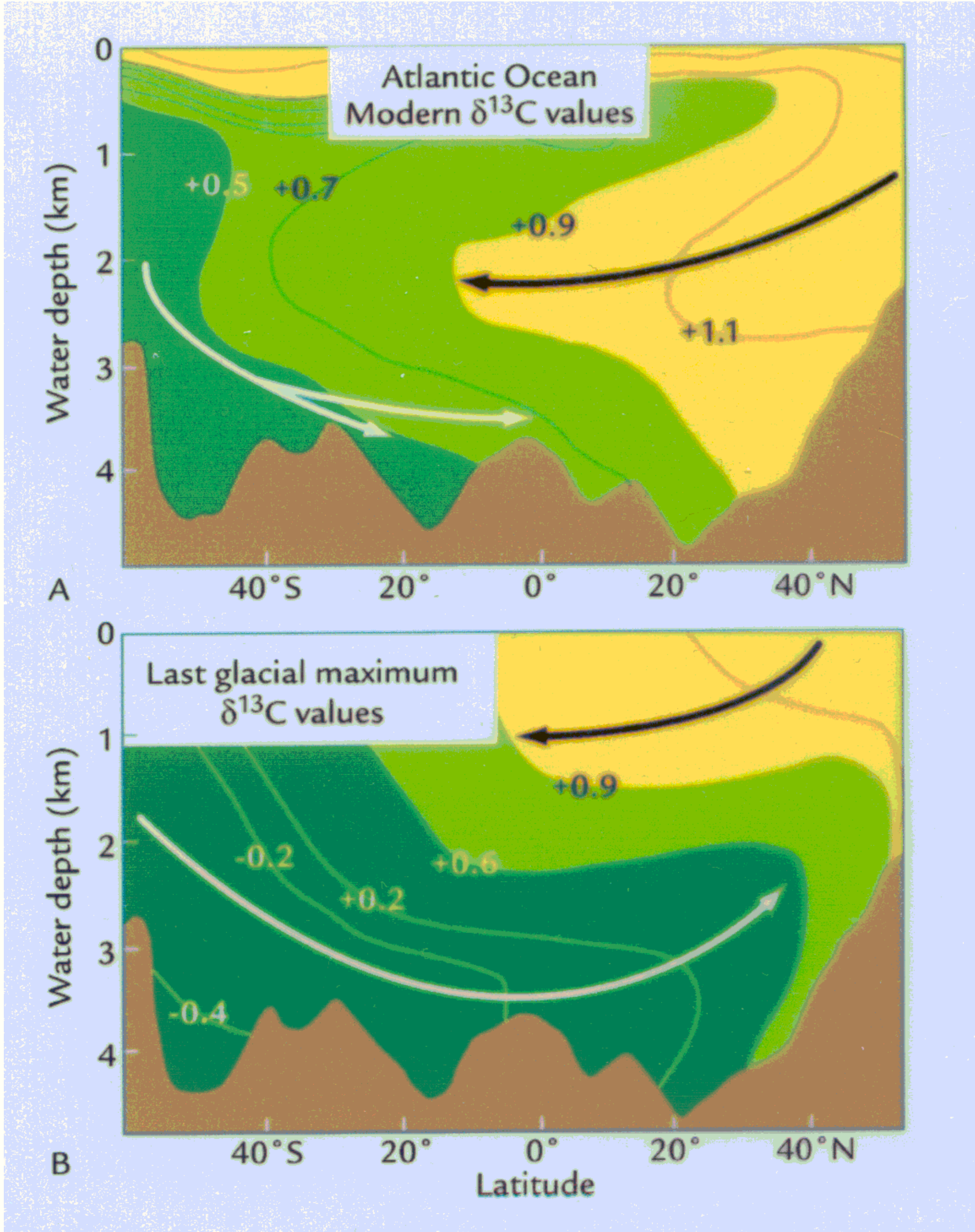
Oxygen isotope record from deep Pacific Ocean sediments



Carbon source: CO2
δ13C = -7‰
Fractionation
-18‰
Fractionation
-6‰
Trees and shrubs (C3) -25‰
Summer grasses (C4) -13‰
Carbon source: Dissolved inorganic C in surface ocean (δ13C initially = 0 ‰)
(Remaining inorganic C = +1‰)
Fractionation
-22‰
Dead organic C
-22‰

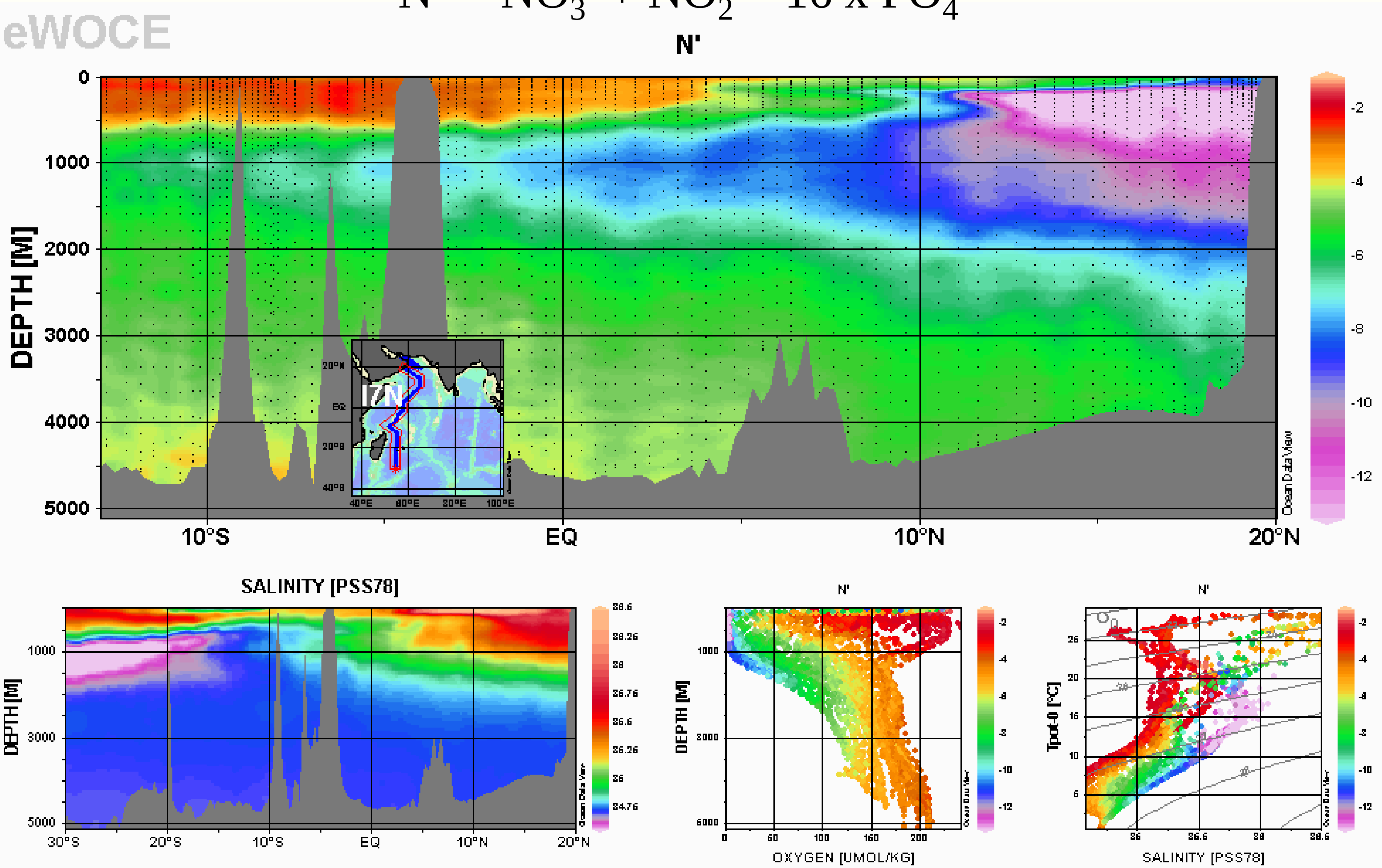

δ13C (‰)
0
+1
+2
Water depth (km)
0
1
2
3
4
5
δ13C
PO4
Seafloor
0
1
2
3
PO4 (μmol/kg)

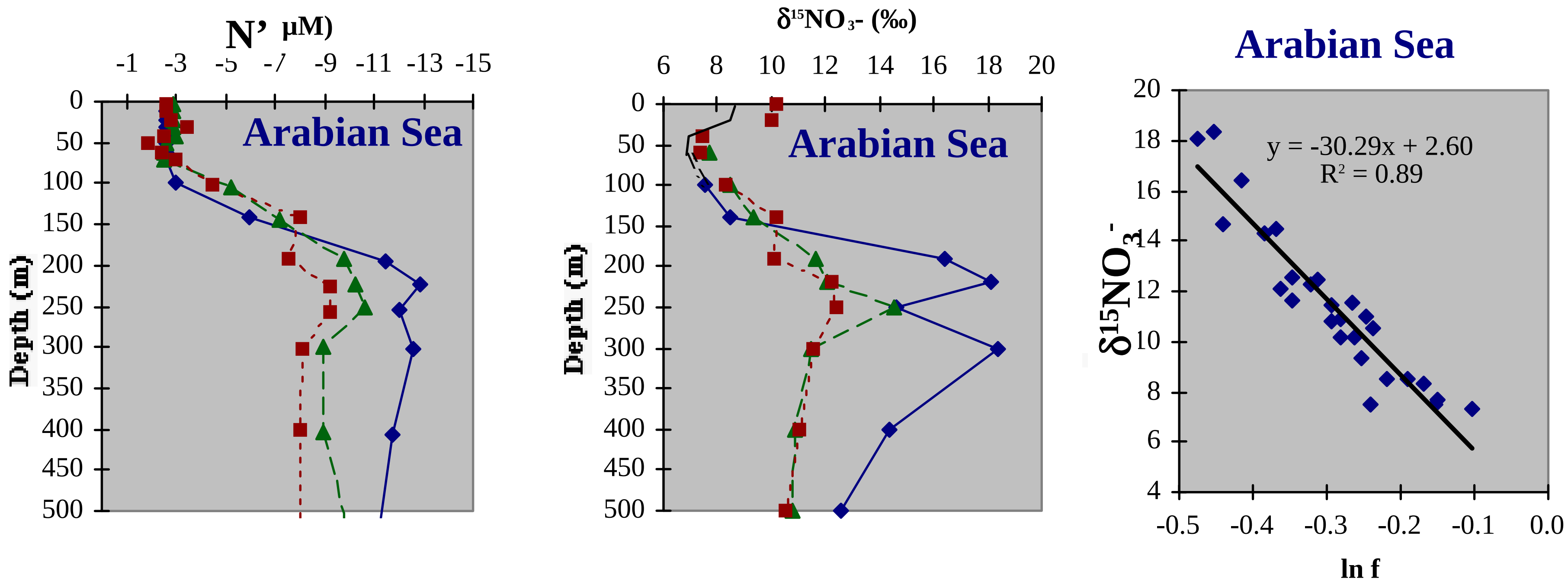

Surface water
Deep Atlantic water
Deep Pacific water
δ13C (‰)
2
1
0
1
0
1
2
3
PO4 (μmol/kg)


Atlantic Ocean
Modern δ13C values
+0.5
+0.7
+0.9
+1.1
Water depth (km)
0
1
2
3
4
A
40°S
20°
0°
20°
40°N
Last glacial maximum
δ13C values
+0.9
-0.2
+0.6
+0.2
-0.4
B
Latitude

Water Column Denitrification Effects

$N' = NO_3^- + NO_2^- - 16 \times PO_4^{-3}$

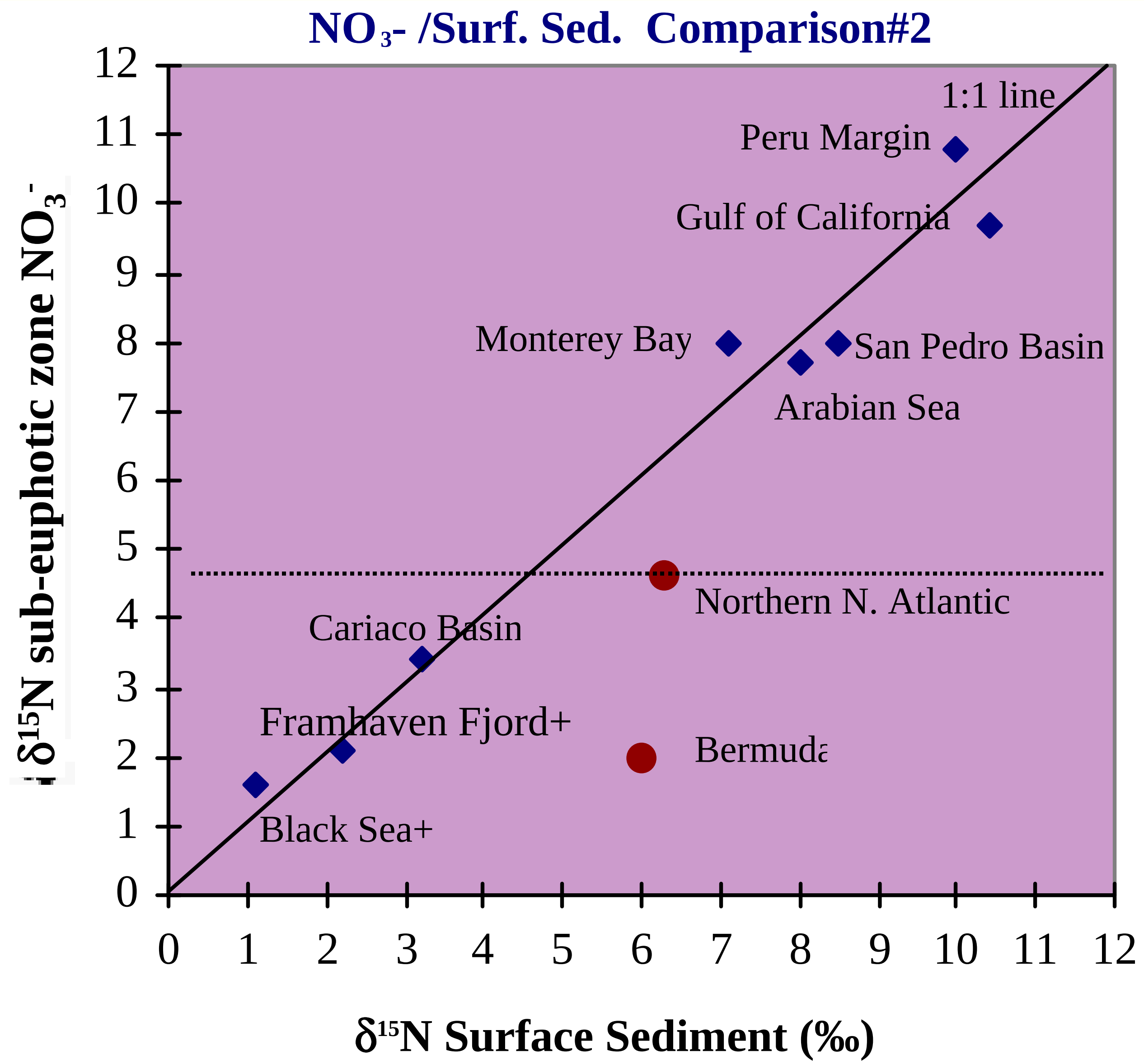




$$\Delta\ \delta^{15}NO_3^- = -\ \varepsilon \times \ln(f)$$

$$f = (NO_3^- + NO_2^-)/(NO_3^- + NO_2^- - N')$$

Preservation of $\delta^{15}N$ Signature



Arabian Sea Sediment Core Results