Stable Isotope Tracers

- Stable Isotopes - Introduction & Notation
- Isotope Fractionation
- Example oceanographic applications

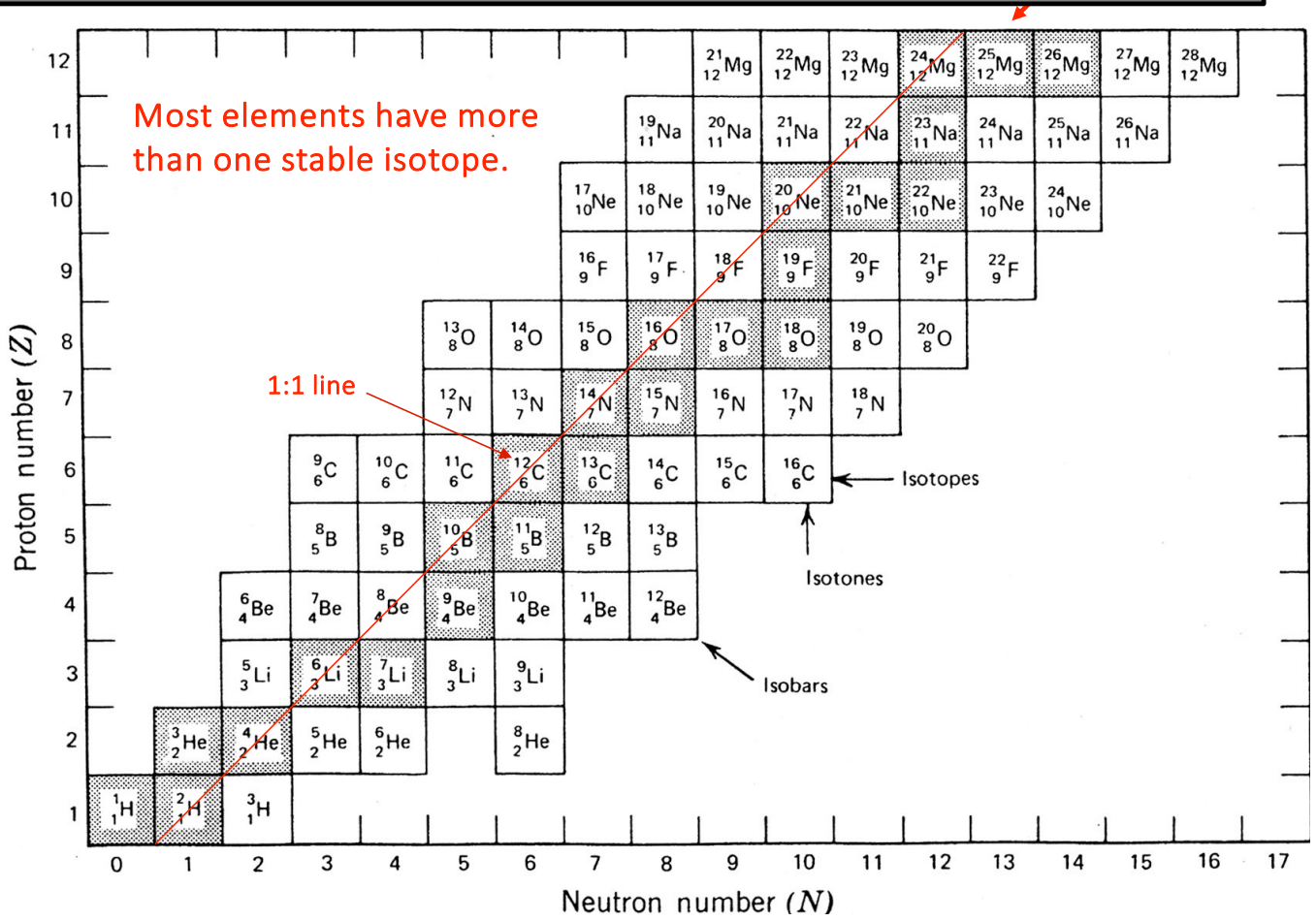
Stable Isotope Tracers

- Trace source/sink and pathways of nutrients and chemicals in the ocean
- Tracers of biological, physical, geological ocean processes
- Record past changes in physical, chemical, and biological processes in the ocean

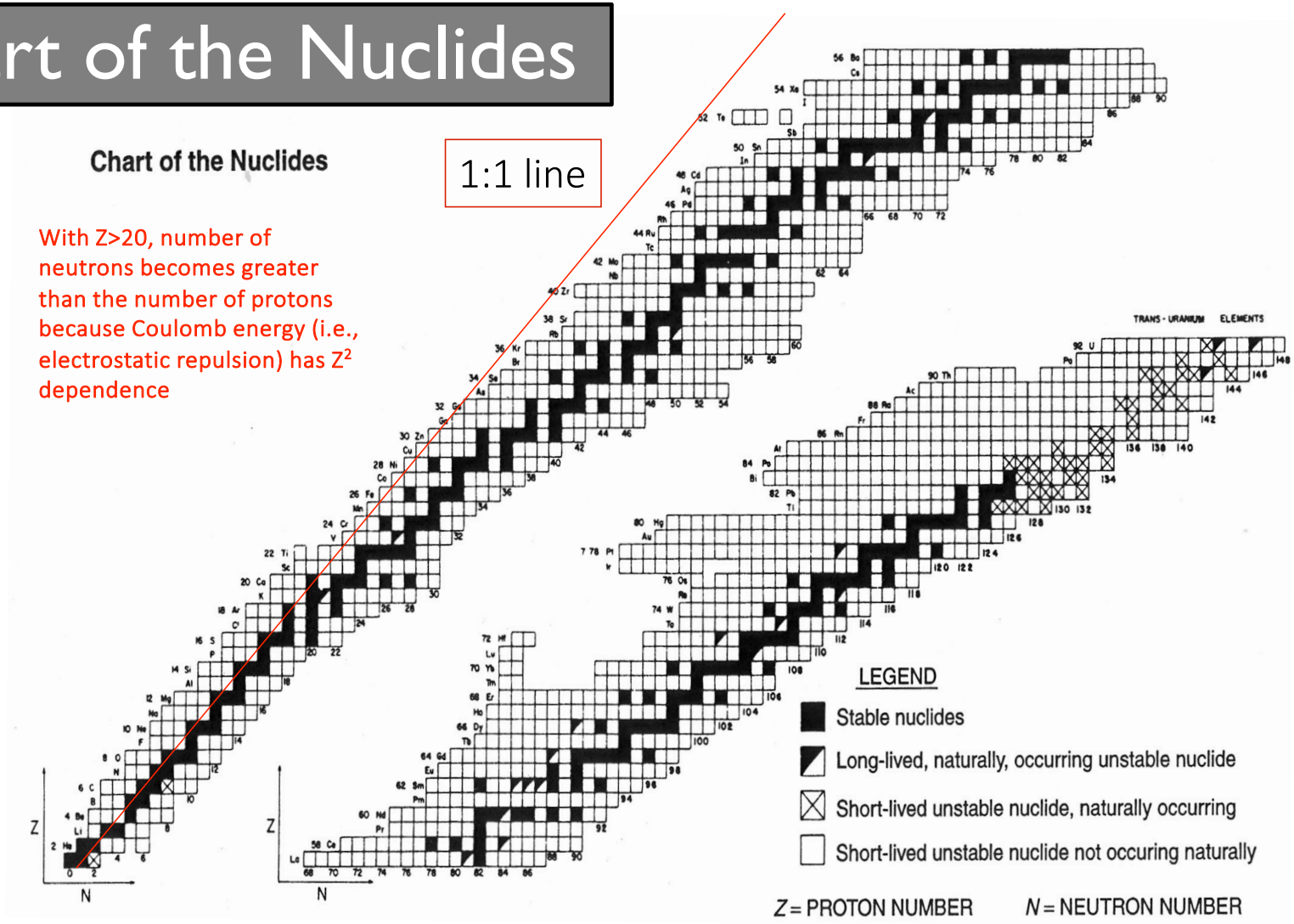
Isotopes of Elements

- The chemical characteristic of an element is determined by the number of protons in its nucleus.
- Atomic Number (Z) = number of protons = defines the chemistry
- Atomic Mass = protons + neutrons (N)
- Isotopes = Atoms with same Z but different N

The chart of the nuclides (protons versus neutrons) for elements 1 (Hydrogen) through 12 (Magnesium)



Full Chart of the Nuclides



Examples: H, He, C, N and O

Element	Symbol	Protons	Neutrons	% Abundance	Half-life
Hydrogen	H	1	0	99.985	
	D (^{2}H)	1	1	0.015	
	T (^{3}H)	1	2	10^{-14} to 10^{-16}	$\tau_{1/2}$ = 12.33 y
Helium	^{3}He	2	1	0.000137	
	^{4}He	2	2	99.999863	
Carbon	^{12}C	6	6	98.89	
	^{13}C	6	7	1.11	
	^{14}C	6	8	10^{-10}	$\tau_{1/2}$ = 5730 y
Nitrogen	^{14}N	7	7	99.634	
	^{15}N	7	8	0.366	
Oxygen	^{16}O	8	8	99.757	
	^{17}O	8	9	0.038	
	^{18}O	8	10	0.205	

All Isotopes of a given element have the same chemical properties, yet there are small differences due to the fact that heavier isotopes typically form stronger bonds and diffuse slightly slower

% abundance is for the average Earth's crust, ocean and atmosphere

Measurement reporting convention (δ or "delta" units):

Delta Notation for ^{18}O:

$$\delta^{18}O = \left[\frac{\left(^{18}O/^{16}O\right)_{Sample} - \left(^{18}O/^{16}O\right)_{Standard}}{\left(^{18}O/^{16}O\right)_{Standard}}\right] \times 1000 = \left[\frac{\left(^{18}O/^{16}O\right)_{Sample}}{\left(^{18}O/^{16}O\right)_{Standard}} - 1\right] \times 1000$$

Generally reported as ratio of a heavy (i.e., rare) isotope to a light (i.e., abundant) isotope

Using a mass spectrometer, isotope ratios can be measured much more precisely than absolute abundances of isotopes

If $\delta > 0$, the sample is *enriched* in the heavy isotope relative to a standard; If $\delta < 0$, the sample is *depleted* in the heavy isotope relative to a standard.

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Example:

If $(^{18}O/^{16}O)_{sample} = 0.995\ (^{18}O/^{16}O)_{Standard}$

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$\delta^{18}O = -0.005 \times 1000 = -5‰$

$\boldsymbol{\varepsilon = \delta_{product} - \delta_{reactant}}$ "difference fractionation factor"

Each isotopic measurement is reported relative to a standard

Element	δ value	Ratio	Standard
Hydrogen	δD	$^{2}H/^{1}H$	Standard Mean Ocean Water (SMOW)
			Standard Light Antarctic Precipitation (SLAP)
Helium	$\delta^{3}He$	$^{3}He/^{4}He$	Atmospheric He
Boron	$\delta^{11}B$	$^{11}B/^{10}B$	NIST SRM 951
Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	Pee Dee Belemnite (PDB)
Nitrogen	$\delta^{15}N$	$^{15}N/^{14}N$	Atmospheric N_2
Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	Standard Mean Ocean Water (SMOW)
			Standard Light Antarctic Precipitation (SLAP)
			Pee Dee Belemnite (PDB)
	$\delta^{17}O$	$^{17}O/^{16}O$	Standard Mean Ocean Water (SMOW)
Sulfur	$\delta^{34}S$	$^{34}S/^{32}S$	Canyon Diablo Troilite (CDT)



http://upload.wikimedia.org/wikipedia/commons/e/e4/Canyon-diablo-meteorite.jpg



http://upload.wikimedia.org/wikipedia/commons/c/cf/Meteor.jpg

Isotope Fractionation

- Change in an isotopic ratio that arises as a result of a chemical or physical process
- Types of isotopic fractionation that cause changes in isotopic compositions:
  - Equilibrium fractionation
  - Kinetic fractionation
  - Mass-independent fractionation
- Fractionation Factor (α):

$\alpha_{A\text{-}B} = R_A / R_B$, where R_A and R_B are isotope ratios in materials A and B

Isotope Fractionation

Example: equilibrium fractionation of oxygen isotopes in liquid water (l) relative to water vapor (g).

$H_2{}^{16}O(l) + H_2{}^{18}O(g) \leftrightarrow H_2{}^{18}O(l) + H_2{}^{16}O(g)$

At 20°C, the equilibrium fractionation factor is:

$\alpha = ({}^{18}O/{}^{16}O)_l / ({}^{18}O/{}^{16}O)_g = 1.0098$

Equilibrium fractionation

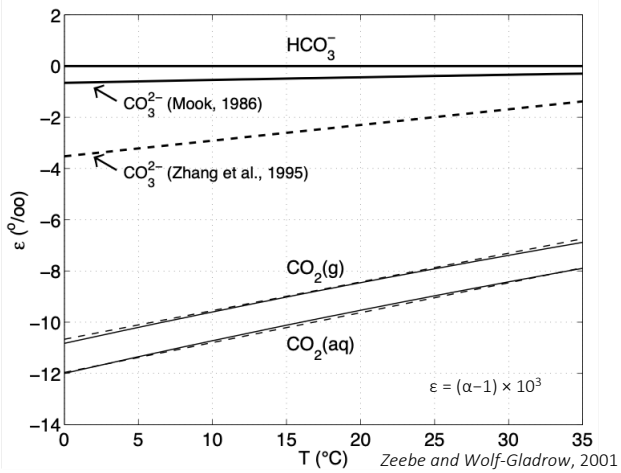
- Exchange reactions in which isotopes are exchanged between two or more species (with isotopic preference).
- Bidirectional (reversible) chemical reactions
- Usually applies to inorganic species
- Temperature dependent
- Generally, the heavy isotope will be concentrated in the phase in which it is most strongly bound (i.e., its lowest energy state).
  - Solid > liquid > vapor
  - Covalent > ionic, etc.

Equilibrium fractionation - Example

The carbonate system involving gaseous CO_2(g), aqueous CO_2 (aq), aqueous bicarbonate HCO_3^- and carbonate CO_3^{2-}.

It is an important system that exhibits equilibrium isotope effects for both carbon and oxygen isotopes. For example:

$^{13}CO_2(g) + H^{12}CO_3^- \leftrightarrow {}^{12}CO_2(g) + H^{13}CO_3^-$



Zeebe and Wolf-Gladrow, 2001

Equilibrium fractionation - Example

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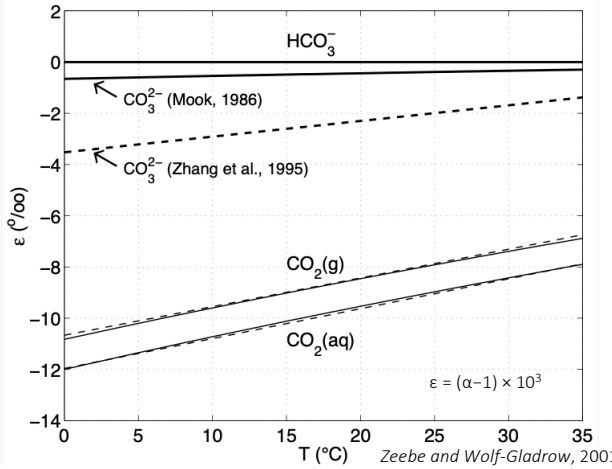
$^{13}CO_2(g) + H^{12}CO_3^- \leftrightarrow {}^{12}CO_2(g) + H^{13}CO_3^-$

The heavier isotope (^{13}C) is preferentially concentrated in the chemical compound in which it is most strongly bound. In this case ^{13}C will be concentrated in HCO_3^- as opposed to $CO_2(g)$.

For this reaction:

$\alpha = (H^{13}CO_3^- / H^{12}CO_3^-) / (^{13}CO_2 / {}^{12}CO_2)$

$\alpha =$ 1.0092 at 0 °C and 1.0068 at 30 °C



Zeebe and Wolf-Gladrow, 2001

Kinetic fractionation

- One isotope reacts, diffuses, or evaporates faster than the other.
- Can be due to chemical, physical, or biological processes.
- Occurs during irreversible reactions like photosynthesis, when the rate of chemical reaction is sensitive to atomic mass.
- Essentially all isotopic effects involved with formation / destruction of organic matter are kinetic.
- Usually, the lighter isotope reacts or diffuses faster.
- Reaction products are enriched in the lighter isotopes; reservoir of reactants is depleted in the lighter isotopes.
- Magnitude of isotope effect is temperature and pressure dependent.

Kinetic fractionation - An Ideal (Gas)Example

$^{12}C^{16}O_2$ (mass = 12 + 2 x 16 = 44)
$^{13}C^{16}O_2$ (mass = 13 + 2 x 16 = 45)

In an ideal gas, the average kinetic energy of all molecules is the same:

$$E_k = \frac{1}{2}mv^2$$

$$E_k = \frac{1}{2}m_A v_A^{\ 2} = \frac{1}{2}m_B v_B^{\ 2}$$

$$\frac{v_A}{v_B} = \left(\frac{m_B}{m_A}\right)^{1/2} = \left(\frac{45}{44}\right)^{1/2} = 1.011$$

As an ideal gas, $^{12}CO_2$ diffuses 1.1% faster than $^{13}CO_2$.

In reality, molecular collisions and intermolecular forces are important, effectively reducing the impact of the mass difference between 12 and 13 CO_2

We predict that due to non-ideality, in gaseous diffusion, $^{12}CO_2$ will diffuse 0.44% faster than $^{13}CO_2$.

Kinetic fractionation

All isotope effects involving organic matter are kinetic. Example:

$^{12}CO_2 + H_2O \rightarrow {}^{12}CH_2O + O_2$ faster
$^{13}CO_2 + H_2O \rightarrow {}^{13}CH_2O + O_2$ slower

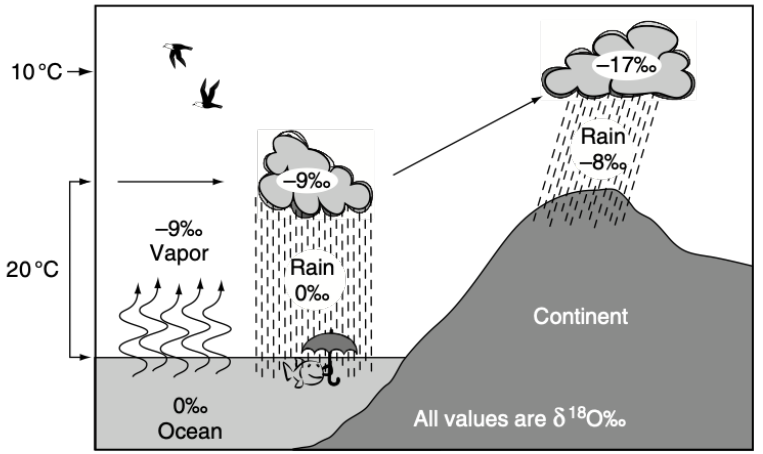
Thus organic matter gets depleted in ^{13}C during photosynthesis (i.e., $\delta^{13}C$ becomes more negative).

Terrestrial plants: ca. -19‰ (range -26 to -7‰)
Marine plants: ca. -14‰ (range -22 to -8‰)

Rayleigh Distillation

- Fractionation occurs when water molecules evaporate from sea surface.
- Equilibrium effect when water molecules condense from vapor to liquid form (rain is heavier than vapor).
- Vapor becomes progressively lighter (i.e., δD and $\delta^{18}O$ get lower) with distance from source.

- Evaporation from ocean creates depleted clouds.
- Air masses transported to higher latitude/altitude where it is cooler.
- Water lost due to rain; raindrops are enriched in ^{18}O relative to cloud.
- Cloud gets lighter



Emerson & Hedges, 2008

Rayleigh Distillation

Example: Evaporation – Condensation Processes

$\delta^{18}O$ in cloud vapor and condensate (rain) plotted versus the fraction of remaining vapor for a Raleigh process.

The isotopic composition of the residual vapor is a function of the fractionation factor between vapor and water droplets. The drops are enriched in ^{18}O. The vapor is progressively depleted.

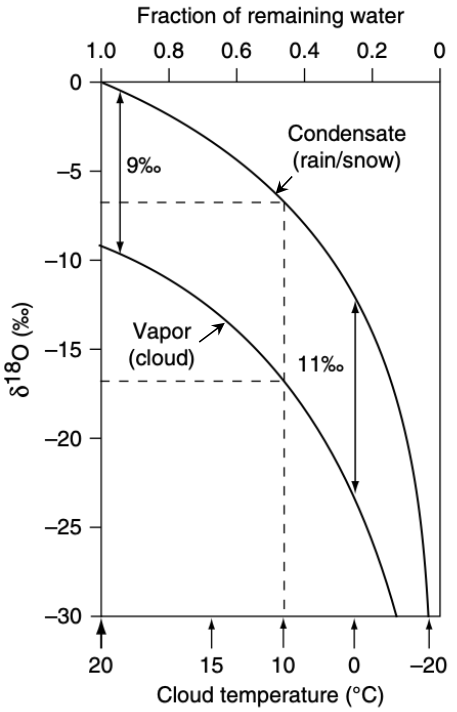
$$\frac{R_V}{R_{V_0}} = f^{(\alpha-1)}$$

R_V is the isotopic ratio of the vapor

R_{V_0} is the initial isotopic ratio of the vapor

f is the fraction of vapor remaining

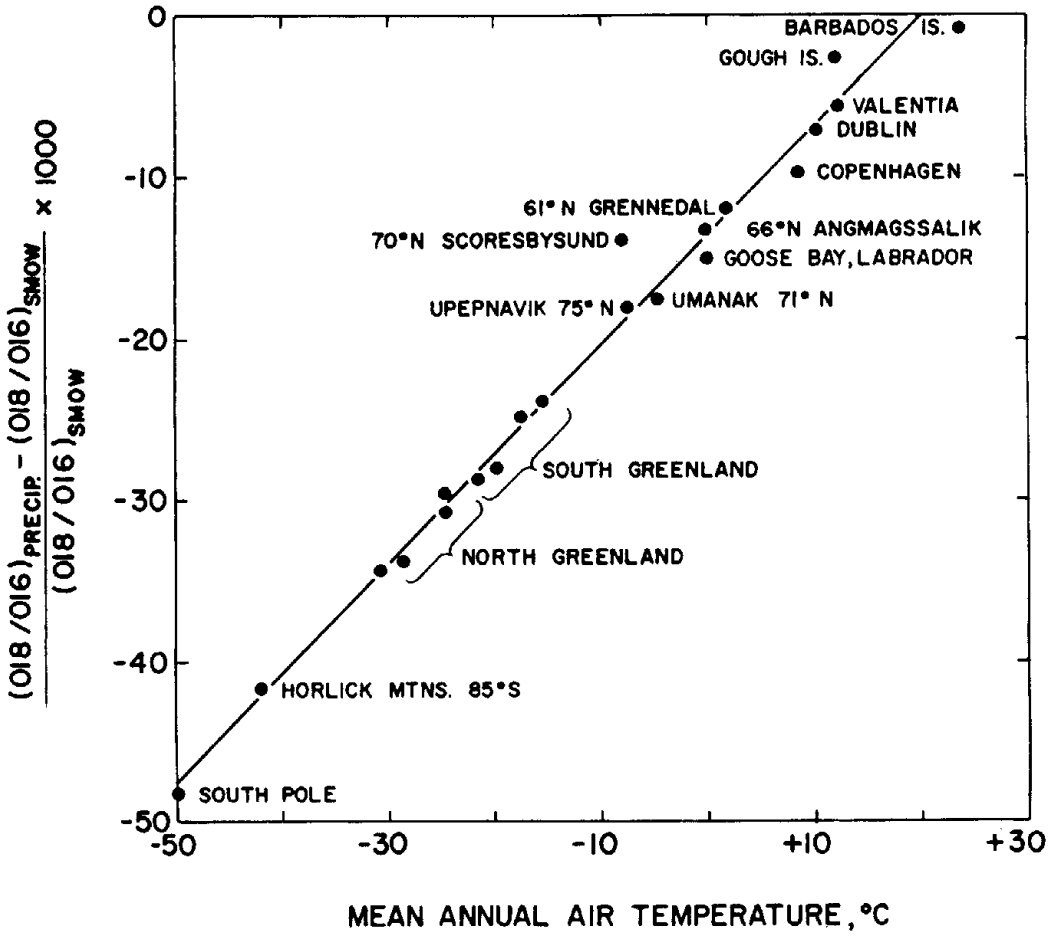
α is the fractionation factor



Fractionation increases with decreasing temperature

Emerson & Hedges, 2008

$\delta^{18}O$ in Average Rain vs. Temperature



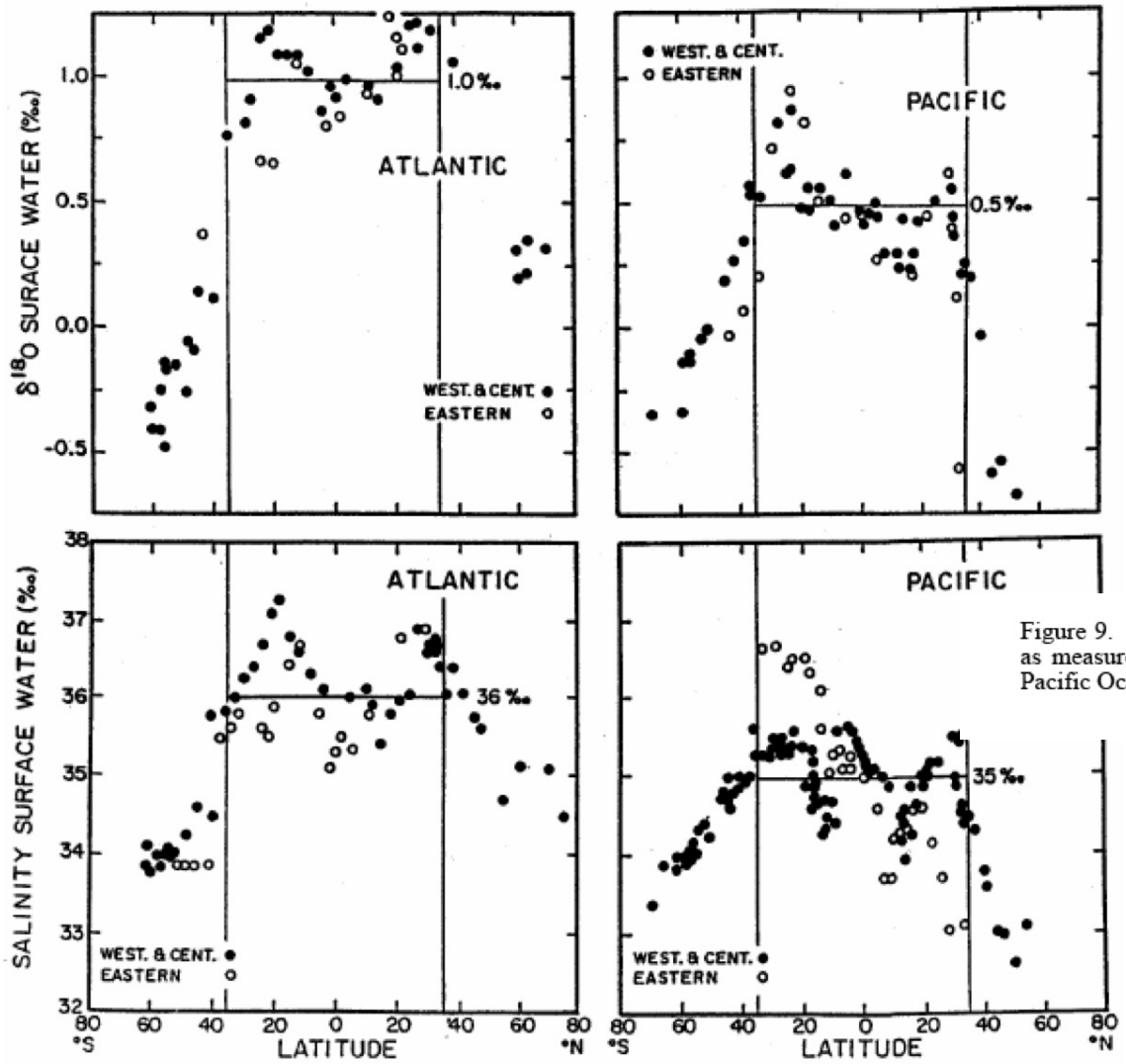


Figure 9. Latitude dependence oxygen isotope composition (upper) and salinity (lower) as measured by Harmon Craig on samples of surface waters in the open Atlantic and Pacific Oceans obtained during the GEOSECS expeditions.

Examples: Stable Isotope Applications in Oceanography

- ^{3}He to study deep ocean circulation in the Pacific
- ^{15}N to close the ocean N budget
- ^{18}O to determine freshwater balance in the Arctic Ocean
- ^{18}O as an indicator of the ice ages

^{3}He Plume from East Pacific Rise

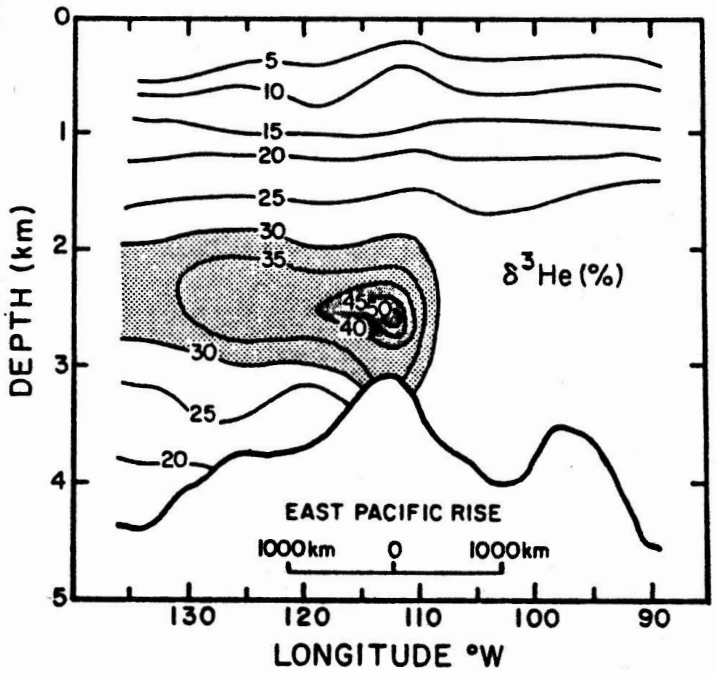
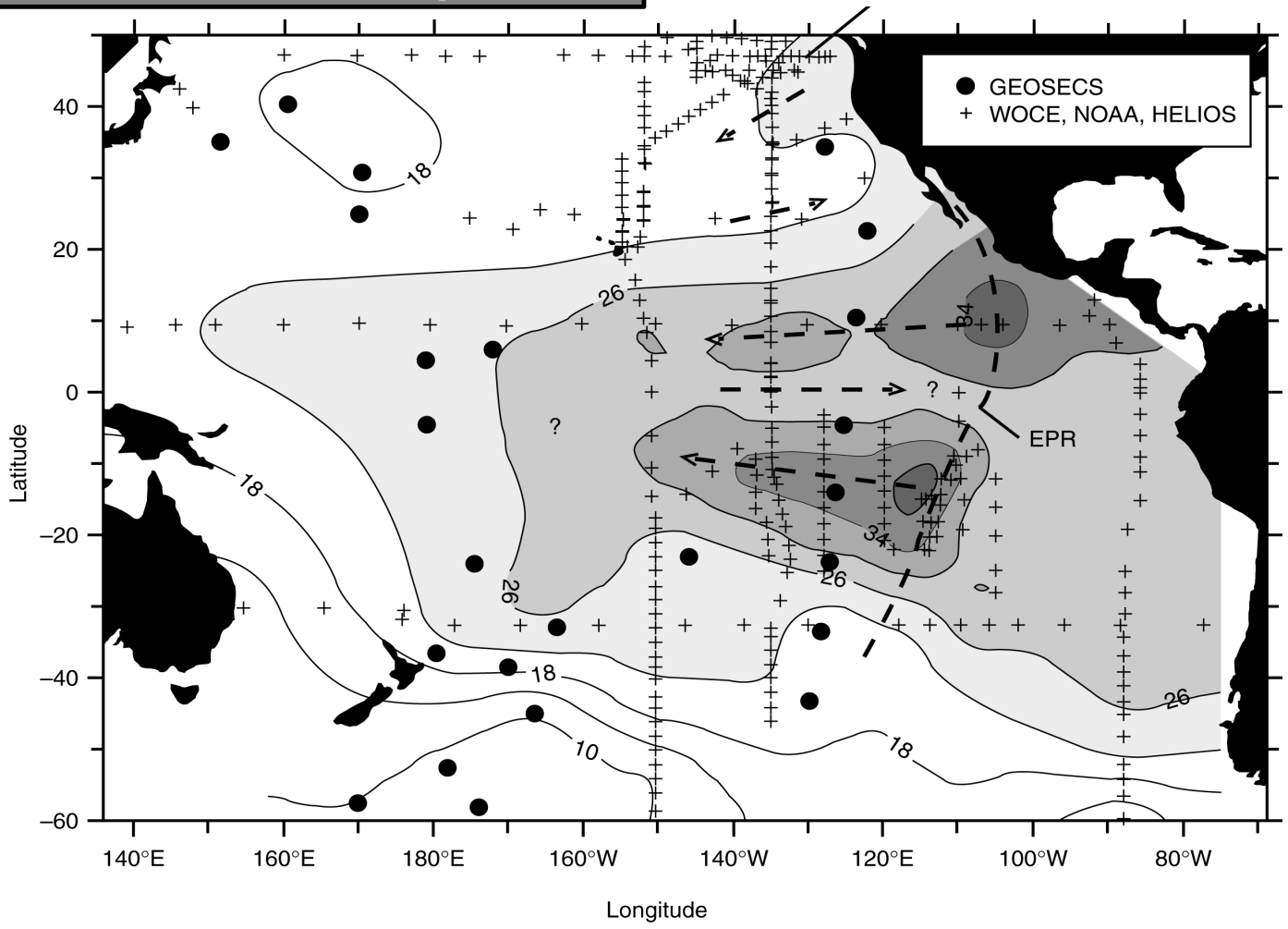


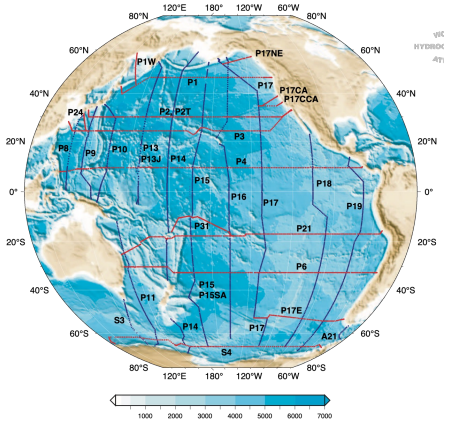
Figure 7-8. Section of excess ^{3}He content (expressed as δ^3He in percent) across the East Pacific Rise at 15° south (line A-B in figure 7-7). The westward extending plume of ^{3}He originating at the crest of this spreading center is quite apparent. The measurements on which this diagram is based were made by John Lupton in the Laboratory of Harmon Craig at the Scripps Institution of Oceanography (280).

Broecker and Peng, 1982

^{3}He at 2500 m depth



^{3}He Plume from Loihi Seamount (Hawaii)



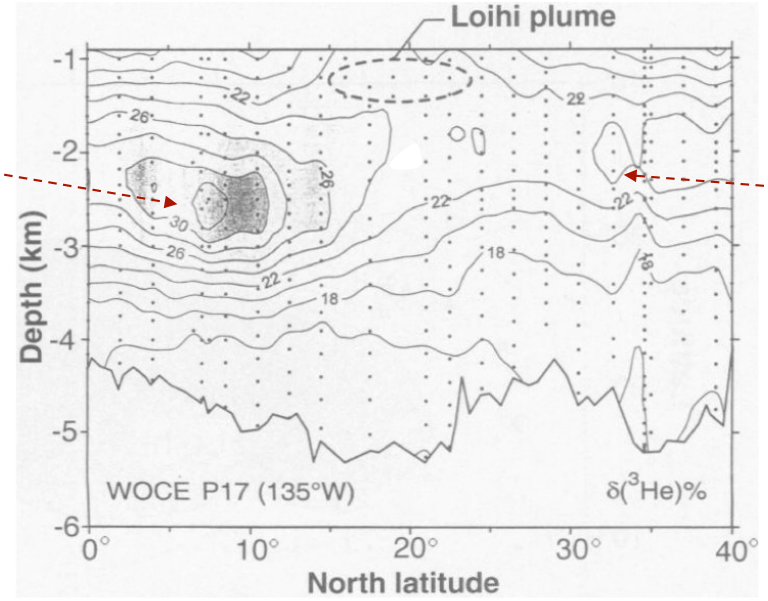


Fig. 5. δ(^{3}He)% contoured in section view for WOCE line P17 along 135°W. In this section, the Loihi plume appears as an upturning of the δ(^{3}He) contours in the depth range from 900 to 1400 m, between latitudes 15° and 25°N as indicated by the dashed ellipse. The plume core centered at 8°N and a depth of 2500 m is helium from the EPR, whereas the weaker signal north of 32°N and at a depth of 2000 m is from the JdFR.

Lupton, 1996

^{3}He at 1100 m depth

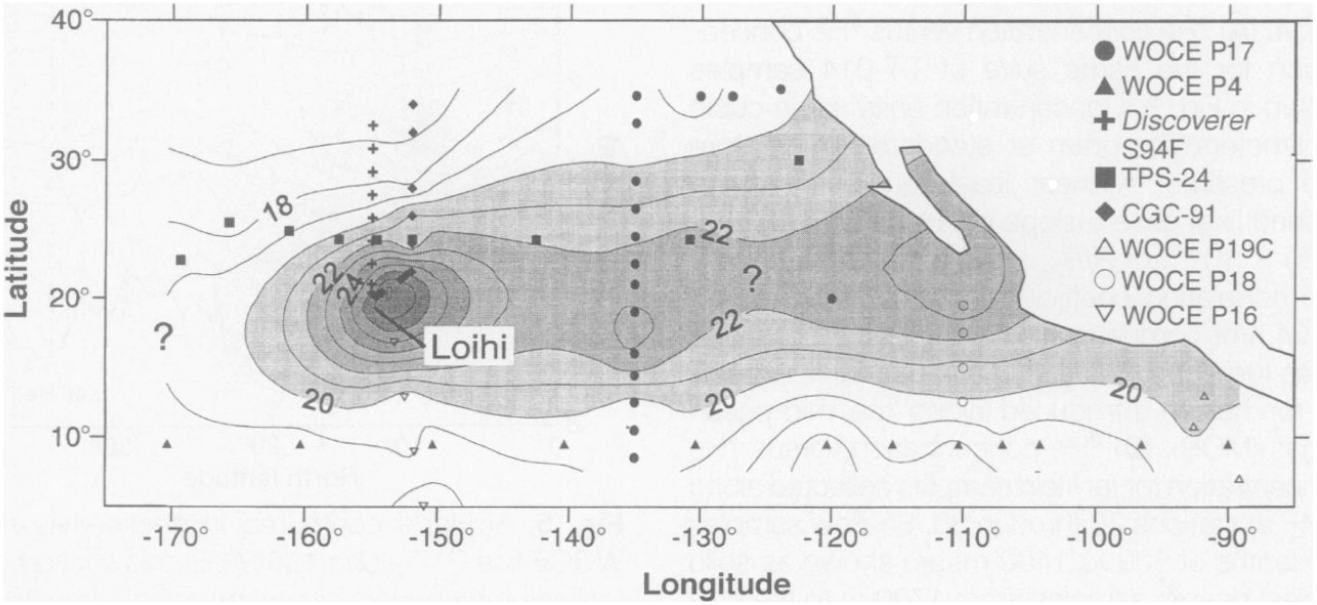


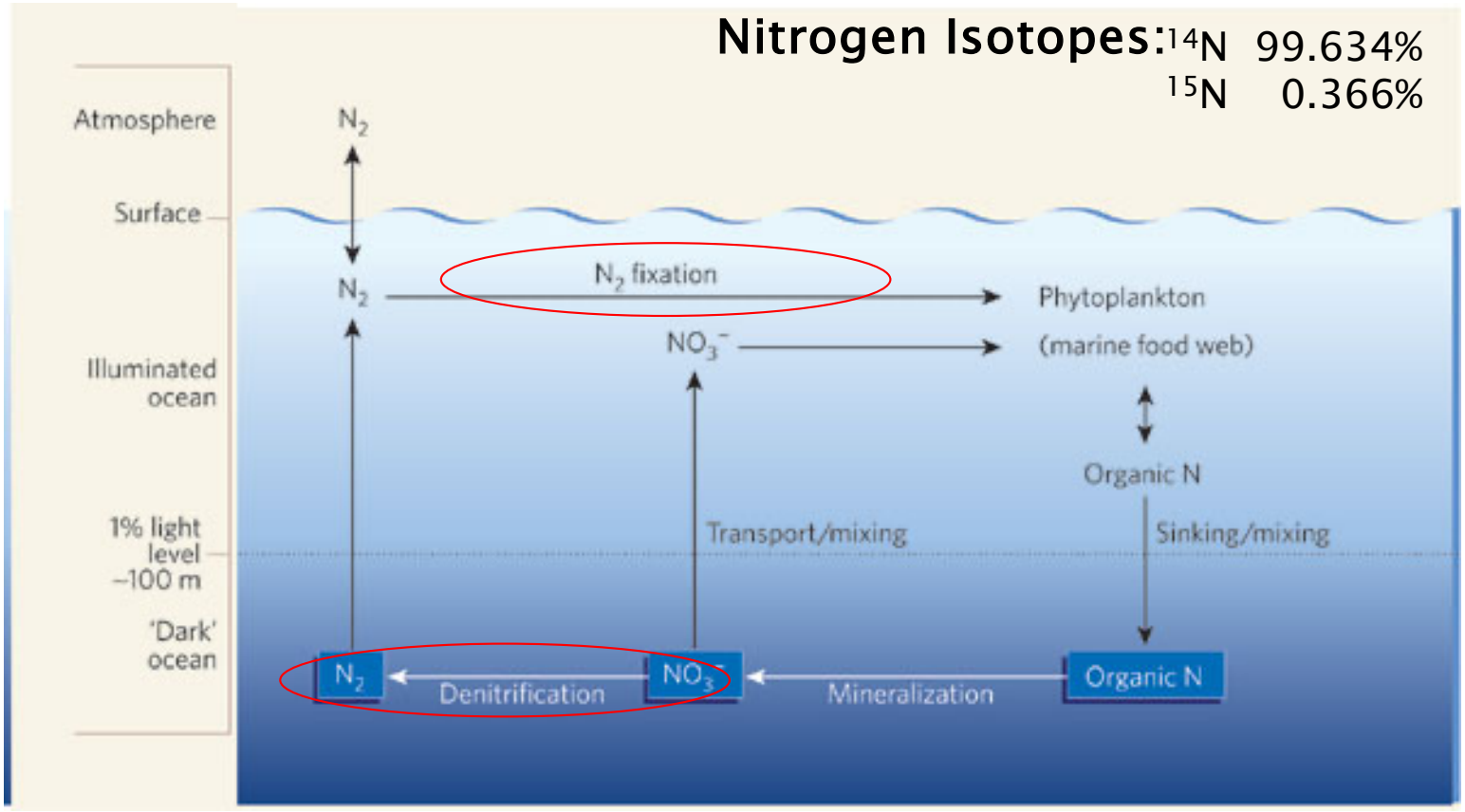
Fig. 6. $\delta(^3He)\%$ contoured on a surface at a depth of 1100 m, showing the broad lateral extent of the Loihi plume. In some cases, bottle data were interpolated to 1100-m deep surface. The contour interval is 1% in $\delta(^3He)$; the accuracy of the measurements is 0.25% (1σ). This figure includes data from eight different expeditions spanning the time interval from 1985 to 1994. Although these data are not synoptic, the sampling period is relatively short compared with the time scale for circulation at this depth. Helium data along WOCE lines P4 and P16 were provided by W. Jenkins (*4, 23*).

Lupton, 1996

Examples: Stable Isotope Applications in Oceanography

- ^{3}He to study deep ocean circulation in the Pacific
- ^{15}N to close the ocean N budget
- ^{18}O to determine freshwater balance in the Arctic Ocean
- ^{18}O as an indicator of the ice ages

Schematic of Ocean Nitrogen Cycle



The Global Nitrogen Budget-one example

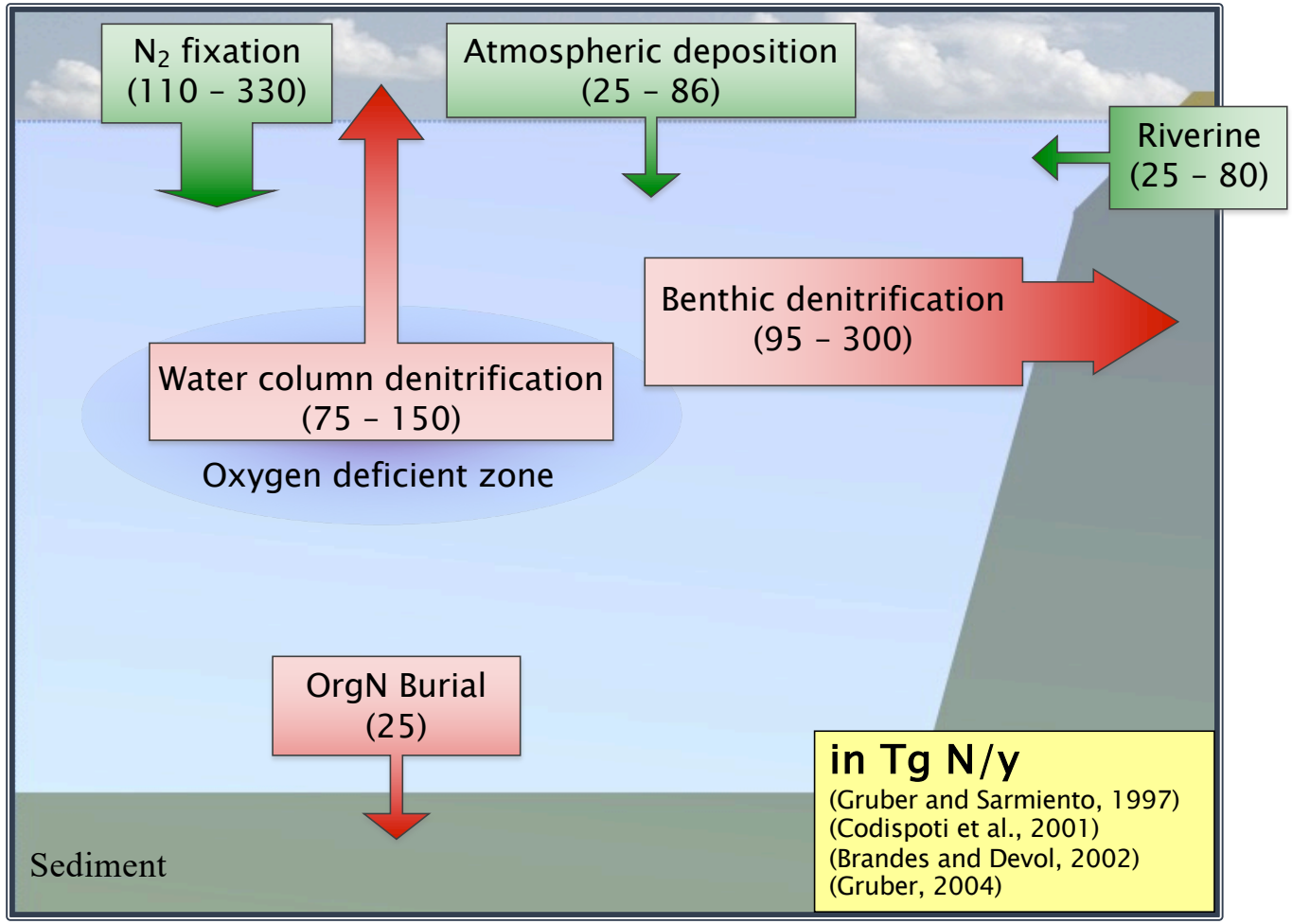
(Brandes et al, 2002)

Table 1. Fluxes and Isotopic Values for Source and Sink Nitrogen Budgets[a]

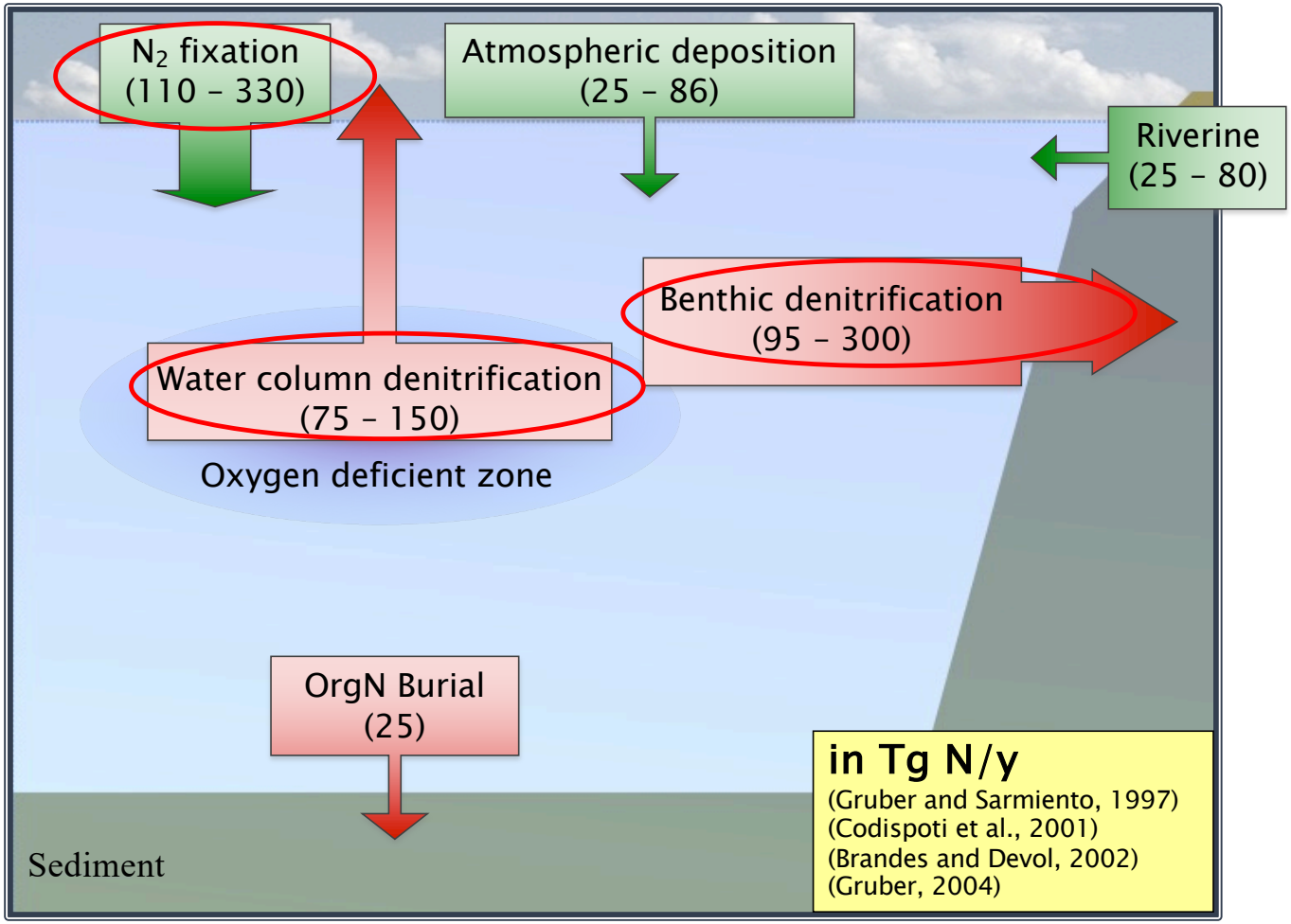
Term	Flux, Tg N yr^{-1}	Isotopic Value, ‰
Riverine source	25	4 (±4)
Atmosphere sources (DON + DIN)	25	−4 (±5)
Nitrogen fixation	110–330	−1 (±1)
Total sources	160–380	−1
Sedimentary denitrification	−200–280	3.5 (±2)
Water column denitrification	−75	−20 (±3)
Organic burial	−25	6 (±4)
Total sinks	−300–380	−1
Net	−200–0	−1 (±2)

[a]Values in parentheses for isotopic values are estimated variances for each term. See text for references.

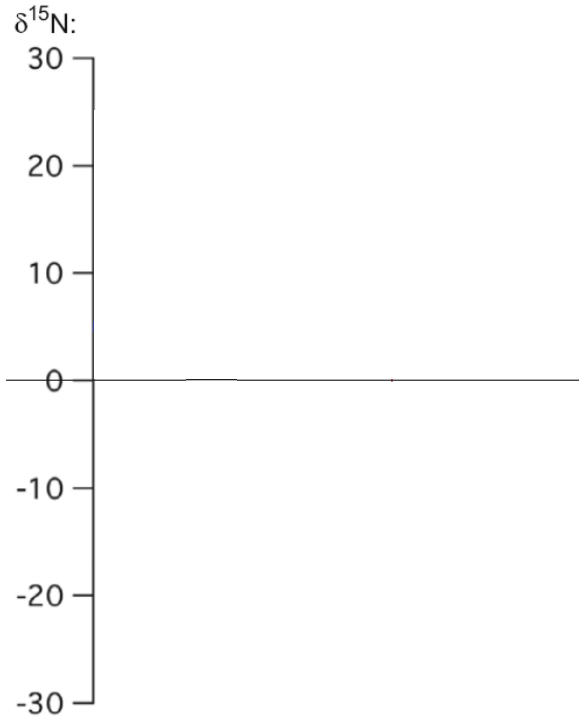
N Budget: Sources and Sinks



N Budget: Sources and Sinks

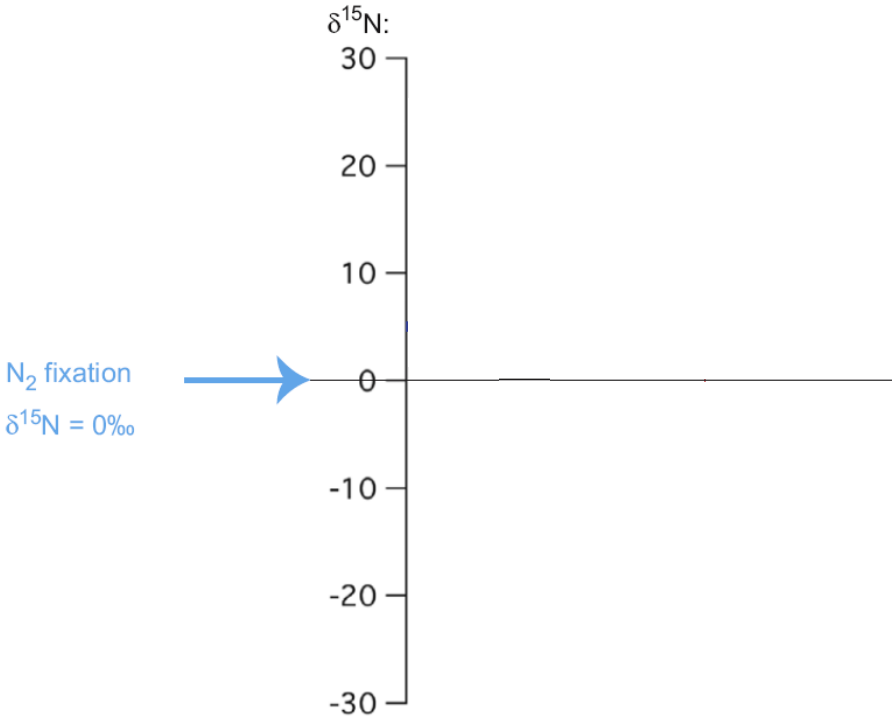


Marine N isotope budget



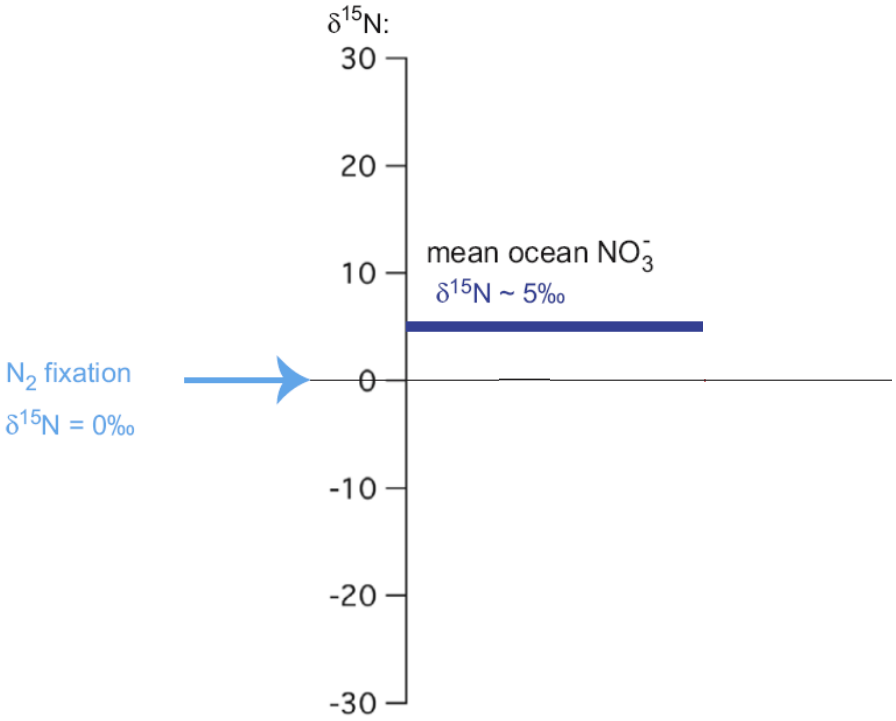
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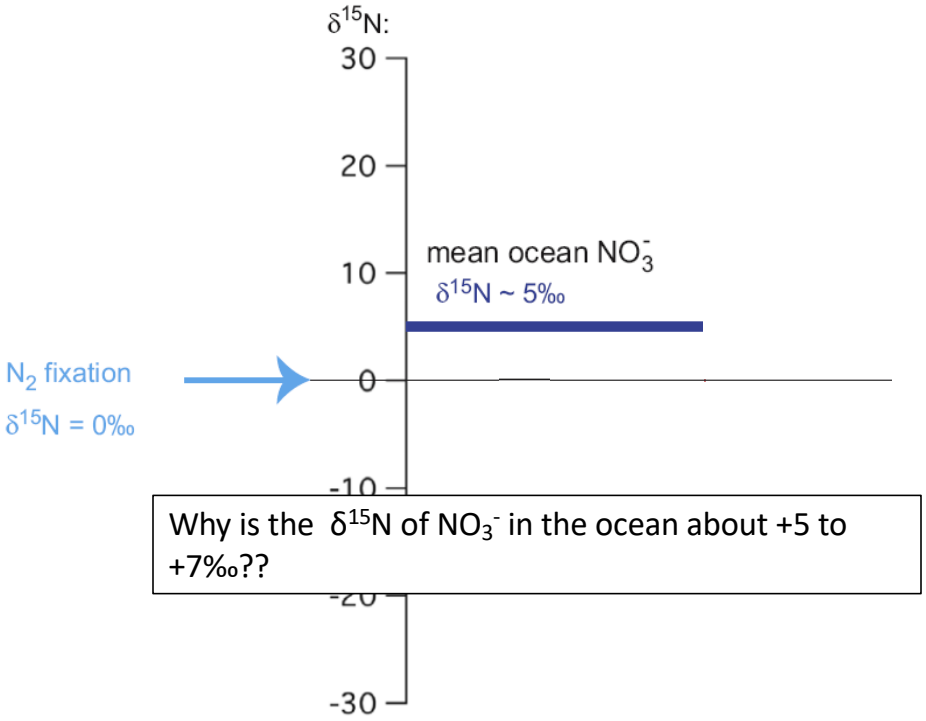
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Marine N isotope budget



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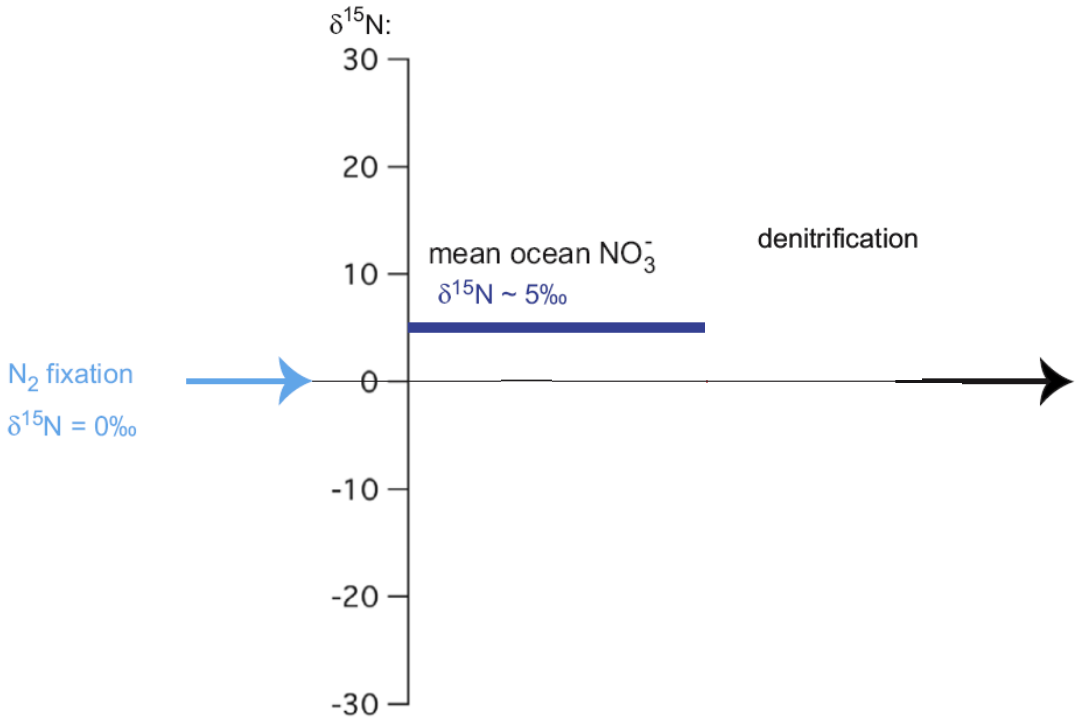
Marine N isotope budget



Why is the $\delta^{15}N$ of NO_3^- in the ocean about +5 to +7‰??

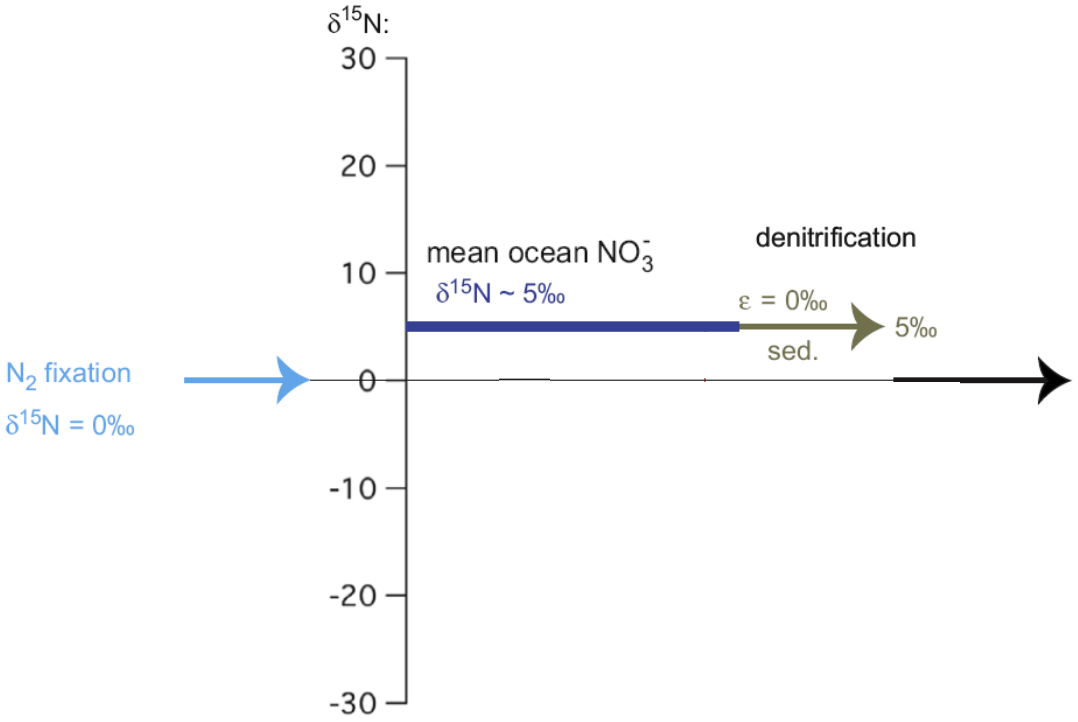
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Marine N isotope budget



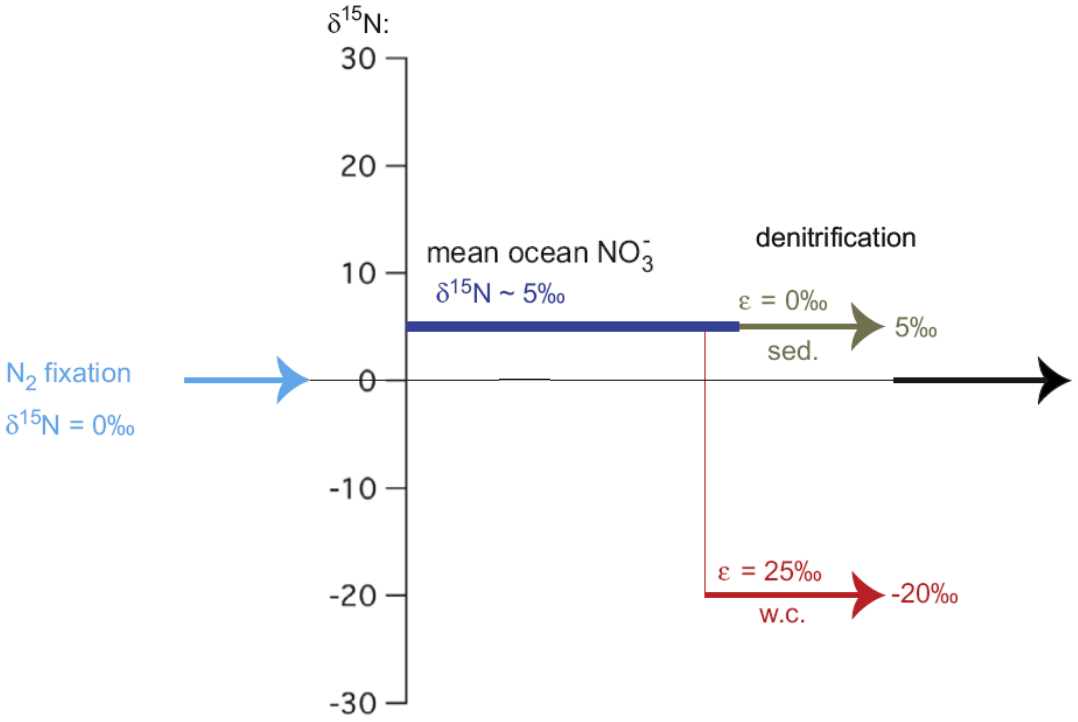
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Marine N isotope budget



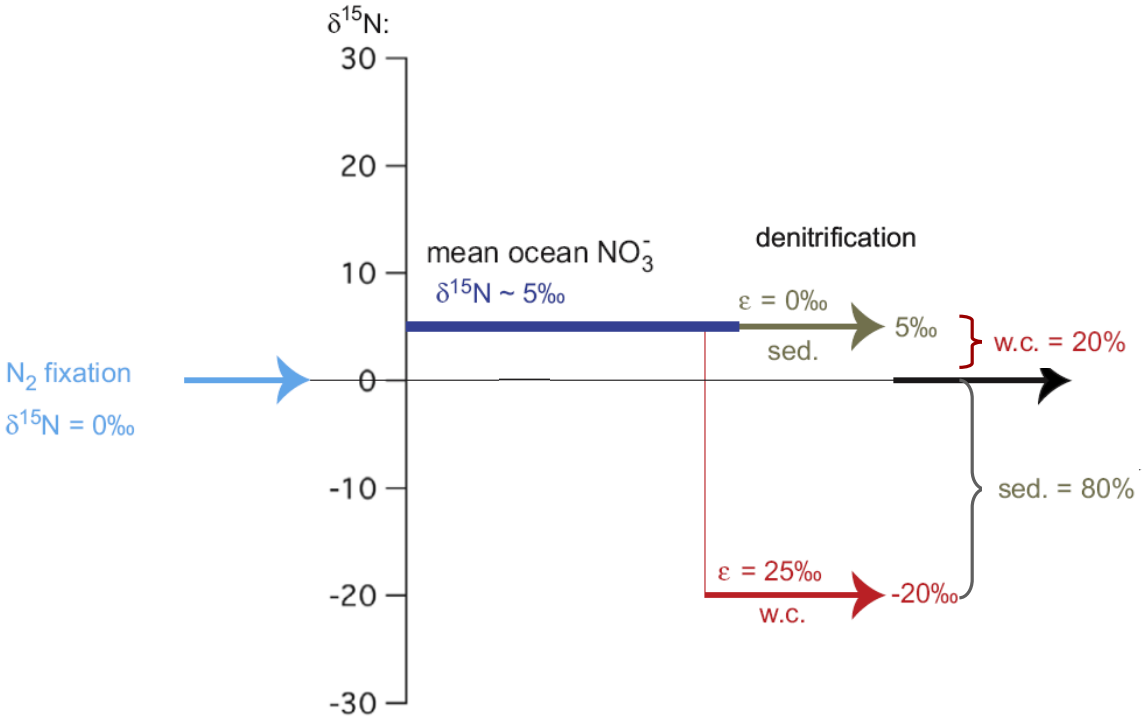
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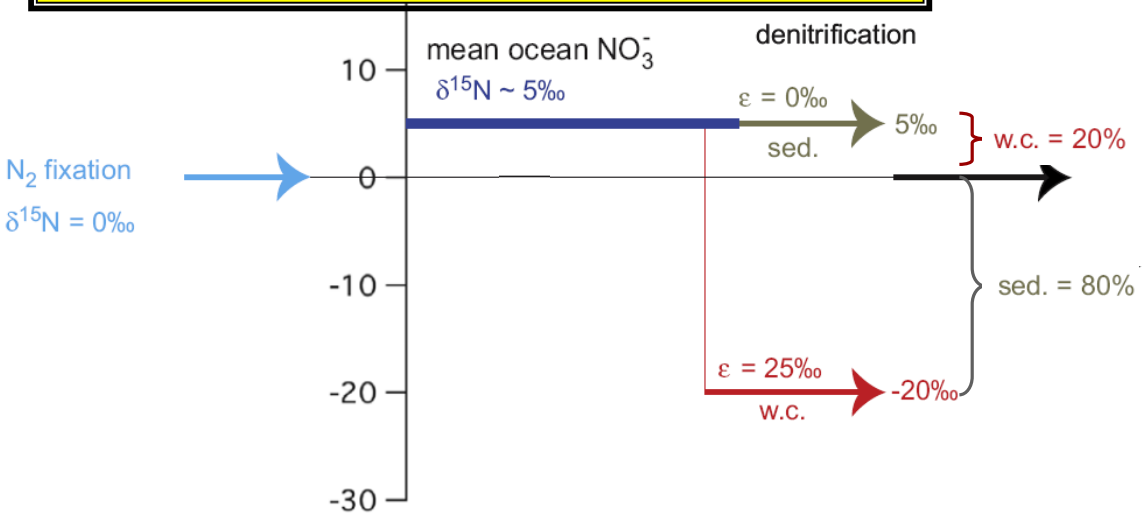


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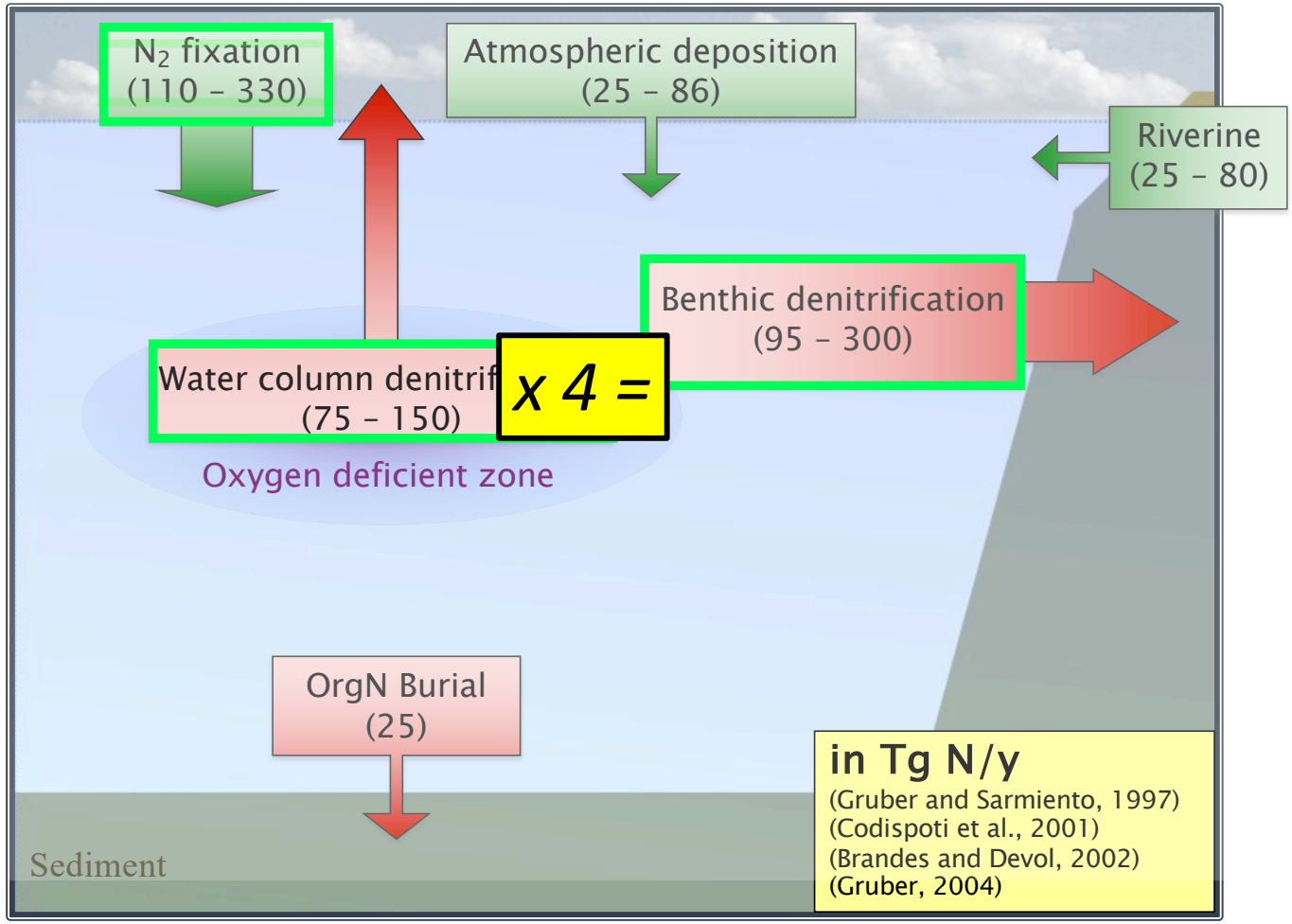
$\delta^{15}N$:

$$\frac{\textit{water column denitrification}}{\textit{sedimentary denitrification}} = \frac{1}{4}$$

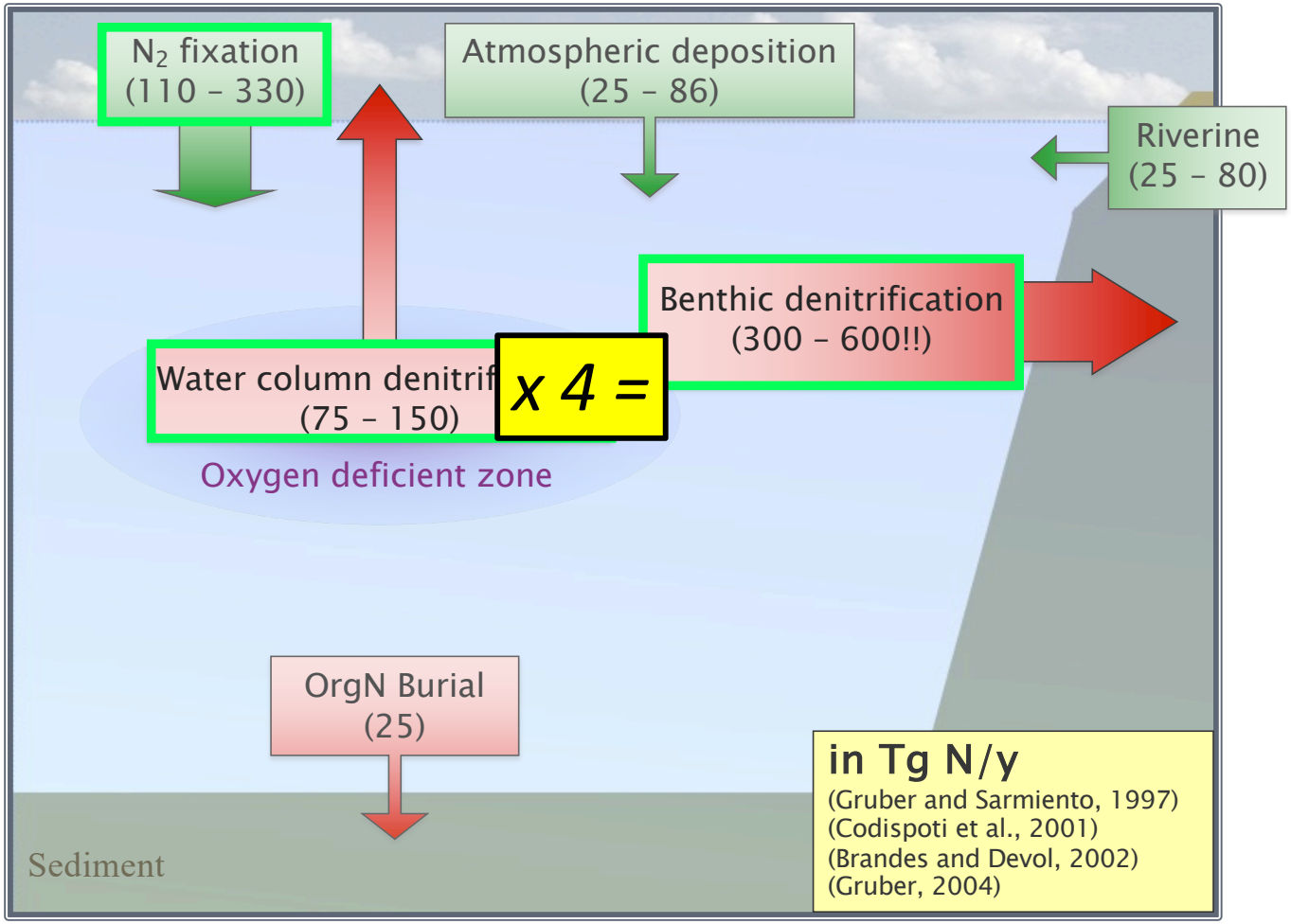


(Brandes and Devol 2002)
(Sigman et al. 2009)

The Marine Nitrogen Budget



The Marine Nitrogen Budget



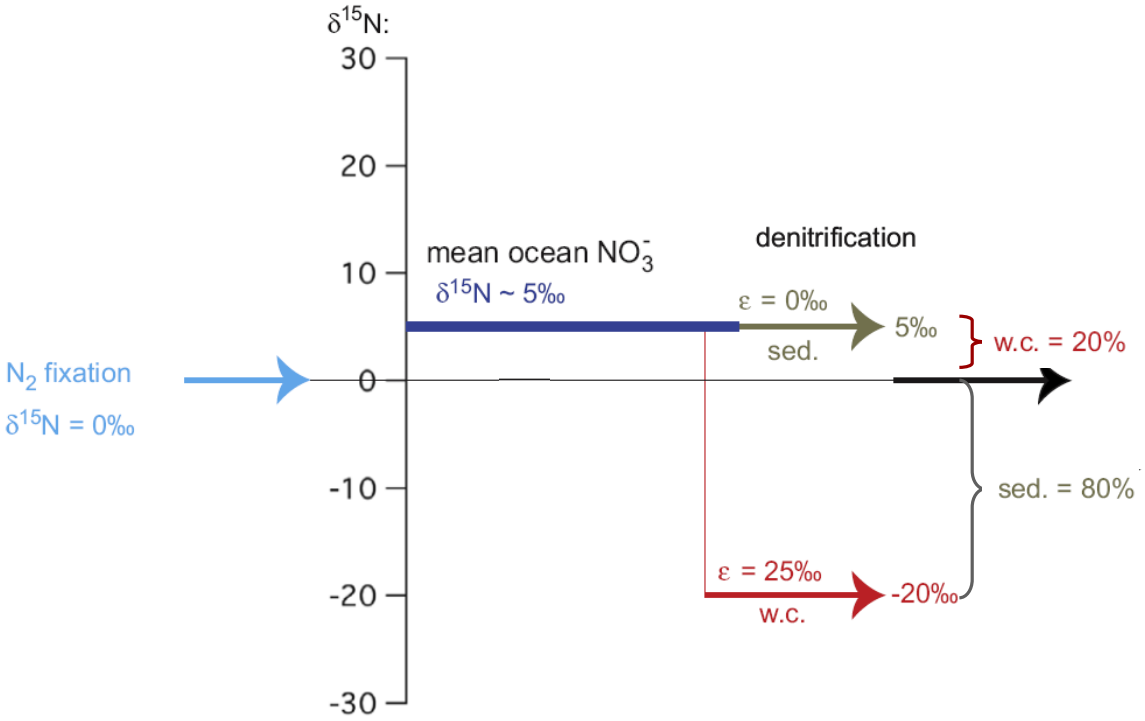
The Marine Nitrogen Budget

Water column denitrification	Benthic denitrification	Net (Tg N/y)	Time to deplete N inventory
75	300	> -200	< 3000 y

The Marine Nitrogen Budget

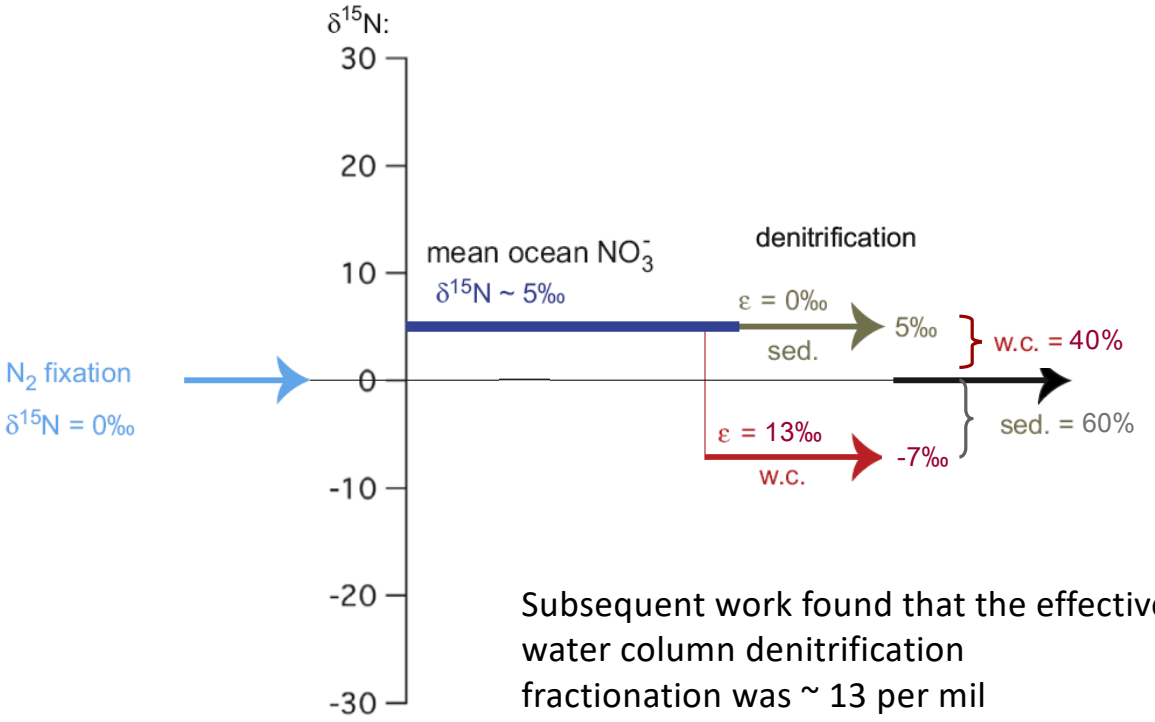
Water column denitrification	Benthic denitrification	Net (Tg N/y)	Time to deplete N inventory
75	300	> -200	< 3000 y
150	600	> -575	< 1000 y

Marine N isotope budget



(Brandes and Devol 2002)
(Sigman et al. 2009)

Marine N isotope budget



Subsequent work found that the effective water column denitrification fractionation was ~ 13 per mil

(Brandes and Devol 2002)
(Sigman et al. 2009)

The Marine Nitrogen Budget

Water column denitrification	$\varepsilon_{W.C.}$	W.C.:Benthic	Benthic denitrification	Net (Tg N/y)
75	25‰	1:4	300	~ -200

With a water column denitrification fractionation of ~ 13 per mil

The Marine Nitrogen Budget

Water column denitrification	$\varepsilon_{W.C.}$	W.C.:Benthic	Benthic denitrification	Net (Tg N/y)
75	25‰	1:4	300	~ -200
75	13‰	1:1.5	113	~ -13

This closes the Nitrogen budget!

Altabet et al. 2007

Examples: Stable Isotope Applications in Oceanography

- ^{3}He to study deep ocean circulation in the Pacific
- ^{15}N to close the ocean N budget
- ^{18}O to determine freshwater balance in the Arctic Ocean
- ^{18}O as an indicator of the ice ages

Freshwater balance in the Arctic Ocean

Balances of mass, salt, $\delta^{18}O$, and nutrients allow us to separate the contributions of the individual freshwater sources

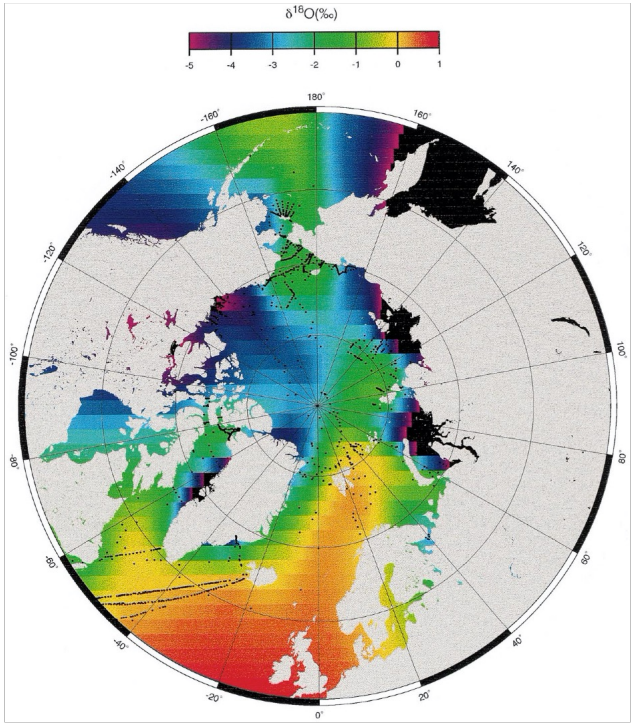


Fig. 7. Distribution of $\delta^{18}O$ in the surface waters (depth 15 m) of the Arctic Ocean and the adjacent seas.

Schlosser et al., 1999

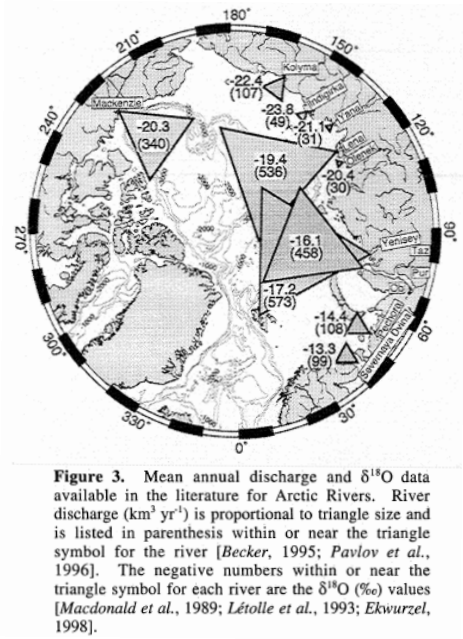


Figure 3. Mean annual discharge and $\delta^{18}O$ data available in the literature for Arctic Rivers. River discharge ($km^3\ yr^{-1}$) is proportional to triangle size and is listed in parenthesis within or near the triangle symbol for the river [*Becker*, 1995; *Pavlov et al.*, 1996]. The negative numbers within or near the triangle symbol for each river are the $\delta^{18}O$ (‰) values [*Macdonald et al.*, 1989; *Létolle et al.*, 1993; *Ekwurzel*, 1998].

$$f_a + f_p + f_r + f_i = 1,$$

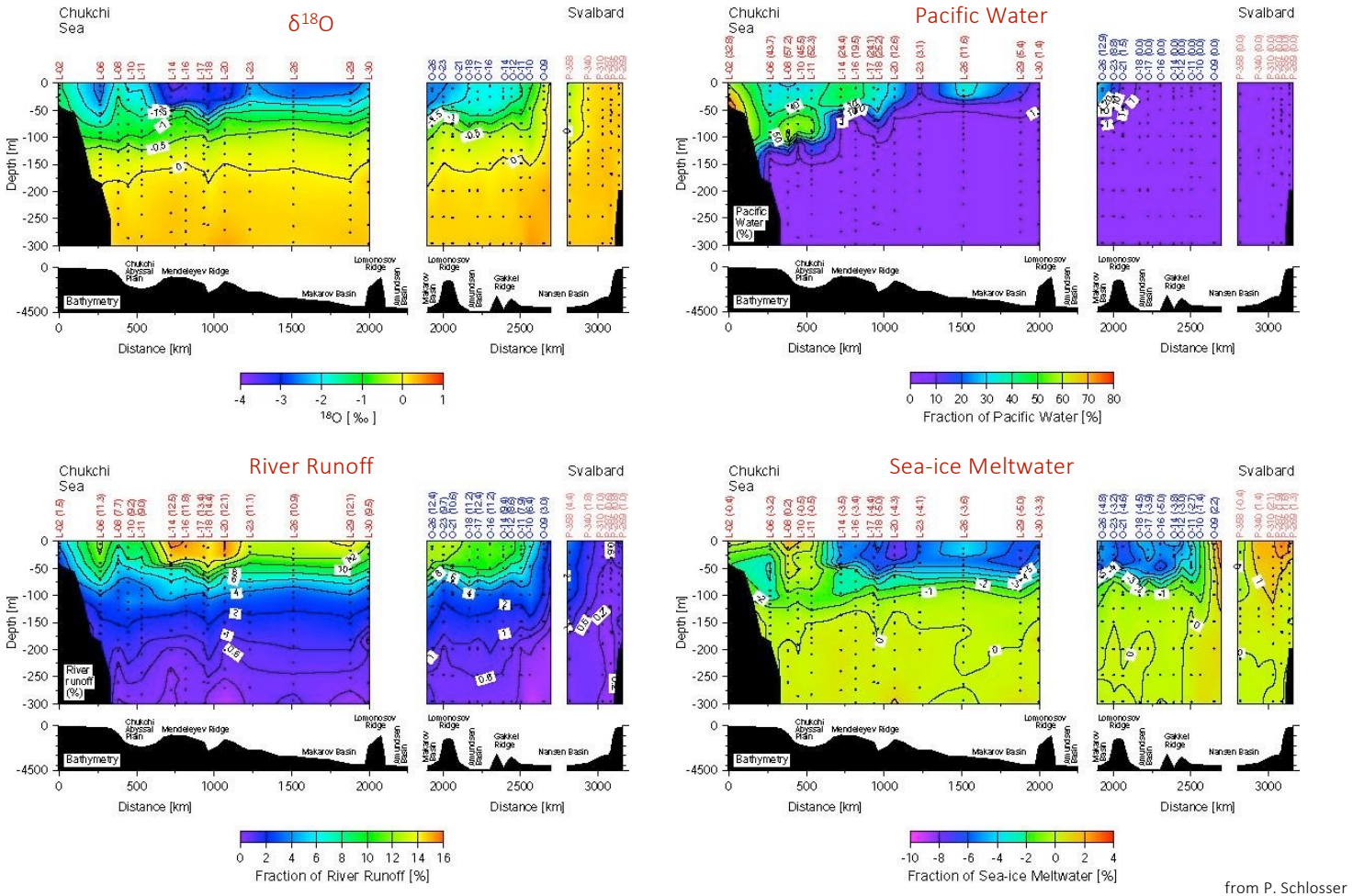
$$f_a S_a + f_p S_p + f_r S_r + f_i S_i = S_m,$$

$$f_a \delta^{18}O_a + f_p \delta^{18}O_p + f_r \delta^{18}O_r + f_i \delta^{18}O_i = \delta^{18}O_m,$$

$$f_a PO_4{}^*_a + f_p PO_4{}^*_p + f_r PO_4{}^*_r + f_i PO_4{}^*_i = PO_4{}^*_m,$$

Ekwurzel et al., 2001

Freshwater balance in the Arctic Ocean

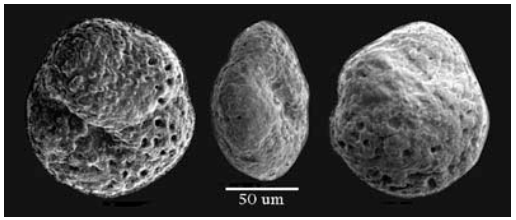


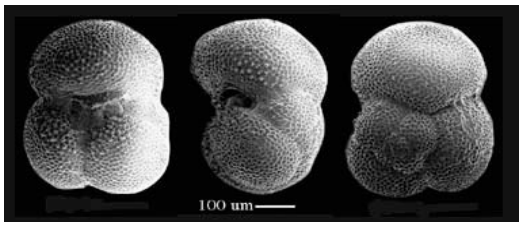
from P. Schlosser

Examples: Stable Isotope Applications in Oceanography

- ^{3}He to study deep ocean circulation in the Pacific
- ^{15}N to close the ocean N budget
- ^{18}O to determine freshwater balance in the Arctic Ocean
- ^{18}O as an indicator of the ice ages

$\delta^{18}O$ in Marine $CaCO_3$

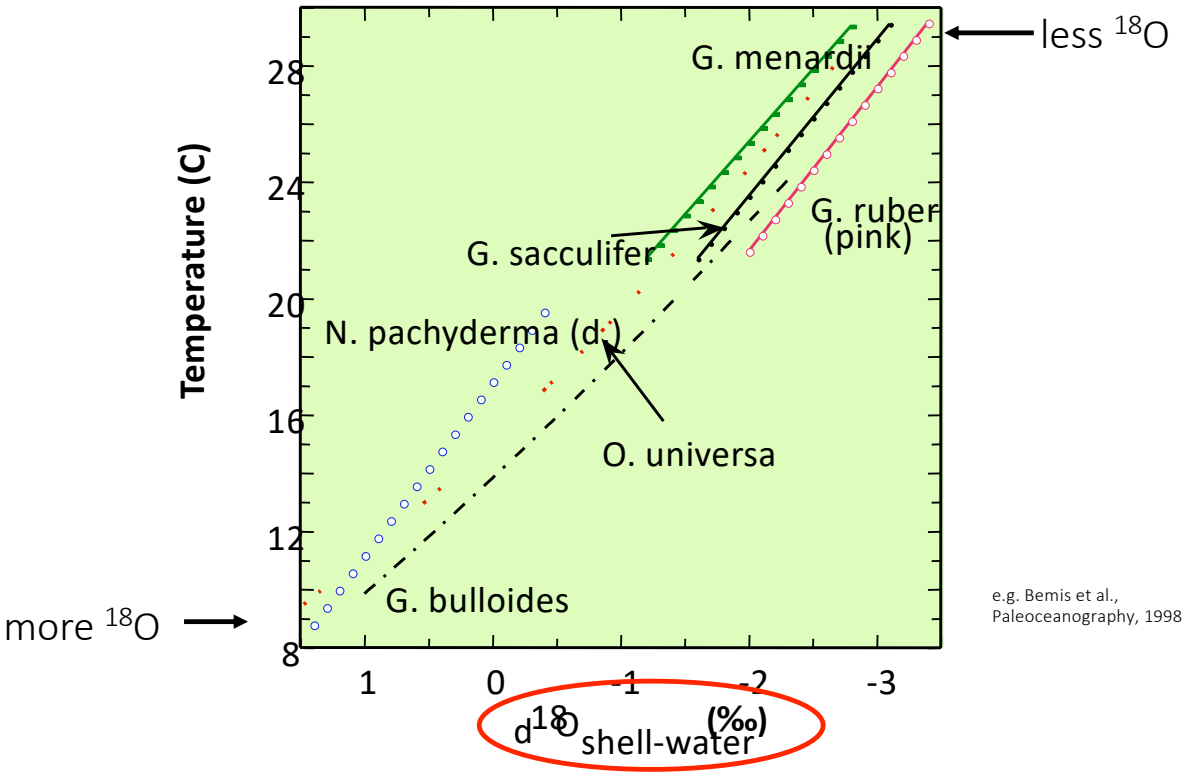




The $\delta^{18}O$ of the $CaCO_3$ is a function of:

1) Temp of seawater that foraminifera are growing in:
   - Warmer water → lighter $\delta^{18}O$ in $CaCO_3$
2) $\delta^{18}O$ of seawater that foraminifera are growing in:
   - Depends on latitude
   - Depends on sea level

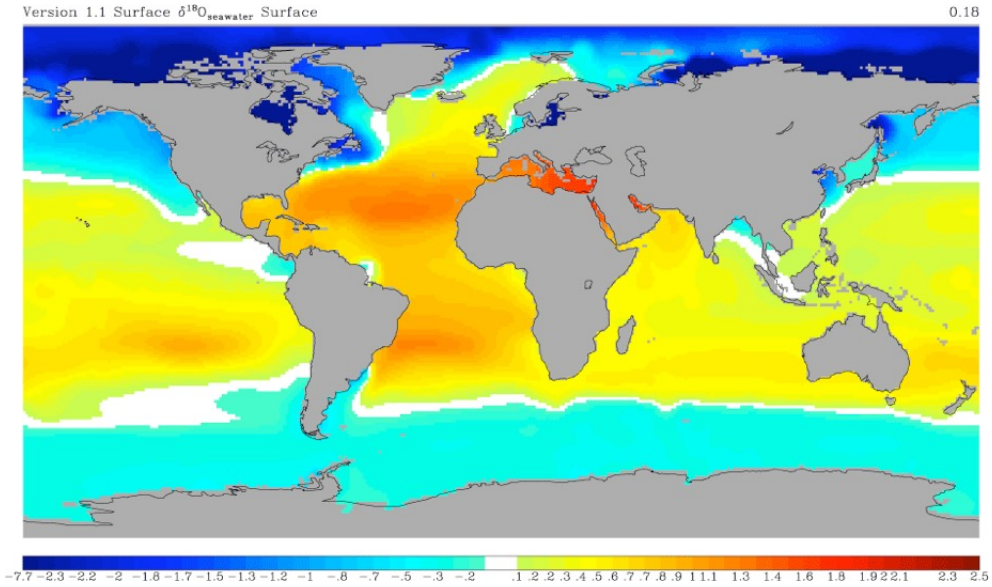
$\delta^{18}O$ Paleothermometer



e.g. Bemis et al., Paleoceanography, 1998

Temperature dependence of equilibrium fractionation between ^{16}O and ^{18}O during precipitation of $CaCO_3$

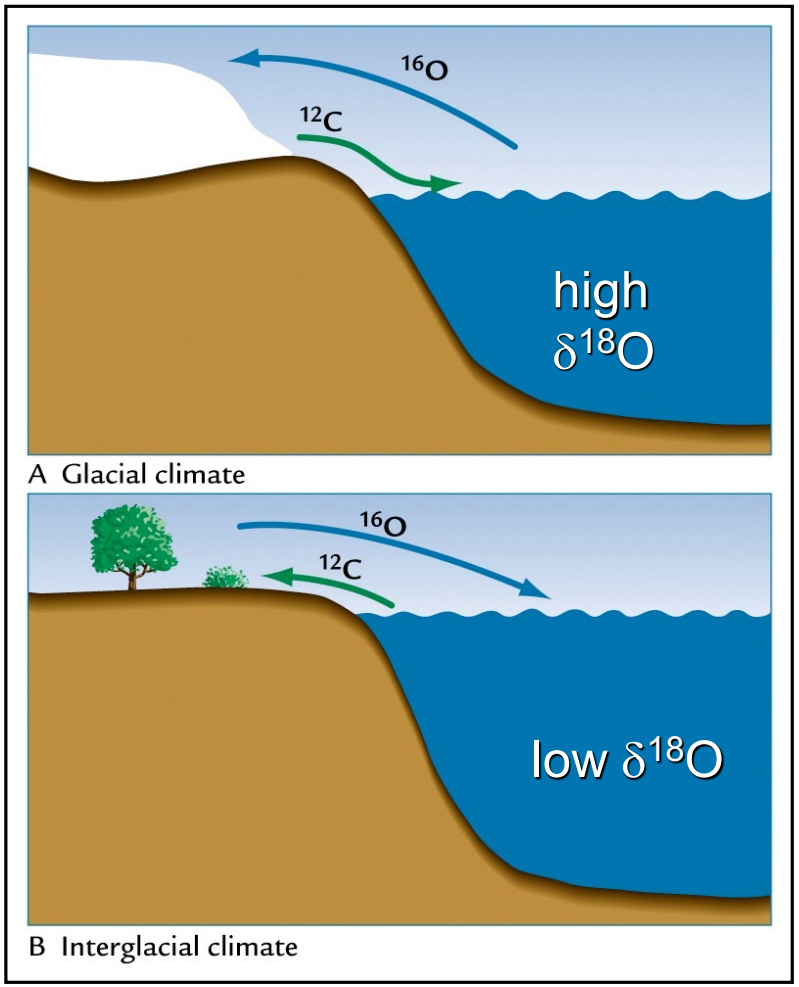
Gridded Surface Seawater $\delta^{18}O$



Note the higher $\delta^{18}O_{sw}$ in the evaporation belts and the lower $\delta^{18}O_{sw}$ in the high latitudes, which are dominated by excess precipitation.

Any $\delta^{18}O$-temperature relationship depends primarily on the $\delta^{18}O$ of the water from which the carbonate is precipitated.

http://data.giss.nasa.gov/o18data/



Changes in ice volume also influence $\delta^{18}O$ of the ocean

$\delta^{18}O$ in marine carbonates and paleotemperature records Vostok ice core

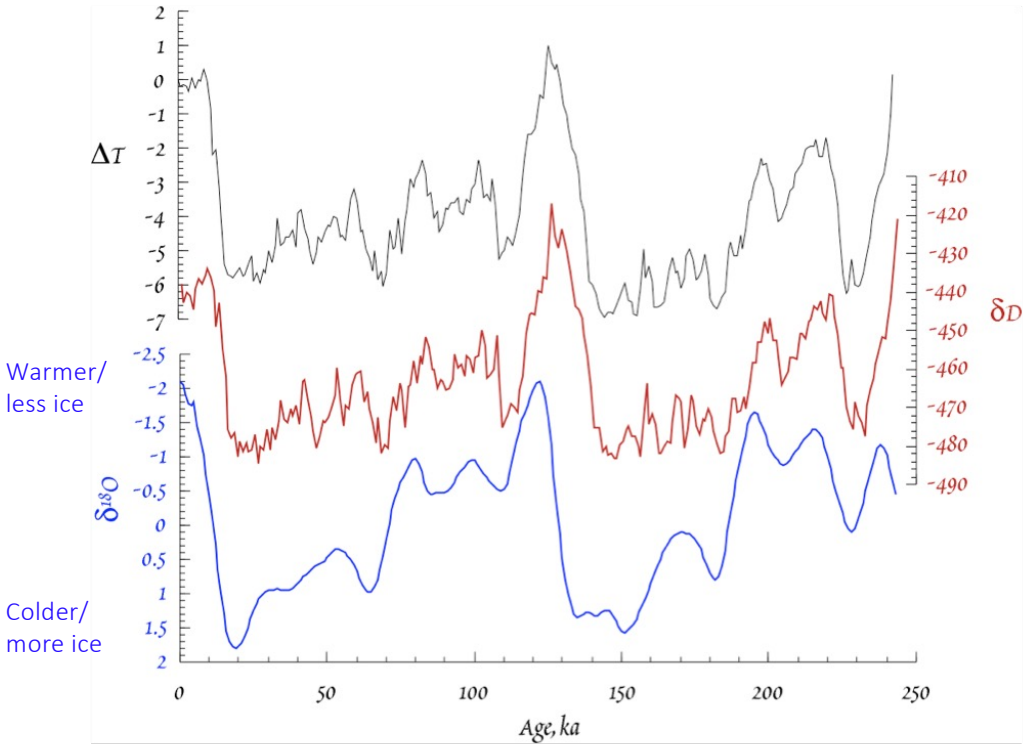


Figure 9.26. The lower curve shows smoothed $\delta^{18}O$ for marine carbonates (SPECMAP), the middle curve shows δD of ice in the Vostok ice core, and the upper curve the temperature calculated from δD at Vostok at the time of deposition of the ice relative to the present mean annual temperature. Vostok data is from Jouzel, et al., (1987, 1993, 1996).

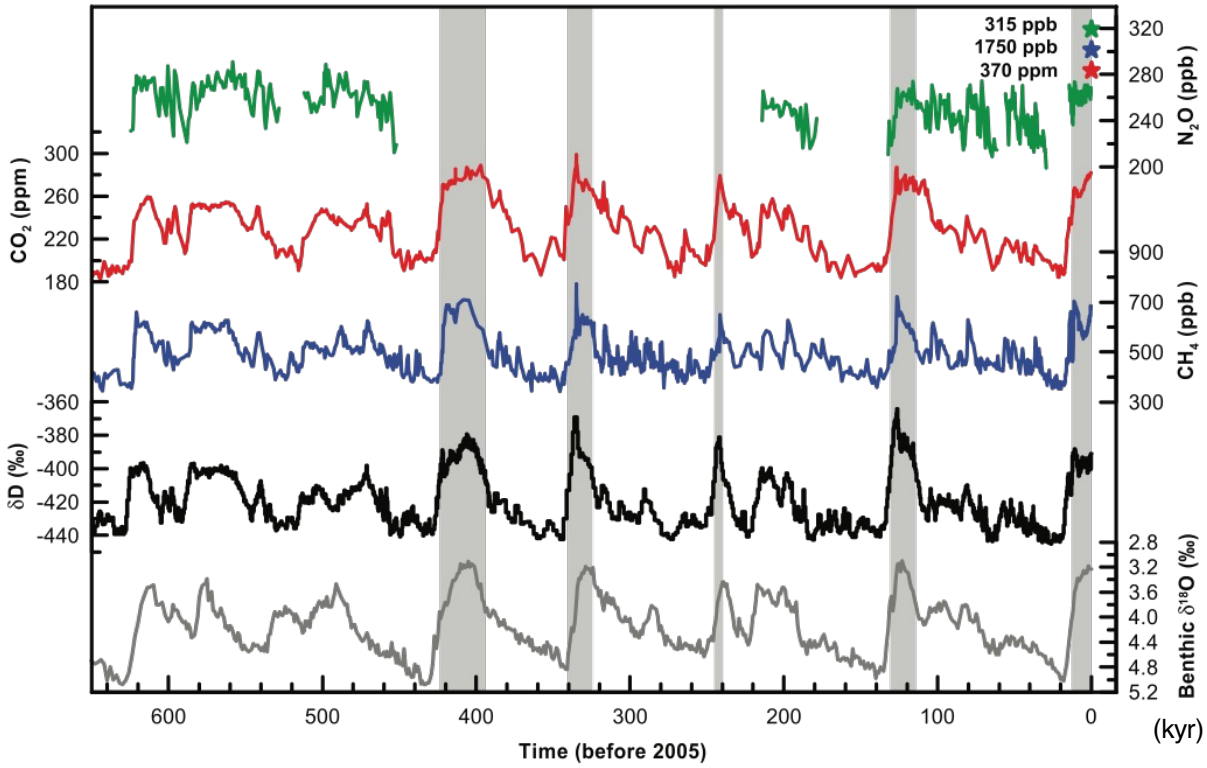


Figure 6.3. *Variations of deuterium (δD; black), a proxy for local temperature, and the atmospheric concentrations of the greenhouse gases CO_2 (red), CH_4 (blue), and nitrous oxide (N_2O; green) derived from air trapped within ice cores from Antarctica and from recent atmospheric measurements (Petit et al., 1999; Indermühle et al., 2000; EPICA community members, 2004; Spahni et al., 2005; Siegenthaler et al., 2005a,b). The shading indicates the last interglacial warm periods. Interglacial periods also existed prior to 450 ka, but these were apparently colder than the typical interglacials of the latest Quaternary. The length of the current interglacial is not unusual in the context of the last 650 kyr. The stack of 57 globally distributed benthic $\delta^{18}O$ marine records (dark grey), a proxy for global ice volume fluctuations (Lisiecki and Raymo, 2005), is displayed for comparison with the ice core data. Downward trends in the benthic $\delta^{18}O$ curve reflect increasing ice volumes on land. Note that the shaded vertical bars are based on the ice core age model (EPICA community members, 2004), and that the marine record is plotted on its original time scale based on tuning to the orbital parameters (Lisiecki and Raymo, 2005). The stars and labels indicate atmospheric concentrations at year 2000.*

IPCC Fourth Assessment Report, Working Group I Report "The Physical Science Basis", Chapter 6 Palaeoclimate