Lecture 1 overview

- Sources and sinks of material to the ocean
- Box models and residence times
- Major elements
- Biological and trace elements
- Ocean thermohaline circulation

Why cover stable isotopes?

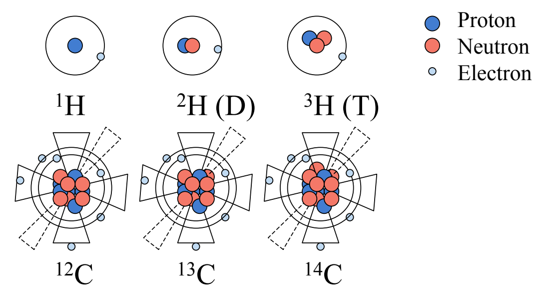
- Unique tracers of biogeochemical processes:
  - Trace source and sink processes important for the inventories of major nutrients and chemical constituents.
  - Record past changes in physical and biological processes affecting the ocean.

Lecture 2: Introduction to Stable Isotopes

- Definitions
- Measurement
- Theories and Models
- Applications in Marine Chemistry
  - Physical and chemical processes
  - Biological processes
  - Paleoceanography

Definitions

- Isotopes are atoms that contain the same number of protons but differ in the number of neutrons.



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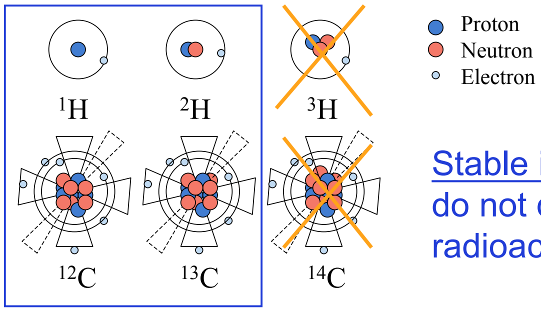

Stable isotopes do not decay radioactively

Definitions

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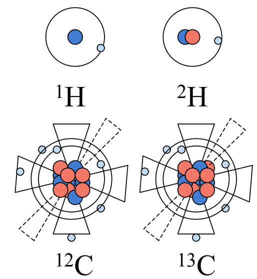


$\Delta m/m$

1.00

0.08

The difference in masses among stable isotopes is relatively larger for smaller mass atoms

Common Light Stable Isotopes

Element	Stable Isotopes	Average Abundance	Element	Stable Isotopes	Average Abundance
Hydrogen	^{1}H	99.985	Oxygen	^{16}O	99.762
	^{2}H (D)	0.015		^{17}O	0.038
Carbon	^{12}C	98.90		^{18}O	0.200
	^{13}C	1.10	Sulfur	^{32}S	95.02
Nitrogen	^{14}N	99.63		^{33}S	0.75
	^{15}N	0.37		^{34}S	4.21
				^{36}S	0.02

Isotope Ratios

- Isotope ratios can be measured more precisely than absolute abundances of isotopes.
- Generally, isotope ratios are reported as the ratio of a heavy (rare) isotope to a light (primary) isotope:
  - $^{13}R_{CO2} = {}^{13}CO_2/{}^{12}CO_2$
  - $^{15}R_{N2} = {}^{15}N_2/{}^{14}N_2$

Delta Notation

- Isotopic ratios expressed relative to a standard using delta notation: $\delta = [R_{sample}/R_{std} - 1]$
- R_{sample} is the isotopic ratio of a sample (e.g., $^{18}R_{sample} = {}^{18}O/{}^{16}O_{sample}$)
- R_{std} is the isotopic ratio of the standard, or reference material
- $R_{sample} < R_{std}$ gives negative δ value and is said to be *depleted*
- $R_{sample} > R_{std}$ gives positive δ value, said to be *enriched*

Example: For a sample with $^{18}O/^{16}O = 0.00198$

$$\delta^{18}O = [0.00198/0.00200 - 1] = -0.010$$

Delta values are often expressed in units of permil (‰) by multiplying by a factor of 1000.
In this example, $\delta^{18}O$ is -0.010 (unitless) or -10‰

Isotope Ratio Standards

International standards used for reporting isotopic values

Element	Standard	Abbrev.
H	Vienna Standard Mean Ocean Water	VSMOW
C	PeeDee Belemnite (carbonate)	PDB
N	Air Nitrogen	N_2(atm.)
O	Vienna Standard Mean Ocean Water	VSMOW
S	Triolite (FeS) from the Canyon Diablo meteorite	CDT

Lecture 2: Introduction to Stable Isotopes

- Definitions
- **Measurement**
- Theories and Models
- Applications in Marine Chemistry
  - Physical processes
  - Chemical processes
  - Biological processes
  - Paleoceanography

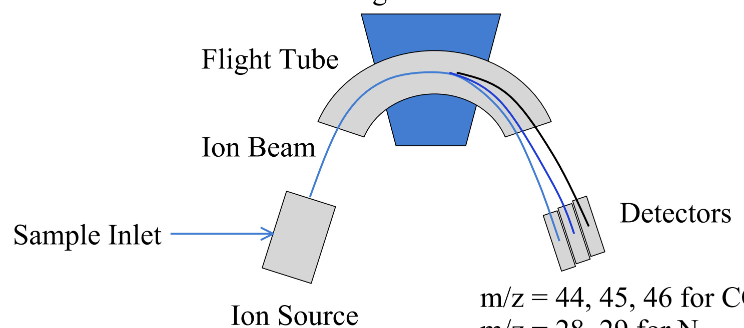
Measuring Isotopic Ratios

- Convert element of interest into a stable gas.
- Purify/separate gas analyte from contaminants (off-line or on-line)
- Measure isotopic ratios on an isotope ratio mass spectrometer (IRMS)

Measuring Isotopic Ratios

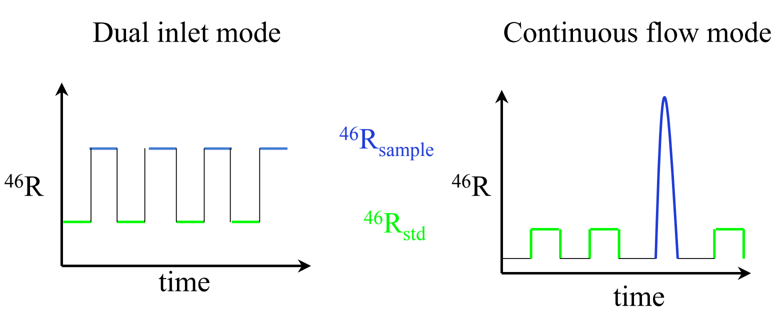
- Example 1: Carbon isotope ratio of calcite shells.
  - Shells ($CaCO_3$) + acid → CO_2
  - CO_2 → IRMS, measure m/z:
    - 44 (^{16}O-^{12}C-^{16}O)
    - 45 (^{16}O-^{13}C-^{16}O or ^{17}O-^{12}C-^{16}O or ^{16}O-^{12}C-^{17}O)
    - 46 (^{18}O-^{12}C-^{16}O or ^{16}O-^{12}C-^{18}O)
- Example 2: Nitrogen and Oxygen isotopic ratios of dissolved nitrate.
  - Dissolved nitrate + denitrifying bacteria → N_2O
  - N_2O →Purify from CO_2 → IRMS, measure m/z:
    - 44 (^{14}N-^{14}N-^{16}O)
    - 45 (^{15}N-^{14}N-^{16}O or ^{14}N-^{15}N-^{16}O or ^{14}N-^{14}N-^{17}O)
    - 46 (^{14}N-^{14}N-^{18}O)

Measuring Isotopic Ratios



m/z = 44, 45, 46 for CO_2, N_2O
m/z = 28, 29 for N_2
m/z = 32, 33, 34 for O_2

Measuring Isotopic Ratios



Lecture 2: Introduction to Stable Isotopes

- Definitions
- Measurement
- **Theories and Models**
- Applications in Marine Chemistry
  - Physical processes
  - Chemical processes
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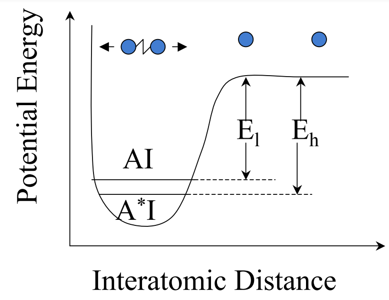
Isotopic Fractionation

- Two types of isotopic fractionation that cause changes in isotopic ratios
  - *Kinetic isotope fractionation*:
    - One isotope reacts, diffuses, or evaporates faster than the other.
    - Can be due to chemical, physical, or biological processes.
    - Usually, the lighter isotope reacts or diffuses faster.
    - Magnitude of isotope effect is temperature, reaction rate, and species dependent
  - *Equilibrium isotope fractionation*:
    - Exchange reactions in which a single atom is exchanged between 2 species (with isotopic preference).
    - Bidirectional (reversible) chemical reactions
    - Temperature dependent

Kinetic Isotope Fractionation



- In a diatomic molecule, substitution with a heavy isotope lowers the *ground state* vibrational energy and makes it marginally more difficult to break the bond

- Reactions of heavy isotopically substituted molecules are marginally slower than light isotopic molecules and "discrimination" against the heavy molecule leads to *kinetic isotope fractionation*:

$$AI \xrightarrow{k_l} A + I$$
$$A^*I \xrightarrow{k_h} A + {}^*I$$

"Fractionation factor": $\alpha_k = k_l/k_h > 1$

"Isotope effect": $\varepsilon_k = (\alpha_k\text{-}1) > 0$

Kinetic Isotope Fractionation

$$AI \xrightarrow{k_l} A + I$$
$$A^*I \xrightarrow{k_h} A + {}^*I$$

- ${}^*I/I_{product} < {}^*I/I_{substrate}$
- Consumption of substrate leaves behind substrate enriched in the heavy isotope, and becomes increasingly enriched as the amount of substrate that is consumed increases
- In turn, the product also becomes proportionately heavier.
- The greater the isotope effect, or isotopic discrimination, the more dramatic the enrichment for the same level of substrate consumption.

Kinetic Isotope Fractionation Models

- Closed system
  - Unidirectional
  - Constant isotope effect
  - No replenishment of reactant
  - No removal of product
- Open system
  - Addition/replenishment of reactant and/or removal of product
  - Unidirectional or bidirectional
  - Constant isotope effect
  - Doesn't have to be at steady state

Kinetic Isotope Fractionation

In closed systems: substrate --> product

$\delta_s \approx \delta_{s0} - \varepsilon * \ln(f)$

ε is the isotope effect (> 0 when $k_l > k_h$)
f is the fraction of substrate remaining ($[S]/[S]_0$)

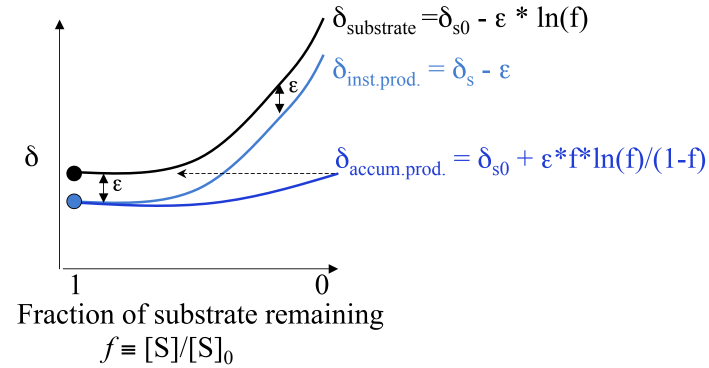
$\delta_{inst.prod.} \approx \delta_s - \varepsilon$

The accumulated product follows from mass balance:

$\delta_{accum.prod} * (1-f) + \delta_s * f \approx \delta_{s0}$
$\delta_{accum.prod.} \approx \delta_{s0} + \varepsilon * f * \ln(f)/(1-f)$

Kinetic Isotope Fractionation

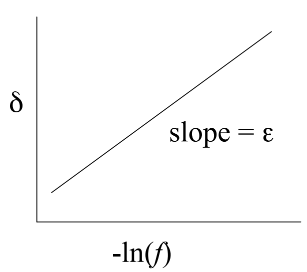
In closed systems: substrate--> product



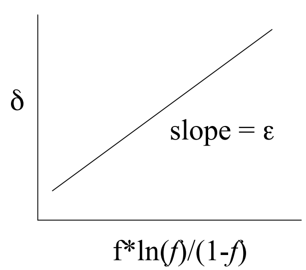
Kinetic Isotope Fractionation

Calculate ε from a closed system reaction by measuring the change in either $\delta_{substrate}$ or $\delta_{accum.prod}$ as a function of f.

$\delta_{substrate} = \delta_{s0} - \varepsilon * \ln(f)$

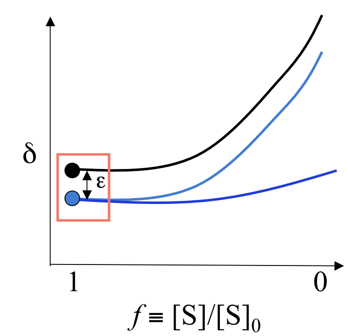


$\delta_{accum.prod.} = \delta_{s0} + \varepsilon * f * \ln(f)/(1-f)$



Kinetic Isotope Fractionation

In cases where very little of the substrate has been consumed ($f \approx 1$): $\varepsilon = \delta_{substrate} - \delta_{prod}$



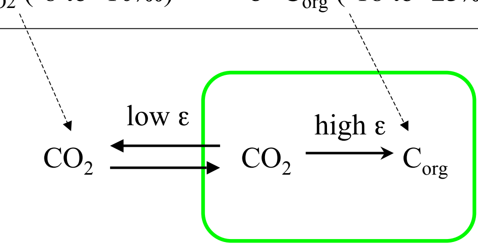
Kinetic Isotope Fractionation

Substrate		Product
CO_2	$\xrightarrow[\varepsilon \approx 20‰]{\text{photosynthesis}}$	C_{org}
$\delta^{13}C_{CO2}$ (-8 to -10‰)		$\delta^{13}C_{org}$ (-18 to -23‰)
NO_3^-	$\xrightarrow[\varepsilon \approx 5\text{-}10‰]{\text{nitrate assimilation}}$	N_{org}
$\delta^{15}N_{NO3}$ (+5‰)		$\delta^{15}N_{org}$ (-1 to +5 ‰)
SO_4^{-2}	$\xrightarrow[\varepsilon \approx 2\text{-}42‰]{\text{sulfate reduction}}$	S^{-2}
$\delta^{34}S_{SO4}$ (+20‰)		$\delta^{34}S_{FeS2}$ (-45‰ to +20 ‰)

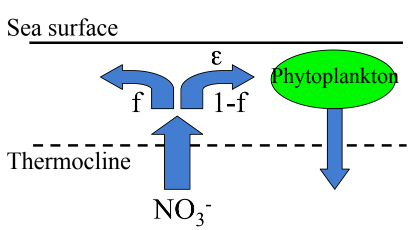
Kinetic Isotope Fractionation

$CO_2 \xrightarrow[\varepsilon \approx 20‰]{\text{photosynthesis}} C_{org}$

$\delta^{13}C_{CO2}$ (-8 to -10‰) $\delta^{13}C_{org}$ (-18 to -23‰)

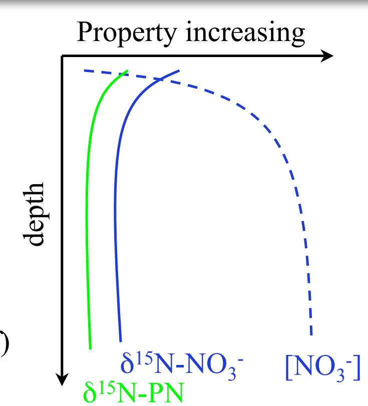


Nitrate Uptake by Phytoplankton

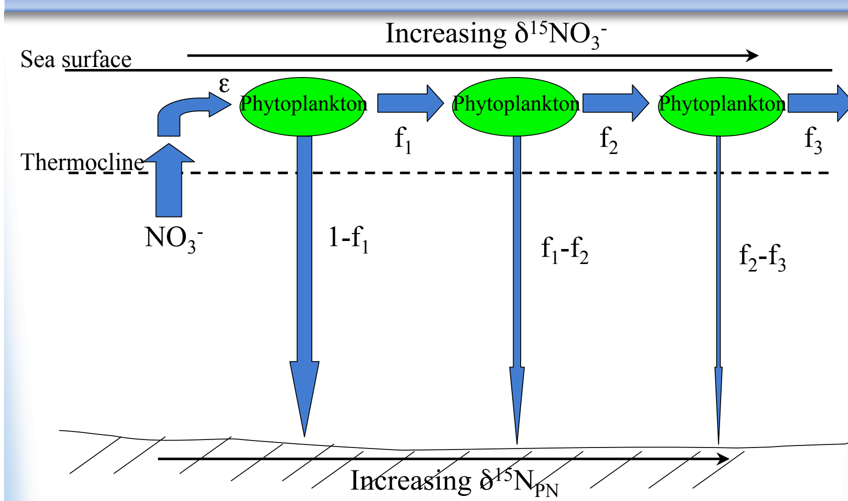


$$\delta^{15}NO_{3,surf} = \delta^{15}NO_{3,deep} - \varepsilon * \ln(f)$$

$$\delta^{15}N_{PN} = \delta^{15}NO_{3,deep} + \varepsilon * f * \ln(f)/(1-f)$$



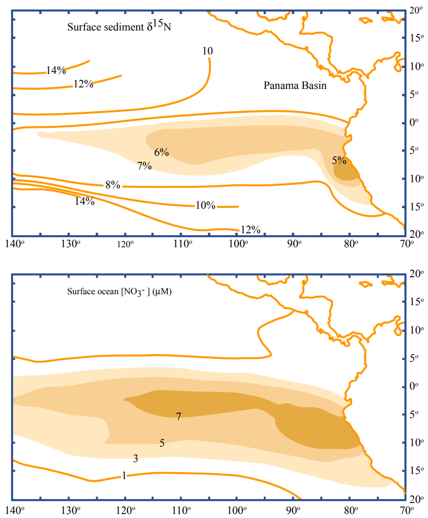
Nitrate Uptake by Phytoplankton



Nitrate Uptake by Phytoplankton

Observed surface $[NO_3^-]$ gradient corresponds to sediment $\delta^{15}N$-PN gradient in expected direction.

Figure by MIT OCW.



Spatial distribution of surface (Holocene) sediment $\delta^{15}N$ values compared with surface ocean $[NO_3^-]$ (b; ref.13) in the eastern tropical pacific Ocean. $\delta^{15}N$ values are from this study (available via e-mail from J.W.F. at jfarrell@brook.edu) and ref. 7. Bulk sediment samples were prepared for $\delta^{15}N$ analysis by freeze-drying and homogenizing by grinding. Sediments were combusted in an online Fisons NA 1500 element analyser and the evolved N_2 was passed to a VG PRISM isotope-ratio mass spectrometer in a continuous flow of He. Results are reported in the δ notation, $\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1]$ per mil, relative to atmospheric N_2 and the measurement precision is better than ±0.3‰. We have assumed that the isotopic composition of the total nitrogen primarily reflects that of marine organic matter, rather than inorganic nitrogen (ammonium) within clay minerals and adsorbed atmospheric N_2. Initial results from Panama basin sediments indicate that inorganic nitrogen constitutes a minor proportion of the total. As drawn, the $\delta^{15}N$ isopleths violate 5% of samples by >0.3‰.

Kinetic Isotope Fractionation Models

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Open System: Steady State Model

Determine fluxes to and from a system based on mass and isotope budgets, e.g. marine nitrogen budget:

Inputs of N to ocean (nitrogen fixation, rivers, atmospheric deposition)

$\sum M_{in}$
$\sum M_{in} * \delta_{in}$

Deep NO_3^-
M_{NO3}
δ_{NO3}

Loss of N from ocean (denitrification, burial)

$\sum M_{out}$
$\sum M_{out} * \delta_{out}$

Open System: Steady State Model

Input of N (nitrogen fixation, rivers, atmospheric deposition)

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Deep NO_3^-
M_{NO3}
δ_{NO3}

Loss of N (denitrification, burial)

$\sum M_{out}$
$\sum M_{out} * \delta_{out}$

Mass Balance: $\sum M_{in} = \sum M_{out}$

Isotope Balance: $\sum M_{in} * \delta_{in} = \sum M_{out} * \delta_{out} = \sum M_{out} * (\delta_{NO3} - \varepsilon_{out})$

Open System: Steady State Model

Mass Balance: $\sum M_{in} = \sum M_{out}$

Isotope Balance: $\sum M_{in} * \delta_{in} = \sum M_{out} * \delta_{out} = \sum M_{out} * (\delta_{NO3} - \varepsilon_{out})$

In: Nitrogen Fixation (125 Tg N/yr, $\delta^{15}N$ = 0‰)
Out: Sedimentary denitrification (? Tg N/yr, $^{15}\varepsilon$ = 0‰)
Water column denitrification (80 Tg N/yr, $^{15}\varepsilon$ = 25‰)

$M_{N2fix} * \delta_{N2fix} = M_{sd} * (\delta_{NO3} - \varepsilon_{sd}) + M_{wd} * (\delta_{NO3} - \varepsilon_{wd})$

(125 Tg N/yr)*(0‰) = (? Tg N/yr)*(5‰ - 0‰) + (80 Tg N/yr)*(5‰ - 25‰)

0 Tg N/yr ‰ = (5‰ * Tg N/yr SD) -1600 Tg N/yr ‰ =>
320 Tg N/yr (Sed. Denit)!

Isotopic Fractionation

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  - *Equilibrium isotope fractionation*:
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Equilibrium Isotope Effects

Example: $CaCO_3$ equilibration with surface seawater

Foraminiferal shell $\leftrightarrow$ Surface seawater

$$CaC^{16}O_3 + H_2{}^{18}O \rightleftharpoons CaC^{16}O_2{}^{18}O + H_2{}^{16}O$$

Equilibrium Isotope Effects

Example: $CaCO_3$ equilibration with surface seawater

Foraminiferal shell $\leftrightarrow$ Surface seawater

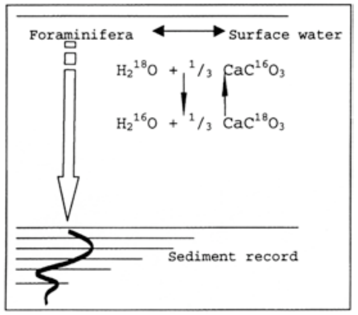
$$CaC^{16}O_3 + H_2{}^{18}O \rightleftharpoons CaC^{16}O_2{}^{18}O + H_2{}^{16}O$$

$$K = \frac{[CaC^{16}O_2{}^{18}O]*[H_2{}^{16}O]}{[CaC^{16}O_3]*[H_2{}^{18}O]} = \frac{[CaC^{16}O_2{}^{18}O]/[CaC^{16}O_3]}{[H_2{}^{18}O]/[[H_2{}^{16}O]}$$

$= R_{CaCO3}/R_{H2O}$

$= \alpha_{equilib}$ (equilibrium fractionation factor) ~ 1.0286 at 25°C

Temperature Dependence



This system is used as a rough paleothermometer:

- Calcite is preserved in marine sediments.
- $\alpha_{equilib}$ varies as a function of temperature (higher value at lower T)

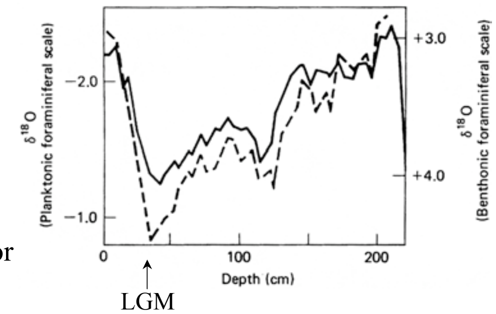
From the dependence of α_{eq} on T:

$$T\,(^\circ C) = 16.9 - 4.2*(\delta^{18}O_{CaCO3} - \delta^{18}O_{H2O}) + 0.13*(\delta^{18}O_{CaCO3} - \delta^{18}O_{H2O})^2$$

Sedimentary Record of $\delta^{18}O_{CaCO3}$

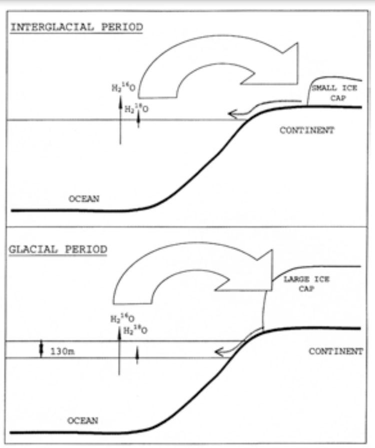
Increasing $\delta^{18}O$-$CaCO_3$ Values

Increasing $\delta^{18}O$-H_2O and/or Increasing α_{eq}



Changing $\delta^{18}O_{CaCO3}$ can reflect changing $\alpha(T)$ but also need to account for changing $\delta^{18}O_{H2O}$…

Ice Volume Effect on $\delta^{18}O_{H2O}$



- Water with low $\delta^{18}O$ is stored in ice caps during the glacial periods, leaving the residual ocean water enriched in ^{18}O
- Approx. 2/3 of the change in planktonic $\delta^{18}O_{CaCO3}$ is due to the increase in $\delta^{18}O_{H2O}$ during glacial periods, the rest is due to lowered sea surface temperature
- Additional caveats due to changes in salinity and "vital" effects, or non-equilibrium nature of foram shells

Summary

- Stable isotopic ratios vary widely in nature
- These variations record the results of chemical, physical, and biological processes
- At equilibrium, isotopes are unequally distributed among molecules or phases and the distribution is determined by thermodynamics
- Kinetic isotope effects arise from slight differences in the rates of reaction involving isotopically substituted molecules
- Because of discrimination against heavy molecules, substrates become enriched in heavy isotopes as a reaction proceeds, and with constant offset (ε) the products also become more enriched