

Introduction to Stable Isotopes

DM Baker

fundamentals

- What is an isotope?
- How do we talk about isotopes? (units and nomenclature)
- Isotopes in natural science (fractionation & mixing)

What are stable isotopes?

- iso = same
 - topos = place

Periodic Table of the Elements																	
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Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca
Na	Mg	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr
Cs	Ba	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Fr	Ra	57-71*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Rf	Ds	89-103*	Rf	Db	Sg	Bh	Hs	Mt	Ds	Cn	Uut	F1	Uup	Lv	Uus		
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			

Review terms

Electron → Tiny subatomic particle with negative charge. Mass $\sim 0.91 \times 10^{-30}$ kg

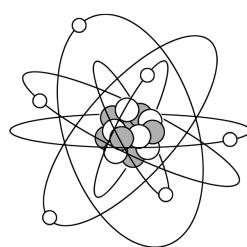
Proton → Subatomic particle with a positive charge. Mass $\sim 1.67 \times 10^{-27}$ kg

Neutron (N) —————> Subatomic particle with no charge. Similar mass to protons

Atomic Number (Z) ————— Integer that expresses the number of protons in nucleus

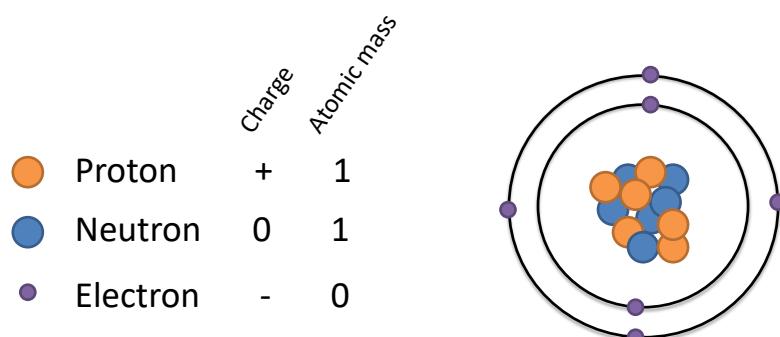
Mass Number (A) —————→ The sum of protons and neutrons in a nucleus: $A = N + Z$

Mass Number A C
 Atomic Number Z 12.011
 Atomic Weight



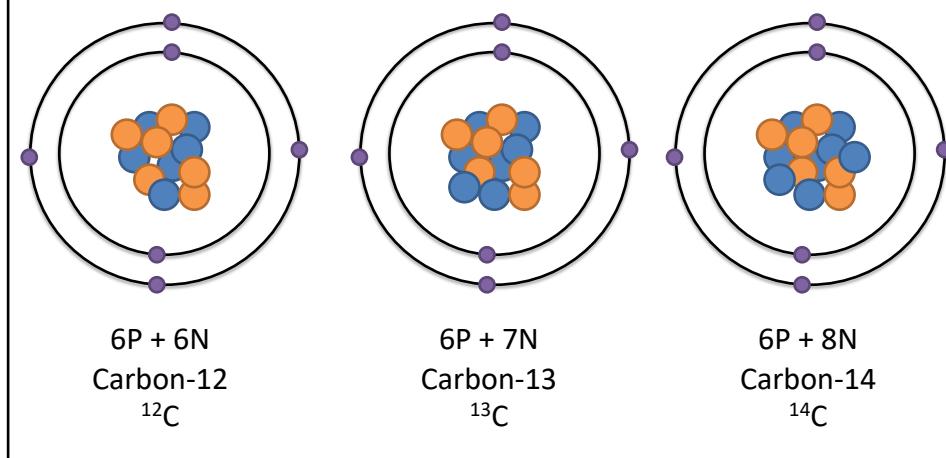
What are stable isotopes?

For example: carbon

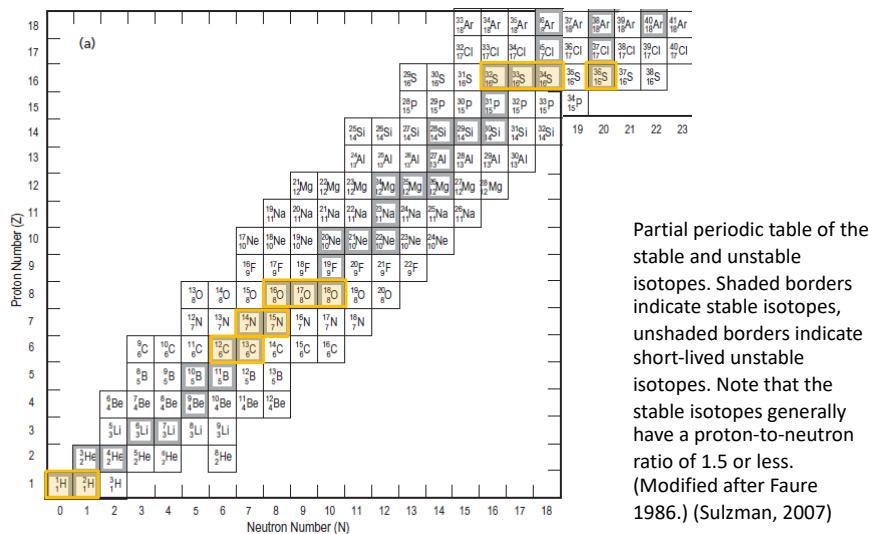


What are stable isotopes?

For example: carbon



What are stable isotopes?



What are stable isotopes?

- Isotope person: one stable isotope has much higher abundance than the other(s)

-Eitaro Wada

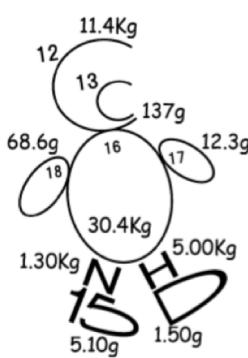


Fig. 1. Isotope content of a human being, the so-called "Isotope Person". In case his body weight is 50.0 kg, He has the heavier isotopes of 225 g within his body.

New terms

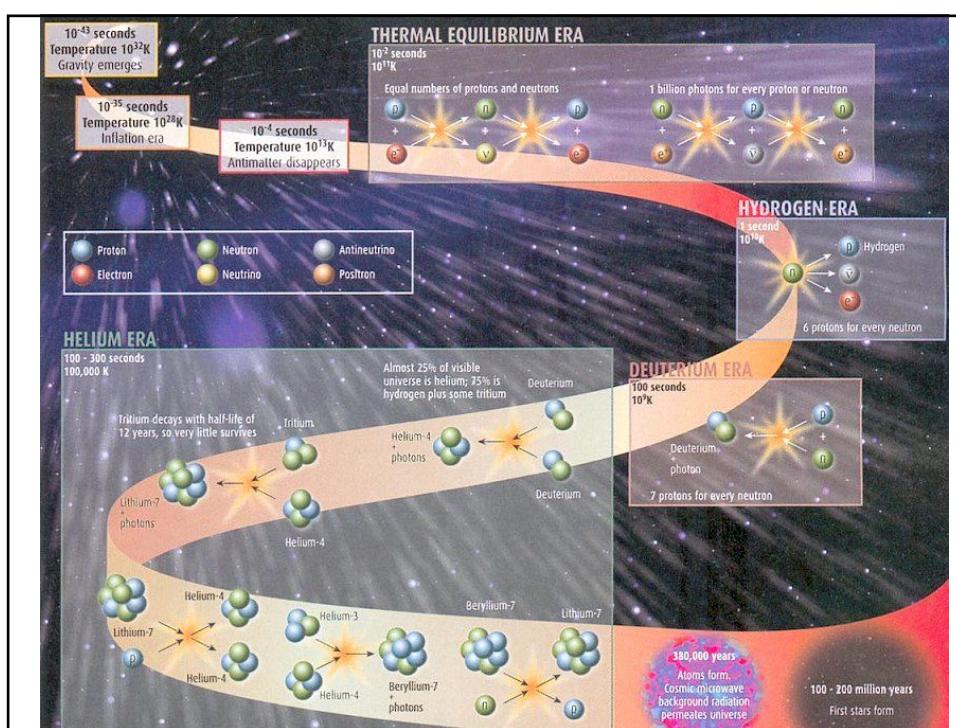
Isotopologues: Isotopic species of the same molecule

- Carbon dioxide (CO_2) has twelve isotopologues:
 $^{12}\text{C}^{16}\text{O}^{16}\text{O}$, $^{12}\text{C}^{16}\text{O}^{17}\text{O}$, $^{12}\text{C}^{16}\text{O}^{18}\text{O}$, $^{12}\text{C}^{17}\text{O}^{17}\text{O}$, $^{12}\text{C}^{17}\text{O}^{18}\text{O}$, $^{12}\text{C}^{18}\text{O}^{18}\text{O}$,
 $^{13}\text{C}^{16}\text{O}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}^{17}\text{O}$, $^{13}\text{C}^{16}\text{O}^{18}\text{O}$, $^{13}\text{C}^{17}\text{O}^{17}\text{O}$, $^{13}\text{C}^{17}\text{O}^{18}\text{O}$, $^{13}\text{C}^{18}\text{O}^{18}\text{O}$
- CO_2 is a symmetric molecule; $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ and $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ are not distinct isotopologues.

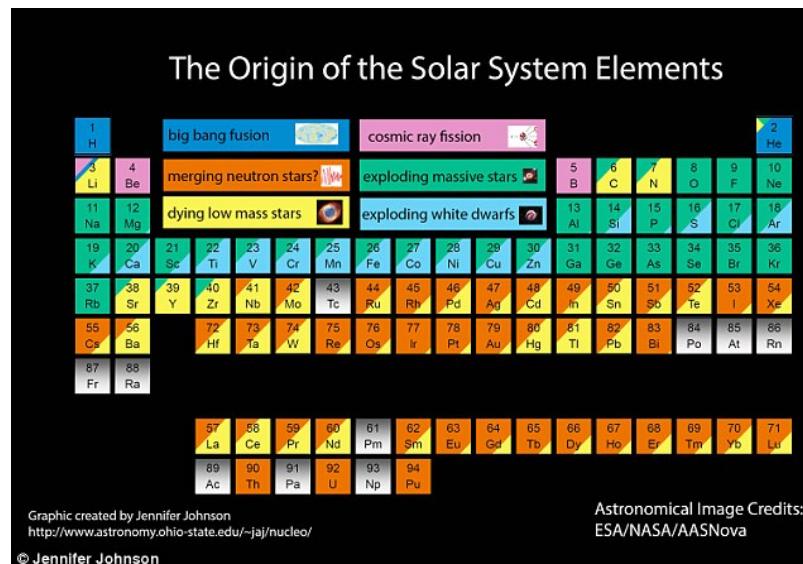


Isotopomers: Isotopologues that differ from one another only in the position of the isotopic elements

- N_2O is **not** a symmetric molecule. Thus, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ are isotopomers of N_2O

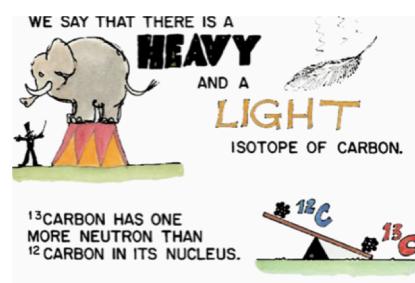


Where did they come from?



Isotope terminology

- Heavy vs. light
- Enriched vs. depleted in ^{13}C , ^{15}N , ^{18}O , ...
- Be careful!



Isotope terminology

$$\text{Isotope ratio: } R(^iE/^jE)_P = \frac{N(^iE)_P}{N(^jE)_P}$$

Where $N(^iE)_P$ and $N(^jE)_P$ are the number of each isotope, iE and jE , of chemical element E in substance P.

Superscripts i and j denote mass numbers of a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively

Rapid Commun. Mass Spectrom. 2011, 25, 2538-2560
(wileyonlinelibrary.com) DOI: 10.1002/rcm.5129

Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results^{t, ‡}

Tyler B. Coplen*

Isotope terminology

$$\text{Isotope ratio: } R(^iE/^jE)_P = \frac{N(^iE)_P}{N(^jE)_P}$$

Examples of isotope pairs:

$^2H/^1H$	$^{18}O/^{16}O$	$^{36}S/^{32}S$	$^{56}Fe/^{54}Fe$	$^{97}Mo/^{95}Mo$
$^7Li/^6Li$	$^{26}Mg/^{24}Mg$	$^{37}Cl/^{35}Cl$	$^{57}Fe/^{54}Fe$	$^{98}Mo/^{95}Mo$
$^{11}B/^{10}B$	$^{29}Si/^{28}Si$	$^{42}Ca/^{40}Ca$	$^{65}Cu/^{63}Cu$	$^{110}Pd/^{104}Pd$
$^{13}C/^{12}C$	$^{30}Si/^{28}Si$	$^{44}Ca/^{40}Ca$	$^{66}Zn/^{64}Zn$	$^{130}Te/^{122}Te$
$^{15}N/^{14}N$	$^{33}S/^{32}S$	$^{53}Cr/^{52}Cr$	$^{82}Se/^{76}Se$	$^{205}Tl/^{203}Tl$
$^{17}O/^{16}O$	$^{34}S/^{32}S$	$^{54}Cr/^{52}Cr$	$^{88}Sr/^{86}Sr$	

Isotope terminology

Isotope ratio: $R(^iE/^jE)_P = \frac{N(^iE)_P}{N(^jE)_P}$

Natural abundance: $^{13}R = \frac{^{13}C}{^{12}C} = \frac{1.108}{98.892} = 0.011204$

Sample 1: $^{13}R = 0.010959$

Sample 2: $^{13}R = 0.011043$

Isotope terminology

relative difference of isotope ratios (δ)

= isotope delta

$$\begin{aligned}\delta^iE_P &= \delta^{i/j}E_P = \frac{R(^iE/^jE)_P - R(^iE/^jE)_{\text{std}}}{R(^iE/^jE)_{\text{std}}} \\ &= \frac{\frac{N(^iE)_P}{N(^jE)_P} - \frac{N(^iE)_{\text{std}}}{N(^jE)_{\text{std}}}}{\frac{N(^iE)_{\text{std}}}{N(^jE)_{\text{std}}}}\end{aligned}$$

$$\delta^iE_P = \frac{R(^iE/^jE)_P}{R(^iE/^jE)_{\text{std}}} - 1 = \frac{N(^iE)_P/N(^jE)_P}{N(^iE)_{\text{std}}/N(^jE)_{\text{std}}} - 1$$

(Coplen 2011)

where $N(^iE)_P$ and $N(^jE)_P$ are the numbers of the two isotopes iE and jE of chemical element E in specimen P, $R(^iE/^jE)_P$ is $N(^iE)_P / N(^jE)_P$ in specimen P, and equivalent parameters follow for the international measurement standard, 'std'.

Superscripts i and j should denote mass numbers of a heavier and a lighter isotope, respectively

Isotope terminology

relative difference of isotope ratios (δ)
= isotope delta

$$\delta^i E_p = \frac{R(iE/jE)_p}{R(iE/jE)_{std}} - 1$$

$$\delta^{13}C_{sample} = \frac{^{13}R_{sample}}{^{13}R_{std}} - 1$$

	^{13}R
Natural abundance	0.011204
Sample 1	0.010959
Sample 2	0.011043

Isotope standards

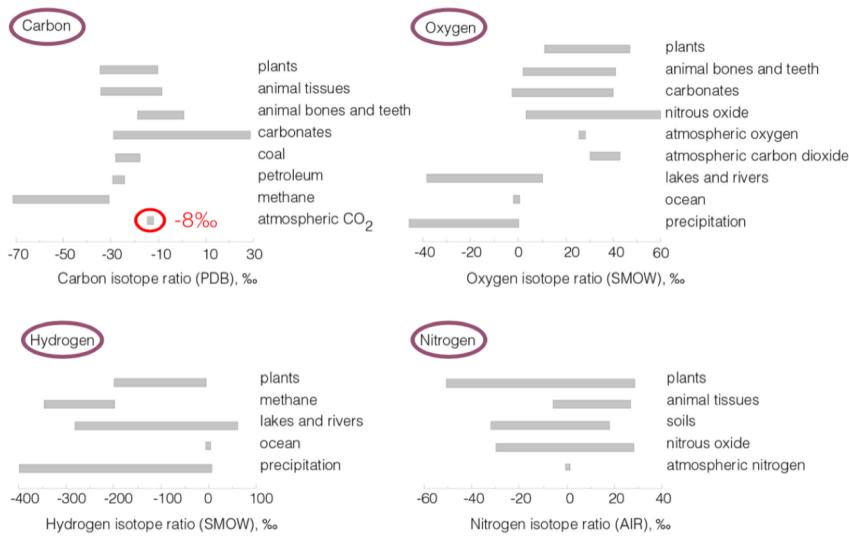
Internationally accepted isotope standards and their isotope ratios:

Acronym	Standard Name	Isotopes	$R_{heavy/Light}$
V-SMOW	Vienna Standard Mean Ocean Water	$^2H/^1H$	0.00015576
V-SMOW	Vienna Standard Mean Ocean Water	$^{18}O/^16O$	0.00200520
V-PDB	Vienna Pee Dee Belemnite	$^{13}C/^12C$	0.0112372
V-PDB	Vienna Pee Dee Belemnite	$^{18}O/^16O$	0.0020672
Air	Atmospheric Air	$^{15}N/^14N$	0.0036765
Air	Atmospheric Air	$^3He/^4He$	1.38×10^{-6}
CDT	Canyon Diablo Troilite	$^{34}S/^32S$	0.04500451

Notes on delta

1. The δ units are **not** the same as molarity or atom percent notation, but are **RATIOS** ($^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$ or $^{2}\text{H}/^{1}\text{H}$).
 - Thus, δ units must be used only for comparison.
2. Because δ values are measured relative to a standard, they can often be negative: for example $\delta^{13}\text{C}$ values in organic samples typically range from -40‰ to -6‰
3. The δ units must be on exactly the same scale to be comparable. (e.g., V-SMOW or V-PDB for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$)
4. Many mathematical calculations should be made by converting δ units to a concentration unit (e.g., atom percent)

Ranges of common isotopes

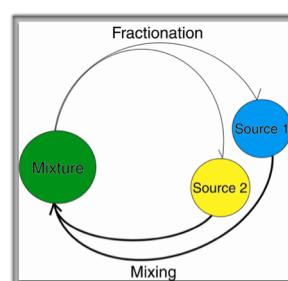


Controls on isotopic composition

- Mixing different isotope sources
- Biogeochemical processes

Mixing of sources

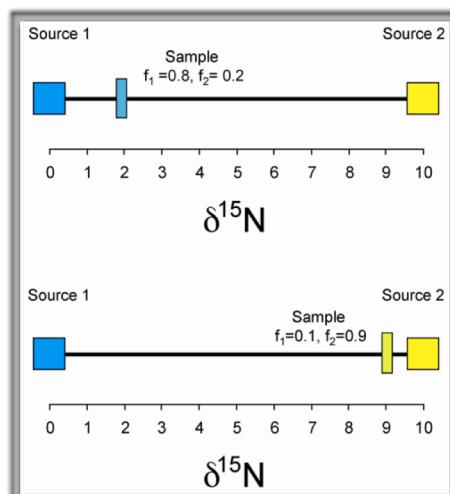
- Conservation of mass



$$\delta^{13}\text{C}_{mix} = f_a \delta^{13}\text{C}_a + f_b \delta^{13}\text{C}_b$$

With f the fraction of source a or b

Mixing of sources



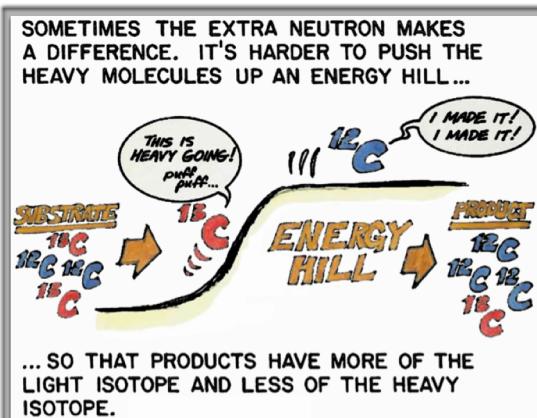
- Mixing=weighted average
- 1 isotope => 2 sources

Controls on isotopic composition

Biogeochemical processes:

- Mass dependent fractionation: kinetic
- Isotope exchange reactions: equilibrium

Isotope effects



Different mass
 ↓
 Different velocity + different bond strength
 ↓
 Different physical behaviour
 ↓
 Fractionation

fractionation

1. Isotopes of the same element undergo the same chemical reactions
 - Because isotopes have same Z (protons) and e (electrons)

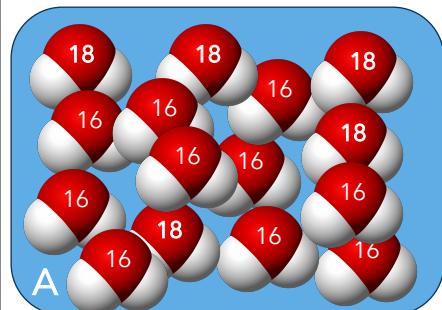


2. But, isotopes do have different thermodynamic properties due to their different masses.
 - Some important properties include: melting point, vapor pressure, diffusion coefficient, and equilibrium and kinetic rate constants of each isotope
3. Thus, different isotopes react at different rates in chemical reactions



4. This leads to isotopic separation/sorting or fractionation.

Isotopic Fractionation: Lighter Goes Faster

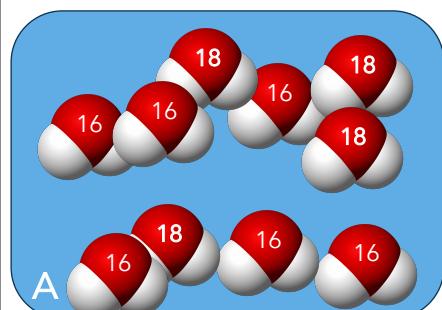


$$\frac{^{18}\text{O}}{^{16}\text{O}} = \frac{5}{15} \longrightarrow \frac{^{18}\text{O}}{^{16}\text{O}} = \frac{4}{10}$$

$$\frac{^{18}\text{O}}{^{16}\text{O}} = \frac{1}{5}$$

Process that occurs during chemical reactions resulting in abundance of heavy isotopes in the **reactant (A)** being different from the abundances of the heavy isotopes in the **product (B)**

Isotopic Fractionation: Expressing the Difference



Fractionation factor in terms of
R = mols of heavy/light

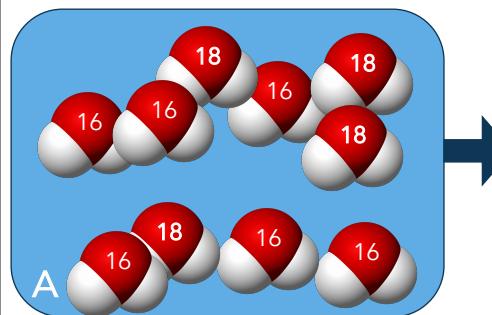
$$\alpha_{A-B} = \frac{R_A}{R_B}$$

Fractionation factor in
terms of delta notation

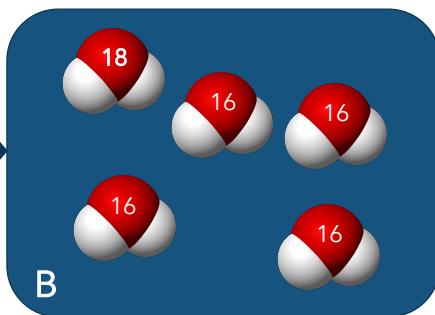
$$\alpha_{A-B} = \frac{(1000 + \delta_A)}{(1000 + \delta_B)}$$

α is the isotopic fractionation factor

Isotopic Fractionation: Expressing the Difference



Isotopic Enrichment



Isotopic Discrimination: Big Delta

$$\varepsilon_{AB} (\text{‰}) = (\alpha - 1) \cdot 1000$$

$$\Delta_{A-B} (\text{‰}) = \delta_A - \delta_B$$

Types of Fractionation

Exchange – Equilibrium (Geologists)

- Complete back-reactions occur.
- Product/reactant offset by constant fractionation factor (α)

Transport or Diffusive – Non-Equilibrium (Biologists and Geologists)

- Kinetic fractionation dealing w/ flux rather than chemical reaction.
- Incomplete back-flux is the rule.

Kinetic – Non-Equilibrium (Biologists)

- Incomplete back-reactions or none occur.
- Product and reactant δ values can evolve in concert (closed system), or product composition determines reactant composition (open system).

Equilibrium isotope effects

The net sum of two opposing kinetic isotope effects
in an exchange reaction

$$\text{Fractionation factor: } \alpha_{eq} = \frac{R_{heavy}}{R_{light}}$$

$$\text{Isotope enrichment: } \varepsilon = (\alpha - 1) * 1000$$

- Often dependent on temperature
- Usually, heavy isotopes concentrate where the bond is strongest

Kinetic (non-equilibrium) isotope effects

Different reaction rates k for heavy and light isotopes, e.g. ^{12}k and ^{13}k for C.

$$\text{Fractionation factor: } \alpha = \frac{^{light}k}{^{heavy}k}$$

$$\text{Kinetic isotope effect: } \varepsilon = (\alpha - 1) * 1000$$

- Most biological reactions
- No or weak dependence on temperature

Different models

Rayleigh model

- Closed system: a constant isotope effect and if the reactant and product N pools are neither replenished nor lost from the system during the transformation

$$\delta^{15}\text{N}_{\text{reactant}} = \delta^{15}\text{N}_{\text{initial}} - \varepsilon \{\ln(f)\}$$

$$\delta^{15}\text{N}_{\text{instantaneous}} = \delta^{15}\text{N}_{\text{reactant}} - \varepsilon$$

$$\delta^{15}\text{N}_{\text{integrated}} = \delta^{15}\text{N}_{\text{initial}} + \varepsilon \{f/(1-f)\} \ln(f)$$

Steady state model

- Open system: reactant N is continuously supplied and partially consumed, with residual reactant N being exported at a steady-state rate

$$\delta^{15}\text{N}_{\text{reactant}} = \delta^{15}\text{N}_{\text{initial}} + \varepsilon(1-f)$$

$$\delta^{15}\text{N}_{\text{product}} = \delta^{15}\text{N}_{\text{initial}} - \varepsilon(f)$$

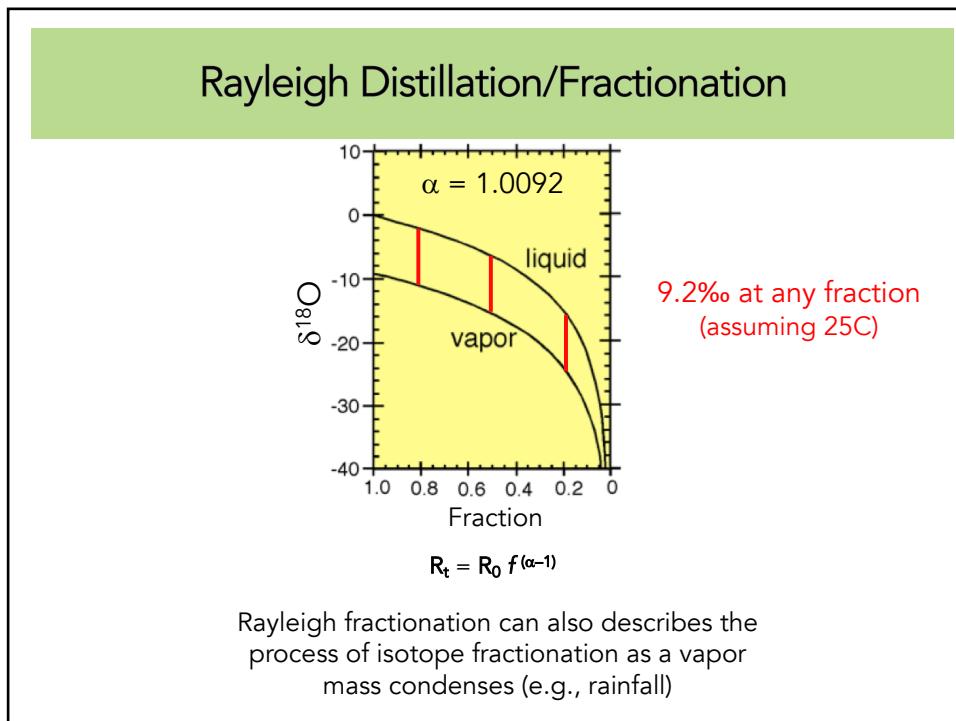
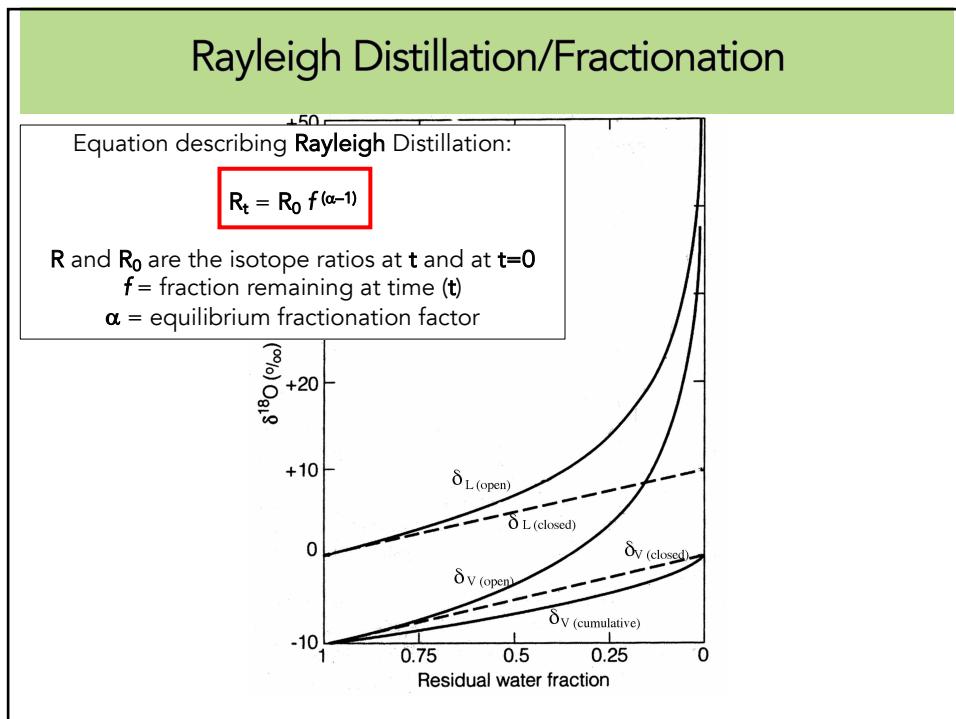
where f is the fraction of the reactant remaining, $\delta^{15}\text{N}_{\text{initial}}$ is the $\delta^{15}\text{N}$ of the initial reactant N pool, and ε is the kinetic isotope effect of the transformation.

Rayleigh Distillation/Fractionation



Evaporation

Vapor is formed from the liquid and the fraction remaining of original liquid declines, as in an evaporating lake or beaker of water.



Kinetic Reactions:

Forward reaction rate is accelerated relative to backward reaction and opportunity for backward mixing diminishes.



Most Biological (Enzyme) Reactions

$$\text{fractionation factor } \alpha = \frac{k_1}{k_2} \begin{array}{l} \text{light isotope} \\ \text{heavy isotope} \end{array}$$

Unidirectional Reactions (e.g., enzyme reactions)
Ratio of reaction rate constants (k) determine fractionation.

Next: measuring isotopes

- Make ions (ionization)
- Separate ions (deflection)
- Count ions (detection)

- Resources:
<https://wwwrcamnl.wr.usgs.gov/isoig/res/>