Isotopes in Environmental Modelling
A Primer

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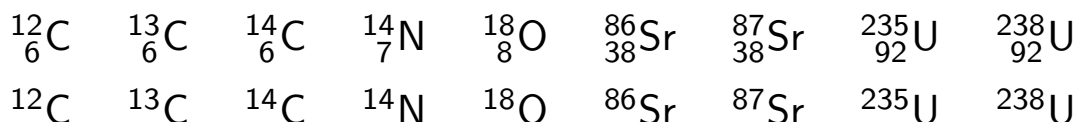Phone: 04-3669771

21st February 2024

Plan

- Introduction: isotope facts and notation
- Isotope ratios, δ's and standards
- Mass balance relationships
- Isotope effects: fractionation, α, ε, Δ
- Evolution equations: approximate and exact

Isotope Notation

- Nuclei of isotopes of a given element E
  - all contain the same number of protons (Z)
  - may have different numbers of neutrons (N)
  - each have a mass number $A = Z + N$

- Isotopes denoted by

$$^A_Z E$$

- Subscript Z generally omitted (redundant)

- Examples:

  $^{12}_6 C$ $^{13}_6 C$ $^{14}_6 C$ $^{14}_7 N$ $^{18}_8 O$ $^{86}_{38} Sr$ $^{87}_{38} Sr$ $^{235}_{92} U$ $^{238}_{92} U$

  $^{12} C$ $^{13} C$ $^{14} C$ $^{14} N$ $^{18} O$ $^{86} Sr$ $^{87} Sr$ $^{235} U$ $^{238} U$

Atomic Weights and Abundances of H, C, N, O Isotopes

Element	Isotope	Atomic weight (Da)	Abundance (atom%)
Hydrogen ($Z=1$)		**1.0079**	
	^{1}H (also: H)	1.007825	99.985
	^{2}H (also: D)	2.014102	0.015
Carbon ($Z=6$)		**12.011**	
	^{12}C	12.00000	98.90
	^{13}C	13.0035	1.10
Nitrogen ($Z=7$)		**14.0067**	
	^{14}N	14.003074	99.63
	^{15}N	15.000109	0.37
Oxygen ($Z=8$)		**15.9994**	
	^{16}O	15.994915	99.76
	^{17}O	16.999131	0.04
	^{18}O	17.999160	0.20

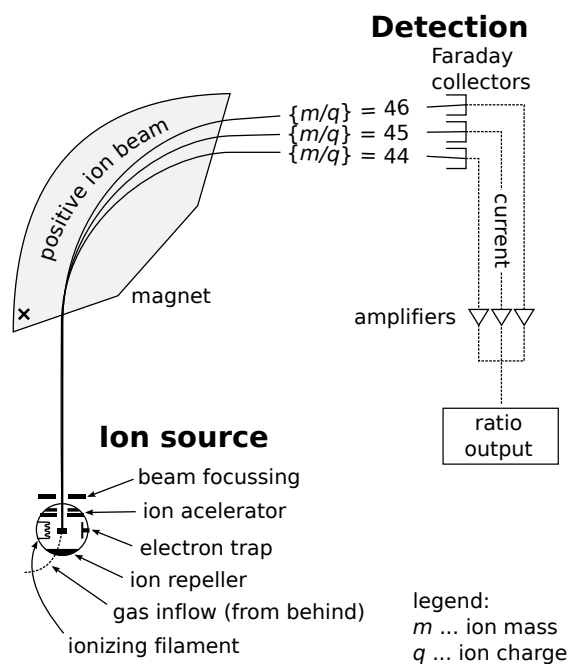Source: Criss (1999)

Miscellaneous Isotope Facts

- 338 naturally occurring nuclides

- 286 of these are said to be *primordial*,
  i. e., have existed since Earth's formation
  - 251 stable isotopes
  - 35 long-lived radioisotopes ($\tau_{1/2} > 100\,\mathrm{Myr}$)

- 52 short-lived radioisotopes ($\tau_{1/2} < 100\,\mathrm{Myr}$)

- Primordial elements have between 1 and 10 stable isotopes
  - Sn has greatest number of stable isotopes: 10
  - Be, F, P (+ 17 others) have only one natural isotope
    (and that is stable)
  - Bi ($\tau_{1/2} = 2.01 \times 10^{19}\,\mathrm{yr}$) and Pa ($\tau_{1/2} = 32{,}760\,\mathrm{yr}$)
    have only one natural isotope (and that is radioactive)

Controls on Isotope Distributions

- Radioactive decay
  - decay of an unstable nucleus to form another (*radiogenic*) one

- Cosmogenic production

- Mixing

- Fractionation during physical and chemical processes
  - isotope exchange reactions: equilibrium effects
  - kinetic processes, where molecules with heavy and light
    isotopes react at different rates: non-equilibrium effects

Usefulness

- Radioactive isotopes
  - act as clocks or dyes (*colors*)

- Stable isotopes
  - act as dyes (*colors*)

- Age determination

- Cycling rate determination

Measuring Isotopic Compositions: Mass Spectrometer

Detection
Faraday collectors

positive ion beam

$\{m/q\} = 46$
$\{m/q\} = 45$
$\{m/q\} = 44$

magnet

×

current

amplifiers

ratio output

Ion source
beam focussing
ion acelerator
electron trap
ion repeller
gas inflow (from behind)
ionizing filament

legend:
m ... ion mass
q ... ion charge

Setup for CO_2

$$m/q = 44: \ ^{12}C(^{16}O)_2{}^+$$

$$m/q = 45: \ ^{13}C(^{16}O)_2{}^+, \ ^{12}C^{16}O^{17}O^+$$

$$m/q = 46: \ ^{12}C^{16}O^{18}O^+, \ ^{13}C^{16}O^{17}O^+,$$
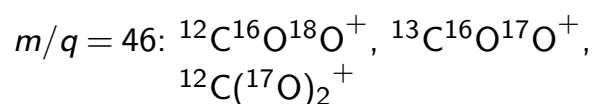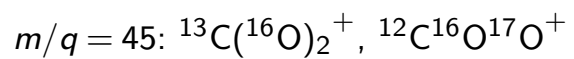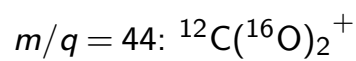$$^{12}C(^{17}O)_2{}^+$$

Image: Wikimedia

Nomenclature for Isotopic Data

- Number of isotopes of mass number i of element E in substance P (number of nuclei):

$$N(^iE)_P$$

- Isotope ratio:

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

- Isotope-number fraction:

$$X(^iE)_P = \frac{N(^iE)_P}{\sum_k N(^kE)_P}$$

(Following Coplen, 2011)

Notation

Most often, context allows to simplify notations without ambiguity

$$N(^iE)_P \rightsquigarrow {}^iN_P$$
$$R(^iE_P/^jE)_P \rightsquigarrow {}^iR_P$$
$$X(^iE)_P \rightsquigarrow {}^iX_P$$

Examples:

$$N(^{18}O)_P \rightsquigarrow {}^{18}N_P$$
$$R(^{18}O/^{16}O)_P \rightsquigarrow {}^{18}R_P$$
$$X(^{18}O)_P \rightsquigarrow {}^{18}X_P$$

$$R(^{17}O/^{16}O)_P \rightsquigarrow {}^{17}R_P$$
$$X(^{17}O)_P \rightsquigarrow {}^{17}X_P$$

Reference Standards: δ Notation

Precise absolute isotope ratio measurements difficult

Example: NBS-19 calcite

- standard reference material for carbon isotope measurements
- $^{13}R_{\mathrm{NBS19}} = 0.011\,202 \pm 0.000\,028$: relative error 2.5‰
- relative deviation of ^{13}R of NBS19 from that of another material can be measured to within ± 0.003‰

Routine measurements made by comparing a sample's isotope ratio to that of a reference material

- with a constant and homogeneous isotopic composition
- ideally a *standard reference material (SRM)*, but often specific to a given laboratory
- with an isotopic composition possibly not precisely known

Reference Standards: δ Notation
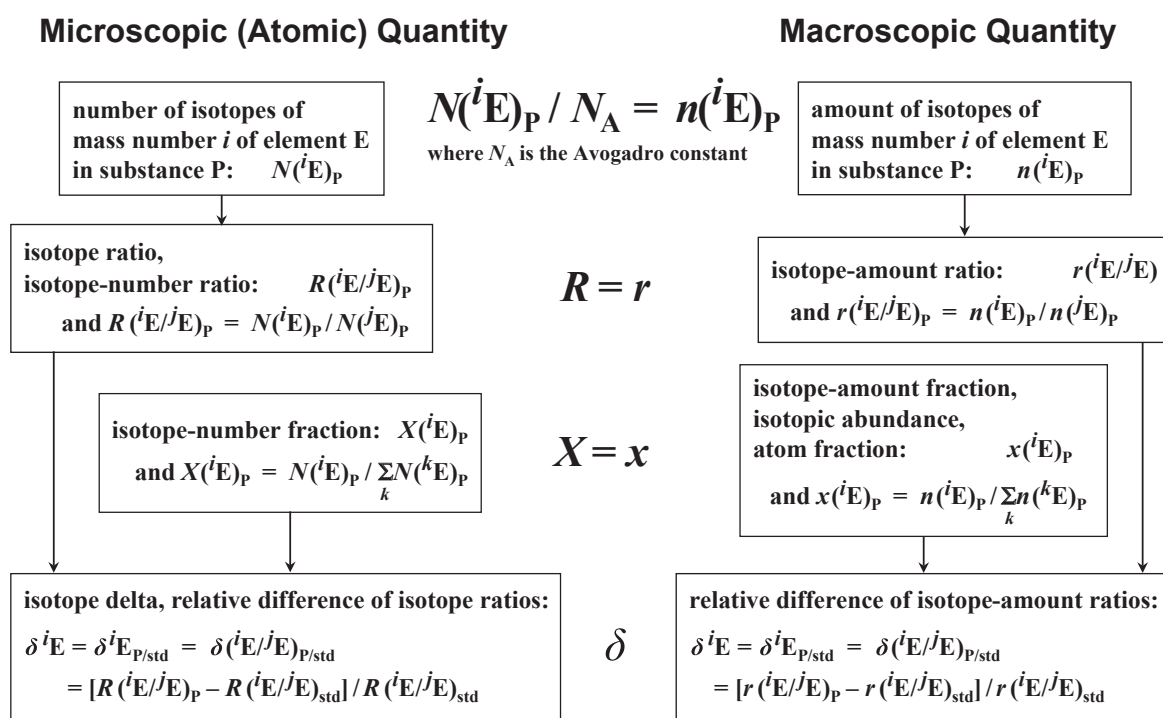
- Measured isotope ratio of sample P reported as the relative difference with respect to a standard

$$\delta(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P/std}} = \frac{R(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P}} - R(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{std}}}{R(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{std}}} = \frac{R(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P}}}{R(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{std}}} - 1$$

- Other notations: $\delta(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P/std}} = \delta\,^{i}\mathrm{E}_{\mathrm{P/std}} = \delta\,^{i}\mathrm{E}$

- δ values typically of the order of 10^{-3}: expressed in ‰

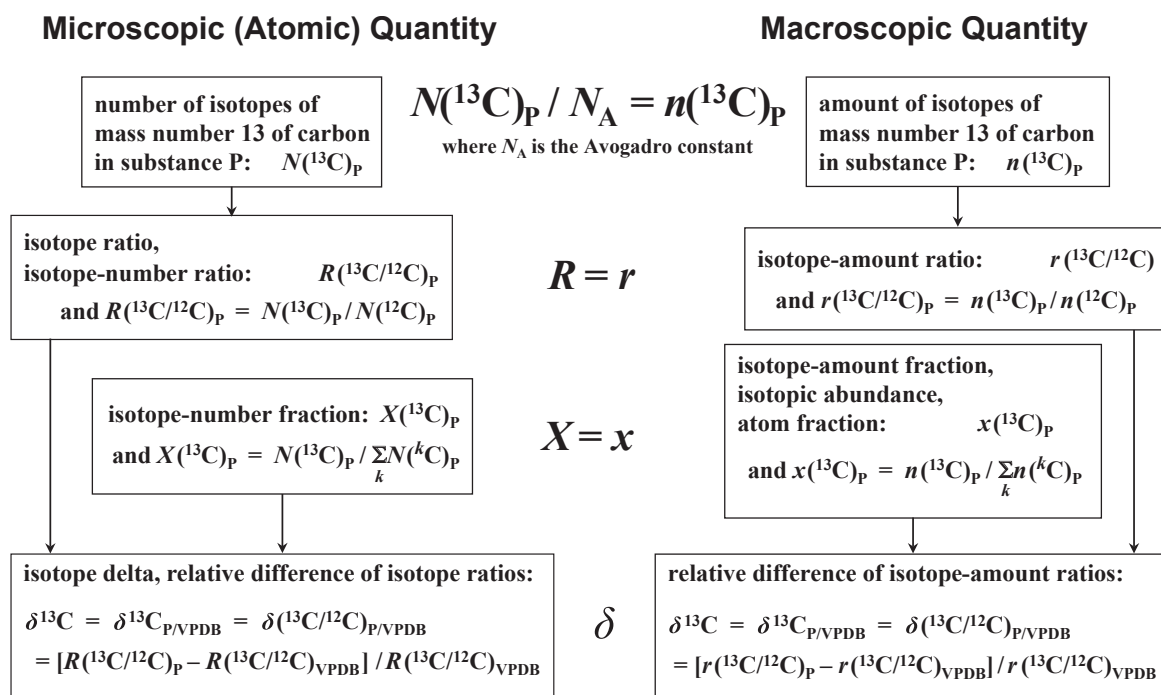- **No extraneous scaling factor 1000** to be included **in the definition!**

Reference Standards: δ Notation

- $\delta(^iE/^jE)_{P/std} < 0$: $R(^iE/^jE)_P < R(^iE/^jE)_{std}$
  $\rightarrow$ isotopic composition of P *lighter* than that of the standard

- $\delta(^iE/^jE)_{P/std} = 0$: $R(^iE/^jE)_P = R(^iE/^jE)_{std}$

- $\delta(^iE/^jE)_{P/std} > 0$: $R(^iE/^jE)_P > R(^iE/^jE)_{std}$
  $\rightarrow$ isotopic composition of P *heavier* than that of the standard

Expressing Isotope Abundances: General Definitions

Microscopic (Atomic) Quantity

| number of isotopes of mass number *i* of element E in substance P: $N(^iE)_P$ |

$$N(^iE)_P / N_A = n(^iE)_P$$

where N_A is the Avogadro constant

Macroscopic Quantity

| amount of isotopes of mass number *i* of element E in substance P: $n(^iE)_P$ |

| isotope ratio, isotope-number ratio: $R(^iE/^jE)_P$ and $R(^iE/^jE)_P = N(^iE)_P / N(^jE)_P$ |

$$R = r$$

| isotope-amount ratio: $r(^iE/^jE)$ and $r(^iE/^jE)_P = n(^iE)_P / n(^jE)_P$ |

| isotope-number fraction: $X(^iE)_P$ and $X(^iE)_P = N(^iE)_P / \sum_k N(^kE)_P$ |

$$X = x$$

| isotope-amount fraction, isotopic abundance, atom fraction: $x(^iE)_P$ and $x(^iE)_P = n(^iE)_P / \sum_k n(^kE)_P$ |

| isotope delta, relative difference of isotope ratios: $\delta^iE = \delta^iE_{P/std} = \delta(^iE/^jE)_{P/std}$ $= [R(^iE/^jE)_P - R(^iE/^jE)_{std}] / R(^iE/^jE)_{std}$ |

$$\delta$$

| relative difference of isotope-amount ratios: $\delta^iE = \delta^iE_{P/std} = \delta(^iE/^jE)_{P/std}$ $= [r(^iE/^jE)_P - r(^iE/^jE)_{std}] / r(^iE/^jE)_{std}$ |

Source: Coplen (*Rapid Commun. Mass Spectrom.*, 2011)

Example: ^{13}C and ^{12}C

Microscopic (Atomic) Quantity   **Macroscopic Quantity**

number of isotopes of mass number 13 of carbon in substance P: $N(^{13}C)_P$

$$N(^{13}C)_P / N_A = n(^{13}C)_P$$
where N_A is the Avogadro constant

amount of isotopes of mass number 13 of carbon in substance P: $n(^{13}C)_P$

isotope ratio, isotope-number ratio: $R(^{13}C/^{12}C)_P$
and $R(^{13}C/^{12}C)_P = N(^{13}C)_P / N(^{12}C)_P$

$$R = r$$

isotope-amount ratio: $r(^{13}C/^{12}C)$
and $r(^{13}C/^{12}C)_P = n(^{13}C)_P / n(^{12}C)_P$

isotope-number fraction: $X(^{13}C)_P$
and $X(^{13}C)_P = N(^{13}C)_P / \sum_k N(^kC)_P$

$$X = x$$

isotope-amount fraction, isotopic abundance, atom fraction: $x(^{13}C)_P$
and $x(^{13}C)_P = n(^{13}C)_P / \sum_k n(^kC)_P$

isotope delta, relative difference of isotope ratios:
$$\delta^{13}C = \delta^{13}C_{P/VPDB} = \delta(^{13}C/^{12}C)_{P/VPDB}$$
$$= [R(^{13}C/^{12}C)_P - R(^{13}C/^{12}C)_{VPDB}] / R(^{13}C/^{12}C)_{VPDB}$$

$$\delta$$

relative difference of isotope-amount ratios:
$$\delta^{13}C = \delta^{13}C_{P/VPDB} = \delta(^{13}C/^{12}C)_{P/VPDB}$$
$$= [r(^{13}C/^{12}C)_P - r(^{13}C/^{12}C)_{VPDB}] / r(^{13}C/^{12}C)_{VPDB}$$

Source: Coplen (*Rapid Commun. Mass Spectrom.*, 2011)

Common Reference Standards

Standard	Ratio	Value (95% confidence)
SMOW	D/H	$0.000\,155\,76 \pm 0.000\,000\,10$
	$^{18}O/^{16}O$	$0.002\,005\,20 \pm 0.000\,000\,43$
	$^{17}O/^{16}O$	$0.000\,373 \pm 0.000\,015$
PDB	$^{13}C/^{12}C$	$0.011\,237\,2 \pm 0.000\,002\,9$
	$^{18}O/^{16}O$	$0.002\,067\,1 \pm 0.000\,002\,1$
	$^{17}O/^{16}O$	$0.000\,379 \pm 0.000\,015$
NBS19	$^{13}C/^{12}C$	$0.011\,202 \pm 0.000\,028$
Air N$_2$	$^{15}N/^{14}N$	$0.003\,676\,5 \pm 0.000\,008\,1$
Canyon Diablo Troilite (CDT)	$^{34}S/^{32}S$	$0.045\,004\,5 \pm 0.000\,009\,3$

After Hoefs (2015, Table 1.6, p. 33) and Prohaska et al. (2022).

Distribution of Carbon-13 in Nature
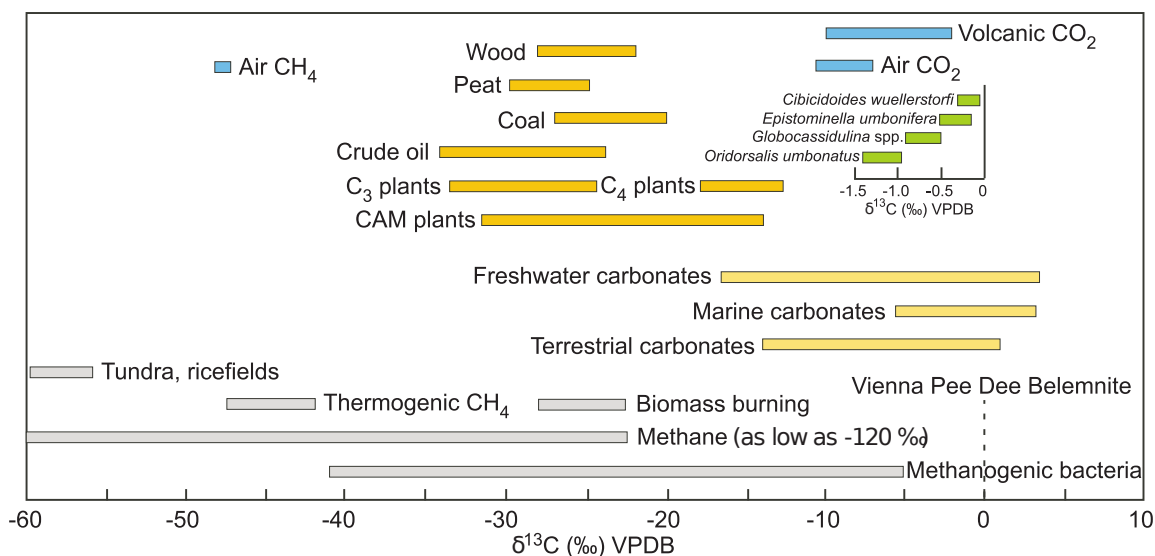
Source: Wagner et al. (Encycl. Geochem. 2007)

Material Balance Relationships

Multicomponent chemical system (Σ) with n parts/compartments
Overall system isotope ratio $R_\Sigma = N(^iE)_\Sigma / N(^jE)_\Sigma$

$$R_\Sigma = \frac{\sum_{p=1}^{n} N(^iE)_p}{N(^jE)_\Sigma} = \frac{N(^iE)_1 + \cdots + N(^iE)_n}{N(^jE)_\Sigma}$$

$$R_\Sigma = \frac{N(^jE)_1}{N(^jE)_\Sigma}\left(\frac{N(^iE)_1}{N(^jE)_1}\right) + \cdots + \frac{N(^jE)_n}{N(^jE)_\Sigma}\left(\frac{N(^iE)_n}{N(^jE)_n}\right)$$

$$= \frac{N(^jE)_1}{N(^jE)_\Sigma}\,R_1 + \cdots + \frac{N(^jE)_n}{N(^jE)_\Sigma}\,R_n$$

Material Balance Relationships

Multicomponent chemical system (Σ) with n parts/compartments
Overall system isotope ratio $R_\Sigma = N(^iE)_\Sigma / N(^jE)_\Sigma$

$$R_\Sigma = \frac{\sum_{p=1}^{n} N(^iE)_p}{N(^jE)_\Sigma} = \frac{N(^iE)_1 + \cdots + N(^iE)_n}{N(^jE)_\Sigma}$$

$$R_\Sigma = \frac{N(^jE)_1}{N(^jE)_\Sigma} \left(\frac{N(^iE)_1}{N(^jE)_1} \right) + \cdots + \frac{N(^jE)_n}{N(^jE)_\Sigma} \left(\frac{N(^iE)_n}{N(^jE)_n} \right)$$

$$R_\Sigma = \sum_{p=1}^{n} \chi_p R_p$$

where χ_p is the system's mole fraction of the *reference isotope* ^jE contained in part p

Mole Fraction vs. Isotope-Number/Isotope-Amount Fraction

Do not confuse

- the *isotope-number fraction* of an isotope ^iE in a substance P

$$X(^iE)_P = \frac{N(^iE)_P}{\sum_k N(^kE)_P}$$

  $\rightarrow$ fraction of ^iE atoms in all E atoms of a given P

- the *mole fraction* χ_p of isotope ^jE of a part p in a system

$$\chi_p = \frac{N(^jE)_p}{N(^jE)_\Sigma} = \frac{N(^jE)_p}{\sum_p N(^jE)_p}$$

  $\rightarrow$ fraction of ^jE atoms in the system that are contained in p

Material Balance Relationships with δ's

Since

$$\delta_{p/\text{std}} = \frac{R_p}{R_\text{std}} - 1 \quad \Leftrightarrow \quad R_p = R_\text{std}(\delta_{p/\text{std}} + 1)$$

$R_\Sigma = \sum_{p=1}^{n} \chi_p R_p$ transforms to

$$R_\text{std}(\delta_{\Sigma/\text{std}} + 1) = \sum_{p=1}^{n} \chi_p R_\text{std}(\delta_{p/\text{std}} + 1) = R_\text{std} \sum_{p=1}^{n} \chi_p(\delta_{p/\text{std}} + 1),$$

which simplifies to

$$\delta_{\Sigma/\text{std}} = \sum_{p=1}^{n} \chi_p \, \delta_{p/\text{std}}$$

Fractionation: Summary Rules

Mass differences between isotopes of a given element lead to different behaviour during physico-chemical processes:

$\Rightarrow$ Fractionation of isotopic ratios

- Equilibrium Fractionation (Bigeleisen, 1965)

  "The heavy isotope goes preferentially to the chemical compound in which the element is bound most strongly."

- Kinetic Fractionation (Bigeleisen, 1949)

  "[. . .] when the different isotopic atoms are chemically bound as molecules in the reacting species, the light molecule usually will have a greater rate constant than the heavy molecule."

Some Physical Properties of Ordinary and Heavy Water

Property	H_2O	D_2O
Molar mass	18.01528	20.02748 g
Vapor pressure at 25 °C	31.672	27.390 hPa
Melting point	0.00	3.82 °C
Boiling point	100.00	101.42 °C
Critical temperature point	373.99	370.74 °C
Density at 25 °C	0.9970	1.1044 $g\,cm^{-3}$
Viscosity at 25 °C	8.93	11.0 mP
Dissociation constant	1.0×10^{-14}	1.95×10^{-15}

Source: Criss (1999)

Equilibrium Fractionation: Fractionation Factor α

For two phases A and B with common isotope pairs, we define

> **Fractionation Factor**
>
> $$\alpha_{A/B} = \alpha_{(A-B)} = \frac{R_A}{R_B}$$

Example:

$$H_2O_{(l)} + HDS_{(g)} \rightleftharpoons HDO_{(l)} + H_2S_{(g)}$$
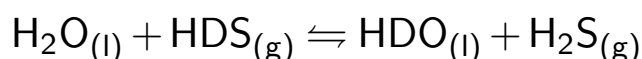
- Phase A: $H_2O + HDO$ (water – 'h2o')
- Phase B: $H_2S + HDS$ (hydrogen sulfide – 'h2s')

$$\alpha_{(h2o-h2s)} = \frac{R(D/H)_{h2o}}{R(D/H)_{h2s}} = \frac{\frac{[HDO]}{[H_2O]}}{\frac{[HDS]}{[H_2S]}} = \frac{[HDO]\,[H_2S]}{[H_2O]\,[HDS]} = K = 2.35$$
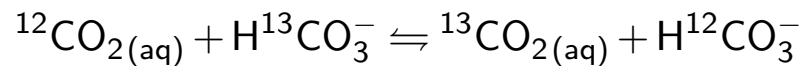
Fractionation Constant

- Fractionation factors involving H isotopes highest

- Most often $\alpha_{(A-B)} \simeq 1$ and for practical usage we define

> ### Fractionation Constant
> $$\varepsilon_{(A-B)} = \alpha_{(A-B)} - 1$$

- Example:

$$^{12}CO_{2\,(aq)} + H^{13}CO_3^- \rightleftharpoons\ ^{13}CO_{2\,(aq)} + H^{12}CO_3^-$$

Fractionation constant and factor at $25\,^\circ C$ (Mook, 1986):

- $\varepsilon_{(CO_2-HCO_3^-)} = -8.97\,\text{\textperthousand} = -0.00897$
- $\alpha_{(CO_2-HCO_3^-)} = \varepsilon_{(CO_2-HCO_3^-)} + 1 = -0.00897 + 1 = 0.99103$

Alternative Quantification of Isotope Effects

- Isotopic difference

$$\Delta_{(A-B)/\text{std}} = \delta_{A/\text{std}} - \delta_{B/\text{std}}$$

- $\ln \alpha_{(A-B)}$ instead of $\alpha_{(A-B)}$
  - for $\alpha_{(A-B)} \simeq 1$, i. e., $\varepsilon_{(A-B)} \ll 1$

$$\ln \alpha_{(A-B)} = \ln(1 + \varepsilon_{(A-B)}) \simeq \varepsilon_{(A-B)}$$

  - for perfect gases, $\ln \alpha_{(A-B)}$ varies as $1/T^2$ and $1/T$ at high and low temperatures, resp.

Fractionation Constant and δ Values

Since $R_\mathrm{A} = R_\mathrm{std}(\delta_\mathrm{A/std} + 1)$ and $R_\mathrm{B} = R_\mathrm{std}(\delta_\mathrm{B/std} + 1)$, we have

$$
\begin{aligned}
\varepsilon_{(\mathrm{A-B})} &= \alpha_{(\mathrm{A-B})} - 1 \\
&= \frac{R_\mathrm{A}}{R_\mathrm{B}} - 1 \\
&= \frac{\delta_\mathrm{A/std} + 1}{\delta_\mathrm{B/std} + 1} - 1 \\
&= \frac{\delta_\mathrm{A/std} - \delta_\mathrm{B/std}}{\delta_\mathrm{B/std} + 1} \\
&= \frac{\Delta_{(\mathrm{A-B})/\mathrm{std}}}{\delta_\mathrm{B/std} + 1}
\end{aligned}
$$

If $\delta_\mathrm{B/std} \ll 1$:

$$\varepsilon_{(\mathrm{A-B})} \simeq \Delta_{(\mathrm{A-B})/\mathrm{std}}$$

Please Notice That . . .

- $\alpha_{(\mathrm{A-B})}$ and $\varepsilon_{(\mathrm{A-B})}$ depend only on $R_\mathrm{A}/R_\mathrm{B}$

- $\Delta_{(\mathrm{A-B})}$ depends on R_A, R_B, and . . . R_std

- $\varepsilon_{(\mathrm{A-B})} \simeq \Delta_{(\mathrm{A-B})}$ is generally an acceptable approximation, but be aware that
  - differences become significant as δ range expands
  - large errors to be expected for D/H calculations in general

Who is Afraid of More Confusion?

- Occasional confusion between fractionation *factor* and fractionation *constant* in the literature
  - fractionation *factor* for multiplication (exact results)
  - fractionation *constant* for addition (approximate results)
  - confusion extends to the usage of the symbols α and ε

- Some authors denote $\alpha - 1$ by Δ instead of ε

- Some authors denote $\delta_A - \delta_B$ by ε

- Always double-check
  - definitions used
  - approximations adopted

- In your own work
  - clearly state adopted definitions and approximations
  - stick to IUPAC recommendations (Coplen, 2011) anyway

Non-Equilibrium fractionation

- kinetic isotope effects: reaction rates of heavy and light isotopes are different
- incomplete or unidirectional processes
- evaporation
- metabolic effects
- diffusion

For a process that transforms

- a substrate or source with one isotope ratio R_S
- to a product with an isotope ratio R_P

we define the isotope effect or fractionation factor

Fractionation Factor

$$\alpha_{S/P} = \alpha_{(S-P)} = \frac{R_S}{R_P}$$

and the related $\varepsilon_{(S-P)}$ and $\Delta_{(S-P)}$ as before.

Mass Balance Equations

Reservoir with content $n \equiv n(E)$:

$$\frac{dn}{dt} = \sum J_{in}(E) - \sum J_{out}(E)$$

where

- $J_{in}(E)$ denotes source terms (input, reaction, ...)
- $J_{out}(E)$ denotes sink terms (output, reaction, decay, ...)
- E includes isotopes ^iE and ^jE:

$$n(E) = n(^jE) + \cdots + n(^iE) + \ldots$$

Question

How are the mass balance equations for ^iE, ^jE and E related?

Problem to Solve

Solve a coupled differential equation problem:

- given
  - t_0 and t_{end} (time interval)
  - $n(t_0) = n_0$
  - $\delta^{13}C(t_0) = \delta_0$
  - fractionation parameters of all involved processes

- determine, for $t_0 \leq t \leq t_{\text{end}}$
  - $n(t)$
  - $\delta^{13}C(t)$

Mass Balance Variables: Exact Relationships

$$n({}^{j}E) = x({}^{j}E) \cdot n(E)$$

$$n({}^{i}E) = x({}^{i}E) \cdot n(E)$$
$$n({}^{i}E) = r({}^{i}E/{}^{j}E) \cdot n({}^{j}E)$$

$$J({}^{j}E) = x({}^{j}E)_J \cdot J(E)$$

$$J({}^{i}E) = x({}^{i}E)_J \cdot J(E)$$
$$J({}^{i}E) = r({}^{i}E/{}^{j}E)_J \cdot J({}^{j}E)$$

Mass Balance Variables: Approximate Relationships

- In common isotope systems (e. g., H, C, N, O), the reference isotope ^jE strongly dominant: $x(^jE) > 98\%$

- In this case:

$$
\begin{aligned}
n(E) &\simeq n(^jE) \\
x(^iE) &\simeq r(^iE/^jE) \\
n(^iE) &\simeq r(^iE/^jE) \cdot n(E) \\[1em]
J(E) &\simeq J(^jE) \\
J(^iE) &\simeq r(^iE/^jE)_J \cdot J(E)
\end{aligned}
$$

Mass Balance Equations for C-13

Exact relationships:

$$
\begin{aligned}
^{13}n &= {}^{13}x \cdot n(C) \\
^{13}n &= {}^{13}r \cdot {}^{12}n \\[1em]
^{13}J &= {}^{13}x_J \cdot J(C) \\
^{13}J &= {}^{13}r_J \cdot {}^{12}J
\end{aligned}
$$

Approximations:

$$
\begin{aligned}
n(C) &\simeq {}^{12}n \\
^{13}n &\simeq {}^{13}r \cdot n(C) \\[1em]
J(C) &\simeq {}^{12}J \\
^{13}J &\simeq {}^{13}r_J \cdot J(C)
\end{aligned}
$$

Approximate Evolution Equation for $\delta^{13}C$

Evolution equations for $n \equiv n(C)$ and ^{13}n:

$$\frac{dn}{dt} = \sum J_{\text{in}}(C) - \sum J_{\text{out}}(C)$$

$$\frac{d\,^{13}n}{dt} = \sum {}^{13}J_{\text{in}} - \sum {}^{13}J_{\text{out}}$$

Introduce approximate relationships for ^{13}n, $^{13}J_{\text{in}}$ and $^{13}J_{\text{out}}$:

$$\frac{d\,^{13}n}{dt} \simeq \frac{d}{dt}({}^{13}r \cdot n)$$

$$\sum {}^{13}J_{\text{in}} - \sum {}^{13}J_{\text{out}} \simeq \sum {}^{13}r_{J_{\text{in}}} \cdot J_{\text{in}}(C) - \sum {}^{13}r_{J_{\text{out}}} \cdot J_{\text{out}}(C)$$

Approximate Evolution Equation for $\delta^{13}C$

Approximate evolution equation for ^{13}n:

$$\frac{d}{dt}({}^{13}r \cdot n) \simeq \sum {}^{13}r_{J_{\text{in}}} \cdot J_{\text{in}}(C) - \sum {}^{13}r_{J_{\text{out}}} \cdot J_{\text{out}}(C)$$

The left-hand side develops as

$$\frac{d}{dt}({}^{13}r \cdot n) = \frac{d\,^{13}r}{dt} \cdot n + {}^{13}r \cdot \frac{dn}{dt}$$

$$= \frac{d\,^{13}r}{dt} \cdot n + {}^{13}r \cdot \left(\sum J_{\text{in}}(C) - \sum J_{\text{out}}(C) \right)$$

Equating the two right-hand sides and rearranging leads to

$$\frac{d\,^{13}r}{dt} \cdot n = \sum ({}^{13}r_{J_{\text{in}}} - {}^{13}r) \cdot J_{\text{in}}(C) - \sum ({}^{13}r_{J_{\text{out}}} - {}^{13}r) \cdot J_{\text{out}}(C)$$

Approximate Evolution Equation for $\delta^{13}C$

Since $^{13}r = {}^{13}r_{std}(\delta^{13}C + 1)$, $^{13}r_{J_{in}} = {}^{13}r_{std}(\delta^{13}C_{J_{in}} + 1)$, etc., we finally get after simplification:

> **$\delta^{13}C$ Equation (*approximate*)**
>
> $$\frac{d\delta^{13}C}{dt} = \left(\sum (\delta^{13}C_{J_{in}} - \delta^{13}C) \cdot J_{in}(C) - \sum (\delta^{13}C_{J_{out}} - \delta^{13}C) \cdot J_{out}(C) \right) \Big/ n$$

where

- $\delta^{13}C_{J_{out}} = \delta^{13}C$ if the process behind J_{out} does not fractionate
- $\delta^{13}C_{J_{out}}$ is derived from $\delta^{13}C$ using the related fractionation information $\Delta_{(S-P)} \simeq \varepsilon_{(S-P)}$

Evolution Equation for ^{13}x

- Repeat the previous developments with ^{13}x instead of ^{13}r:

> **^{13}x Equation (*exact*)**
>
> $$\frac{d^{13}x}{dt} = \left(\sum ({}^{13}x_{J_{in}} - {}^{13}x) \cdot J_{in}(C) - \sum ({}^{13}x_{J_{out}} - {}^{13}x) \cdot J_{out}(C) \right) \Big/ n$$

- ^{13}x, ^{13}r and $\delta^{13}C$ are related by

$$^{13}x = \frac{^{13}r}{1 + {}^{13}r} = \frac{^{13}r_{std}(\delta^{13}C + 1)}{1 + {}^{13}r_{std}(\delta^{13}C + 1)}$$

and

$$\delta^{13}C = \frac{^{13}r}{^{13}r_{std}} - 1 \quad \text{with} \quad ^{13}r = \frac{^{13}x}{1 - {}^{13}x}$$

From

$$\frac{d}{dt}(^{13}r \cdot n) \simeq \sum {}^{13}r_{J_{in}} \cdot J_{in}(C) - \sum {}^{13}r_{J_{out}} \cdot J_{out}(C)$$

and

$$\frac{d}{dt}(^{13}r \cdot n) = \frac{d\,^{13}r}{dt} \cdot n + {}^{13}r \cdot \frac{dn}{dt},$$

one might be tempted to continue with

$$\frac{d\,^{13}r}{dt} \cdot n = \sum {}^{13}r_{J_{in}} \cdot J_{in}(C) - \sum {}^{13}r_{J_{out}} \cdot J_{out}(C) - {}^{13}r \cdot \frac{dn}{dt}$$

to reuse an already calculated dn/dt, writing ...

$$\frac{d\delta^{13}C}{dt} = \left(\sum \delta^{13}C_{J_{in}} \cdot J_{in}(C) - \sum \delta^{13}C_{J_{out}} \cdot J_{out}(C) - \delta^{13}C \cdot \frac{dn}{dt} \right) \bigg/ n$$

- Mathematically speaking, the two are identical

- However, numerically speaking, they are worlds apart:
    - Addition of many small terms in the "*Do*" version:
      terms in $J_{out}(C)$ are even 0 in the absence of fractionation

    - Difference of two or three potentially large terms in the
      "*Don't*" version: danger of *catastrophic cancellation*

Alternatively: Evolution Equations for ^{13}n and n

1. Derive initial condition $^{13}n(t_0) = {}^{13}n_0$ using
   - $^{13}r_0 = {}^{13}r_{\text{std}}(\delta_0 + 1)$
   - $^{13}x_0 = \dfrac{^{13}r_0}{1 + {}^{13}r_0}$
   - $^{13}n_0 = {}^{13}x_0 \cdot n_0$

2. Calculate $n(t)$ and $^{13}n(t)$

3. Whenever $\delta^{13}C(t)$ is required
   - $^{13}x = \dfrac{^{13}n(t)}{n(t)}$
   - $^{13}r = \dfrac{^{13}x}{1 - {}^{13}x}$
   - $\delta^{13}C(t) = \dfrac{^{13}r}{^{13}r_{\text{std}}} - 1$

Useful References

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