

Isotopes in Environmental Modelling A Primer

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Plan

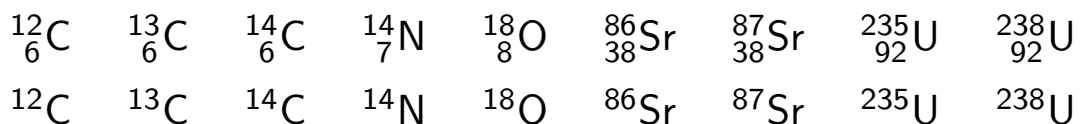
- Introduction: isotope facts and notation
- Isotope ratios, δ 's and standards
- Mass balance relationships
- Isotope effects: fractionation, α , ε , Δ
- Evolution equations: approximate and exact

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



- Subscript Z generally omitted (redundant)
- Examples:



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

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

Source: Criss (1999)

Miscellaneous Isotope Facts

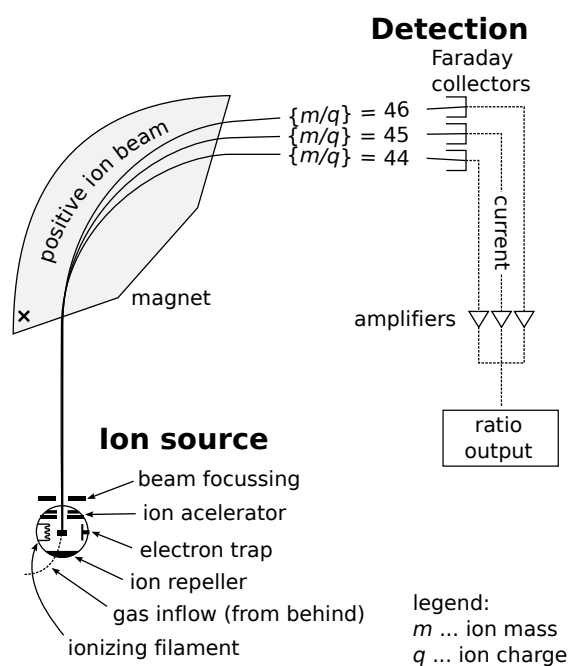
- 338 naturally occurring nuclides
- 286 of these are said to be *primordial*, i. e., have existed since Earth's formation
 - 251 stable isotopes
 - 35 long-lived radioisotopes ($\tau_{1/2} > 100 \text{ Myr}$)
- 52 short-lived radioisotopes ($\tau_{1/2} < 100 \text{ Myr}$)
- Primordial elements have 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 ($\tau_{1/2} = 2.01 \times 10^{19} \text{ yr}$) and Pa ($\tau_{1/2} = 32,760 \text{ yr}$) 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

- Radioactive isotopes
 - act as clocks or dyes (*colors*)
- Stable isotopes
 - act as dyes (*colors*)
- Age determination
- Cycling rate determination

Measuring Isotopic Compositions: Mass Spectrometer



Setup for CO_2

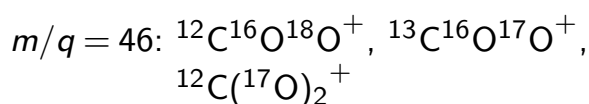
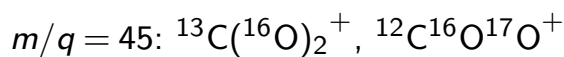
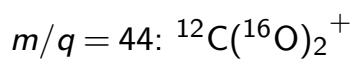


Image: Wikimedia

Nomenclature for Isotopic Data

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

$$N({}^i\text{E})_{\text{P}}$$

- Isotope ratio:

$$R({}^i\text{E}/{}^j\text{E})_{\text{P}} = \frac{N({}^i\text{E})_{\text{P}}}{N({}^j\text{E})_{\text{P}}}$$

- Isotope-number fraction:

$$X({}^i\text{E})_{\text{P}} = \frac{N({}^i\text{E})_{\text{P}}}{\sum_k N({}^k\text{E})_{\text{P}}}$$

(Following Coplen, 2011)

Notation

Most often, context allows to simplify notations without ambiguity

$$\begin{aligned} N({}^i\text{E})_{\text{P}} &\rightsquigarrow {}^iN_{\text{P}} \\ R({}^i\text{E}_{\text{P}}/{}^j\text{E})_{\text{P}} &\rightsquigarrow {}^iR_{\text{P}} \\ X({}^i\text{E})_{\text{P}} &\rightsquigarrow {}^iX_{\text{P}} \end{aligned}$$

Examples:

$$\begin{aligned} N({}^{18}\text{O})_{\text{P}} &\rightsquigarrow {}^{18}N_{\text{P}} \\ R({}^{18}\text{O}/{}^{16}\text{O})_{\text{P}} &\rightsquigarrow {}^{18}R_{\text{P}} \\ X({}^{18}\text{O})_{\text{P}} &\rightsquigarrow {}^{18}X_{\text{P}} \\ R({}^{17}\text{O}/{}^{16}\text{O})_{\text{P}} &\rightsquigarrow {}^{17}R_{\text{P}} \\ X({}^{17}\text{O})_{\text{P}} &\rightsquigarrow {}^{17}X_{\text{P}} \end{aligned}$$

Precise absolute isotope ratio measurements difficult

Example: NBS-19 calcite

- standard reference material for carbon isotope measurements
- $^{13}R_{\text{NBS19}} = 0.011202 \pm 0.000028$: relative error 2.5‰
- relative deviation of ^{13}R of NBS19 from that of another material can be measured to within $\pm 0.003\text{‰}$

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

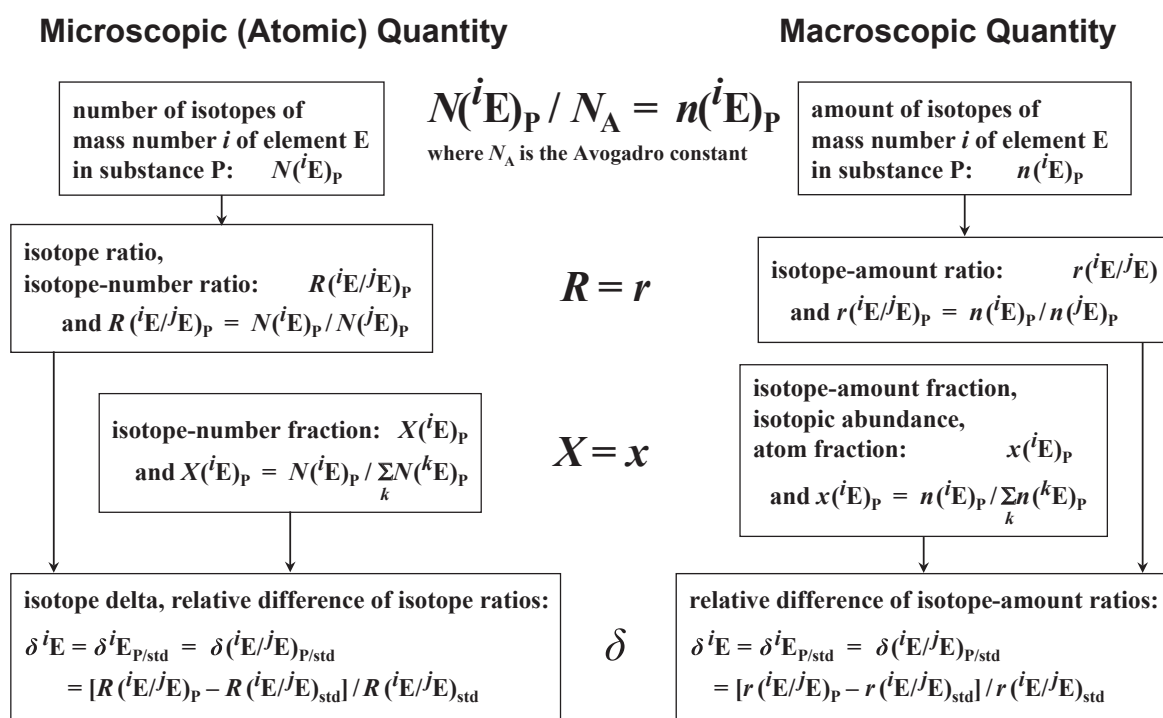
- Measured isotope ratio of sample P reported as the relative difference with respect to a standard

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

- Other notations: $\delta(^i\text{E}/^j\text{E})_{\text{P/std}} = \delta^i\text{E}_{\text{P/std}} = \delta^i\text{E}$
- δ values typically of the order of 10^{-3} : expressed in ‰
- **No extraneous scaling factor 1000 to be included in the definition!**

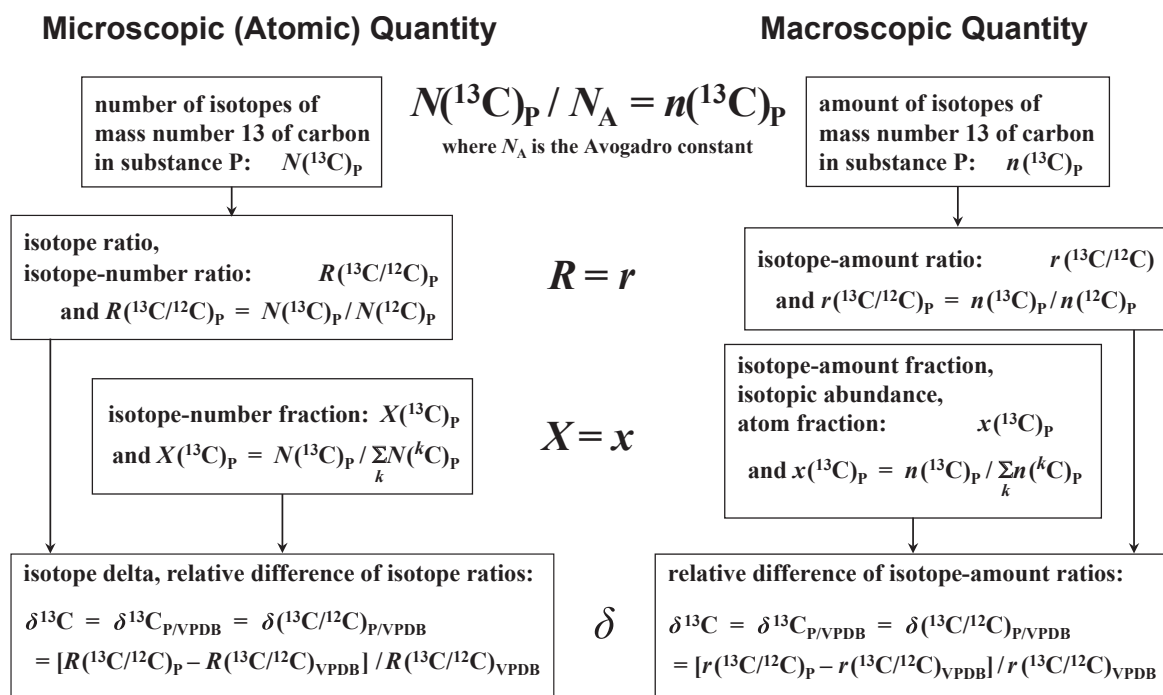
- $\delta(^i\text{E}/^j\text{E})_{\text{P}/\text{std}} < 0$: $R(^i\text{E}/^j\text{E})_{\text{P}} < R(^i\text{E}/^j\text{E})_{\text{std}}$
 → isotopic composition of P *lighter* than that of the standard
- $\delta(^i\text{E}/^j\text{E})_{\text{P}/\text{std}} = 0$: $R(^i\text{E}/^j\text{E})_{\text{P}} = R(^i\text{E}/^j\text{E})_{\text{std}}$
- $\delta(^i\text{E}/^j\text{E})_{\text{P}/\text{std}} > 0$: $R(^i\text{E}/^j\text{E})_{\text{P}} > R(^i\text{E}/^j\text{E})_{\text{std}}$
 → isotopic composition of P *heavier* than that of the standard

Expressing Isotope Abundances: General Definitions



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

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

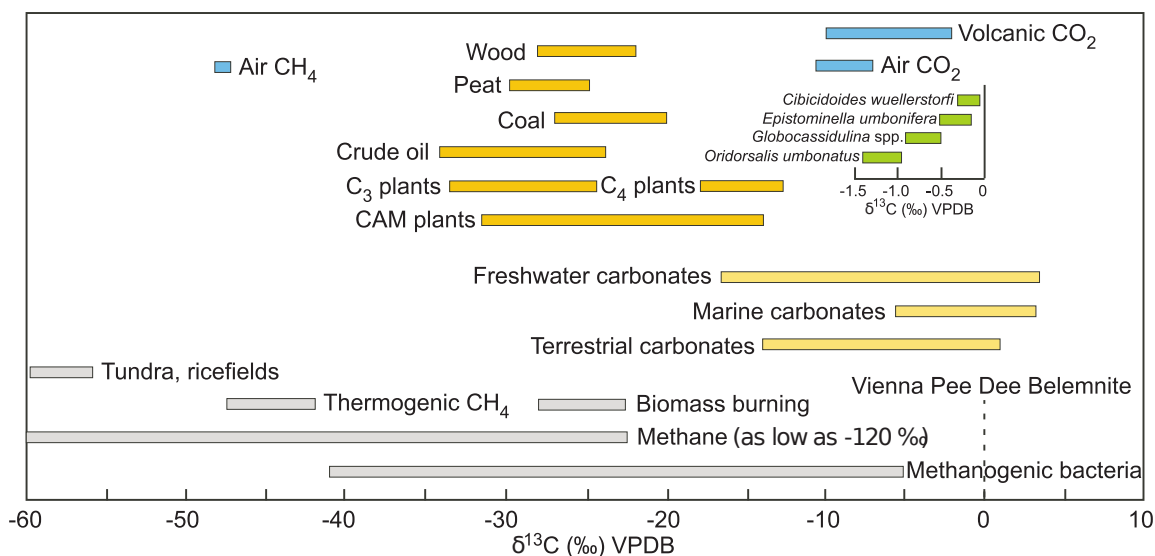


Source: Coplen (*Rapid Commun. Mass Spectrom.*, 2011)

Common Reference Standards

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

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



Source: Wagner et al. (Encycl. Geochem. 2007)

Material Balance Relationships

Multicomponent chemical system (Σ) with n parts/compartments

Overall system isotope ratio $R_{\Sigma} = N(^i\text{E})_{\Sigma} / N(^j\text{E})_{\Sigma}$

$$R_{\Sigma} = \frac{\sum_{p=1}^n N(^i\text{E})_p}{N(^j\text{E})_{\Sigma}} = \frac{N(^i\text{E})_1 + \dots + N(^i\text{E})_n}{N(^j\text{E})_{\Sigma}}$$

$$\begin{aligned} R_{\Sigma} &= \frac{N(^j\text{E})_1}{N(^j\text{E})_{\Sigma}} \left(\frac{N(^i\text{E})_1}{N(^j\text{E})_1} \right) + \dots + \frac{N(^j\text{E})_n}{N(^j\text{E})_{\Sigma}} \left(\frac{N(^i\text{E})_n}{N(^j\text{E})_n} \right) \\ &= \frac{N(^j\text{E})_1}{N(^j\text{E})_{\Sigma}} R_1 + \dots + \frac{N(^j\text{E})_n}{N(^j\text{E})_{\Sigma}} R_n \end{aligned}$$

Material Balance Relationships

Multicomponent chemical system (Σ) with n parts/compartments

Overall system isotope ratio $R_{\Sigma} = N(^iE)_{\Sigma} / N(^jE)_{\Sigma}$

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

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

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

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

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

→ 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

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

→ fraction of jE atoms in the system that are contained in p



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:

⇒ 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.”

Property	H ₂ O	D ₂ O
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)

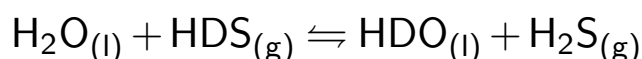
Equilibrium Fractionation: Fractionation Factor α

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:



- Phase A: H₂O + HDO (water – ‘h2o’)
- Phase B: H₂S + HDS (hydrogen sulfide – ‘h2s’)

$$\alpha_{(h2o-h2s)} = \frac{R(D/H)_{h2o}}{R(D/H)_{h2s}} = \frac{\frac{[\text{HDO}]}{[\text{H}_2\text{O}]}}{\frac{[\text{HDS}]}{[\text{H}_2\text{S}]}} = \frac{[\text{HDO}][\text{H}_2\text{S}]}{[\text{H}_2\text{O}][\text{HDS}]} = K = 2.35$$

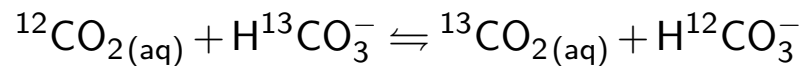
Fractionation Constant

- 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:



Fractionation constant and factor at 25 °C (Mook, 1986):

- $\varepsilon_{(\text{CO}_2-\text{HCO}_3^-)} = -8.97\text{‰} = -0.00897$
- $\alpha_{(\text{CO}_2-\text{HCO}_3^-)} = \varepsilon_{(\text{CO}_2-\text{HCO}_3^-)} + 1 = -0.00897 + 1 = 0.99103$

Alternative Quantification of Isotope Effects

- Isotopic difference

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

- In $\alpha_{(A-B)}$ 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 $R_A = R_{\text{std}}(\delta_{A/\text{std}} + 1)$ and $R_B = R_{\text{std}}(\delta_{B/\text{std}} + 1)$, we have

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

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

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

Please Notice That ...

- $\alpha_{(A-B)}$ and $\varepsilon_{(A-B)}$ depend only on R_A/R_B
- $\Delta_{(A-B)}$ depends on R_A , R_B , and ... R_{std}
- $\varepsilon_{(A-B)} \simeq \Delta_{(A-B)}$ 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 :

$$n(E) = n({}^iE) + \dots + n({}^jE) + \dots$$

Question

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

Solve a coupled differential equation problem:

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

Mass Balance Variables: Exact Relationships

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

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

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

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

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

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

Mass Balance Variables: Approximate Relationships

- In common isotope systems (e. g., H, C, N, O), the reference isotope ${}^j\text{E}$ strongly dominant: $x({}^j\text{E}) > 98\%$
- In this case:

$$n(\text{E}) \simeq n({}^j\text{E})$$

$$x({}^i\text{E}) \simeq r({}^i\text{E}/{}^j\text{E})$$

$$n({}^i\text{E}) \simeq r({}^i\text{E}/{}^j\text{E}) \cdot n(\text{E})$$

$$J(\text{E}) \simeq J({}^j\text{E})$$

$$J({}^i\text{E}) \simeq r({}^i\text{E}/{}^j\text{E})_J \cdot J(\text{E})$$

Mass Balance Equations for C-13

Exact relationships:

$${}^{13}n = {}^{13}x \cdot n(\text{C})$$

$${}^{13}n = {}^{13}r \cdot {}^{12}n$$

$${}^{13}J = {}^{13}x_J \cdot J(\text{C})$$

$${}^{13}J = {}^{13}r_J \cdot {}^{12}J$$

Approximations:

$$n(\text{C}) \simeq {}^{12}n$$

$${}^{13}n \simeq {}^{13}r \cdot n(\text{C})$$

$$J(\text{C}) \simeq {}^{12}J$$

$${}^{13}J \simeq {}^{13}r_J \cdot J(\text{C})$$

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

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

$$\begin{aligned}\frac{dn}{dt} &= \sum J_{\text{in}}(\text{C}) - \sum J_{\text{out}}(\text{C}) \\ \frac{d^{13}n}{dt} &= \sum ^{13}J_{\text{in}} - \sum ^{13}J_{\text{out}}\end{aligned}$$

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

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

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

Approximate evolution equation for ^{13}n :

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

The left-hand side develops as

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

Equating the two right-hand sides and rearranging leads to

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

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

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

$\delta^{13}\text{C}$ Equation (*approximate*)

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

where

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

Evolution Equation for ^{13}X

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

^{13}X Equation (*exact*)

$$\frac{d^{13}\text{X}}{dt} = \left(\sum (^{13}\text{X}_{J_{\text{in}}} - ^{13}\text{X}) \cdot J_{\text{in}}(C) - \sum (^{13}\text{X}_{J_{\text{out}}} - ^{13}\text{X}) \cdot J_{\text{out}}(C) \right) / n$$

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

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

and

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

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 . . .

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

- 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
 - $^{13}r_0 = ^{13}r_{\text{std}}(\delta_0 + 1)$
 - $^{13}x_0 = \frac{^{13}r_0}{1 + ^{13}r_0}$
 - $^{13}n_0 = ^{13}x_0 \cdot n_0$
- ② Calculate $n(t)$ and $^{13}n(t)$
- ③ Whenever $\delta^{13}\text{C}(t)$ is required
 - $^{13}x = \frac{^{13}n(t)}{n(t)}$
 - $^{13}r = \frac{^{13}x}{1 - ^{13}x}$
 - $\delta^{13}\text{C}(t) = \frac{^{13}r}{^{13}r_{\text{std}}} - 1$

Useful References

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