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

$$^{A}_{Z}\mathrm{E}$$

- Subscript Z generally omitted (redundant)
- Examples:

$$^{12}_{6}\mathrm{C} \quad ^{13}_{6}\mathrm{C} \quad ^{14}_{6}\mathrm{C} \quad ^{14}_{7}\mathrm{N} \quad ^{18}_{8}\mathrm{O} \quad ^{86}_{38}\mathrm{Sr} \quad ^{87}_{38}\mathrm{Sr} \quad ^{235}_{92}\mathrm{U} \quad ^{238}_{92}\mathrm{U}$$

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

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

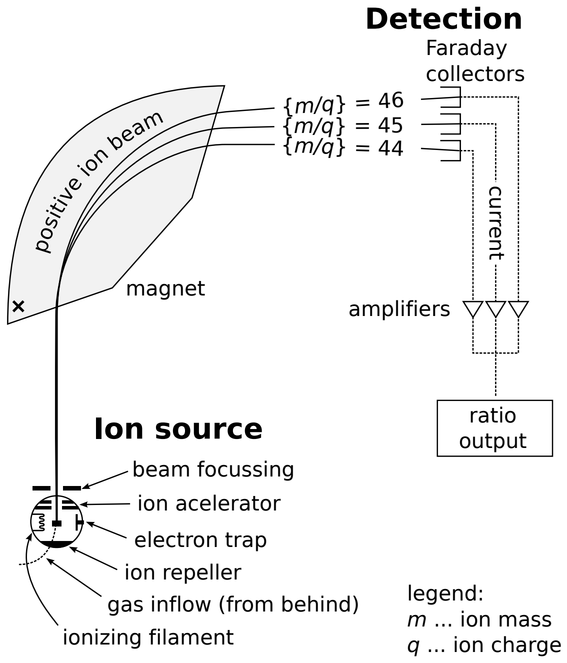

Image: Wikimedia

Setup for CO_2

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

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

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

Nomenclature for Isotopic Data

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

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

- Isotope ratio:

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

- Isotope-number fraction:

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

(Following Coplen, 2011)

Notation

Most often, context allows to simplify notations without ambiguity

$$\begin{aligned} N({}^{i}\mathrm{E})_{\mathrm{P}} &\rightsquigarrow {}^{i}N_{\mathrm{P}} \\ R({}^{i}\mathrm{E}_{\mathrm{P}}/{}^{j}\mathrm{E})_{\mathrm{P}} &\rightsquigarrow {}^{i}R_{\mathrm{P}} \\ X({}^{i}\mathrm{E})_{\mathrm{P}} &\rightsquigarrow {}^{i}X_{\mathrm{P}} \end{aligned}$$

Examples:

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

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

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

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

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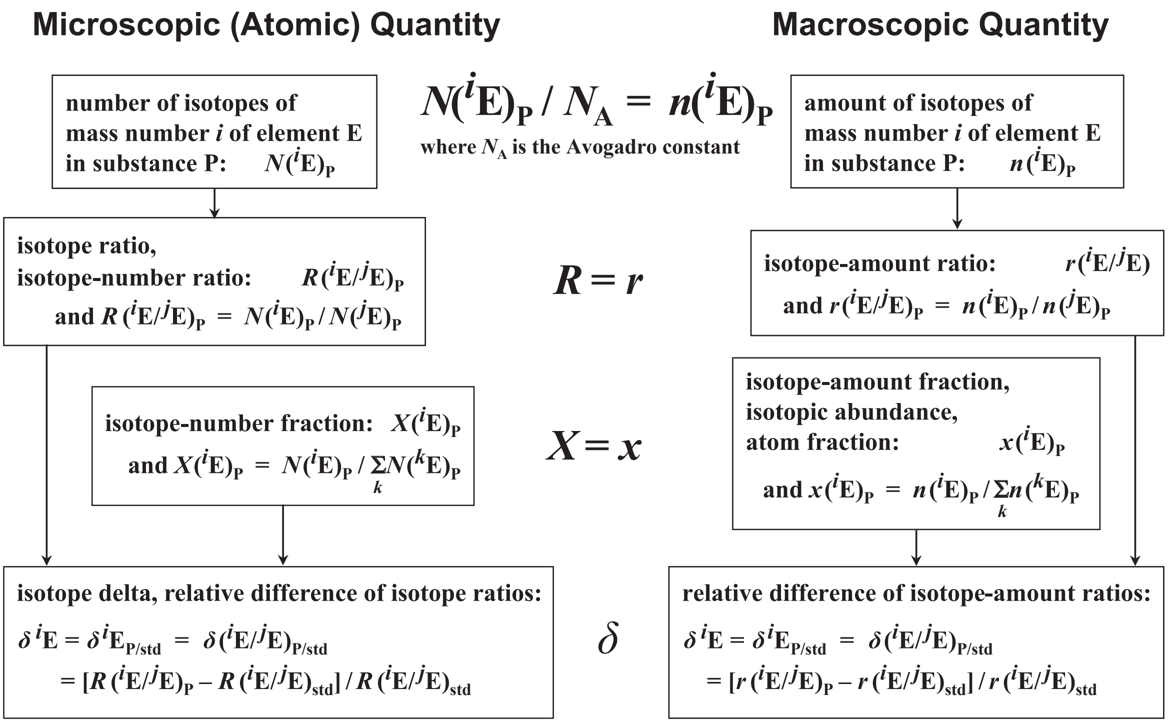
Expressing Isotope Abundances: General Definitions



Microscopic (Atomic) Quantity

Macroscopic Quantity

number of isotopes of mass number i of element E in substance P: $N({}^{i}\mathrm{E})_{\mathrm{P}}$

$$N({}^{i}\mathrm{E})_{\mathrm{P}} / N_{\mathrm{A}} = n({}^{i}\mathrm{E})_{\mathrm{P}}$$

where N_{A} is the Avogadro constant

amount of isotopes of mass number i of element E in substance P: $n({}^{i}\mathrm{E})_{\mathrm{P}}$

isotope ratio, isotope-number ratio: $R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}}$
and $R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} = N({}^{i}\mathrm{E})_{\mathrm{P}} / N({}^{j}\mathrm{E})_{\mathrm{P}}$

$$R = r$$

isotope-amount ratio: $r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})$
and $r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} = n({}^{i}\mathrm{E})_{\mathrm{P}} / n({}^{j}\mathrm{E})_{\mathrm{P}}$

isotope-number fraction: $X({}^{i}\mathrm{E})_{\mathrm{P}}$
and $X({}^{i}\mathrm{E})_{\mathrm{P}} = N({}^{i}\mathrm{E})_{\mathrm{P}} / \sum_{k} N({}^{k}\mathrm{E})_{\mathrm{P}}$

$$X = x$$

isotope-amount fraction, isotopic abundance, atom fraction: $x({}^{i}\mathrm{E})_{\mathrm{P}}$
and $x({}^{i}\mathrm{E})_{\mathrm{P}} = n({}^{i}\mathrm{E})_{\mathrm{P}} / \sum_{k} n({}^{k}\mathrm{E})_{\mathrm{P}}$

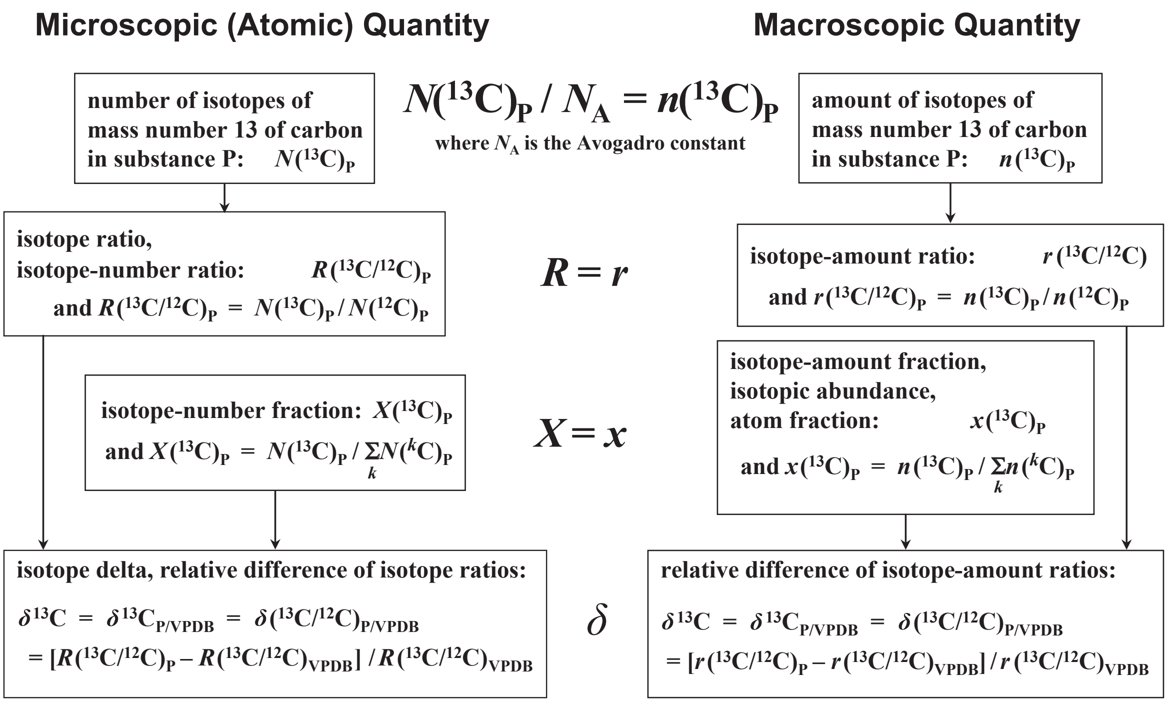
isotope delta, relative difference of isotope ratios:
$\delta^{i}\mathrm{E} = \delta^{i}\mathrm{E}_{\mathrm{P/std}} = \delta({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P/std}}$
$= [R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} - R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{std}}] / R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{std}}$

$$\delta$$

relative difference of isotope-amount ratios:
$\delta^{i}\mathrm{E} = \delta^{i}\mathrm{E}_{\mathrm{P/std}} = \delta({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P/std}}$
$= [r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} - r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{std}}] / r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{std}}$

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: $N(^{13}\mathrm{C})_\mathrm{P}$

$$N(^{13}\mathrm{C})_\mathrm{P} / N_\mathrm{A} = n(^{13}\mathrm{C})_\mathrm{P}$$

where N_A is the Avogadro constant

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

isotope ratio, isotope-number ratio: $R(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P}$

and $R(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P} = N(^{13}\mathrm{C})_\mathrm{P} / N(^{12}\mathrm{C})_\mathrm{P}$

$$R = r$$

isotope-amount ratio: $r(^{13}\mathrm{C}/^{12}\mathrm{C})$

and $r(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P} = n(^{13}\mathrm{C})_\mathrm{P} / n(^{12}\mathrm{C})_\mathrm{P}$

isotope-number fraction: $X(^{13}\mathrm{C})_\mathrm{P}$

and $X(^{13}\mathrm{C})_\mathrm{P} = N(^{13}\mathrm{C})_\mathrm{P} / \sum_k N(^{k}\mathrm{C})_\mathrm{P}$

$$X = x$$

isotope-amount fraction, isotopic abundance, atom fraction: $x(^{13}\mathrm{C})_\mathrm{P}$

and $x(^{13}\mathrm{C})_\mathrm{P} = n(^{13}\mathrm{C})_\mathrm{P} / \sum_k n(^{k}\mathrm{C})_\mathrm{P}$

isotope delta, relative difference of isotope ratios:

$$\delta^{13}\mathrm{C} = \delta^{13}\mathrm{C}_\mathrm{P/VPDB} = \delta(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P/VPDB}$$
$$= [R(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P} - R(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{VPDB}] / R(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{VPDB}$$

$$\delta$$

relative difference of isotope-amount ratios:

$$\delta^{13}\mathrm{C} = \delta^{13}\mathrm{C}_\mathrm{P/VPDB} = \delta(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P/VPDB}$$
$$= [r(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{P} - r(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{VPDB}] / r(^{13}\mathrm{C}/^{12}\mathrm{C})_\mathrm{VPDB}$$

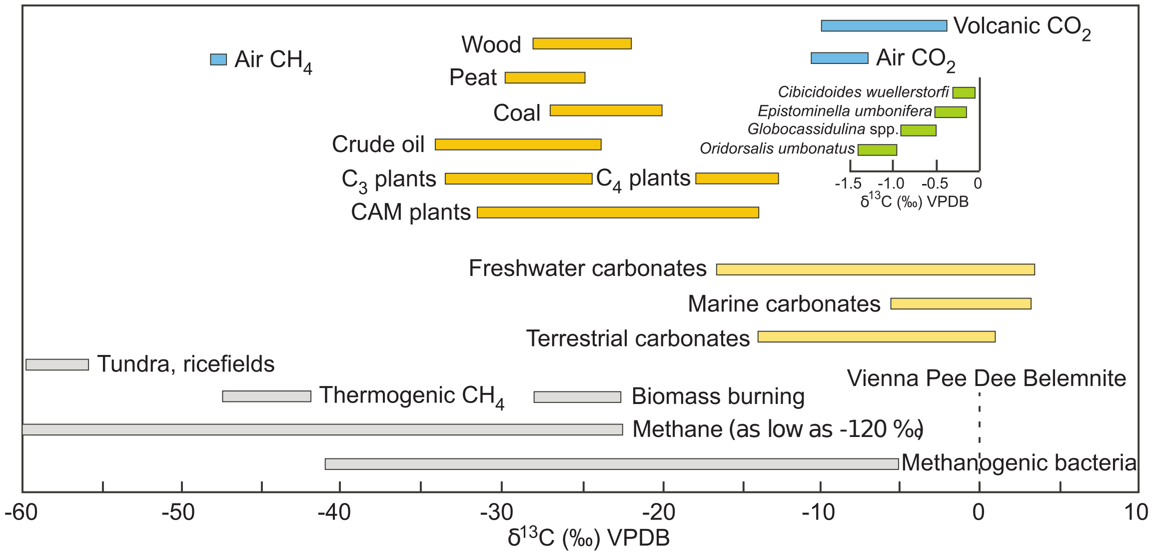
Source: Coplen (*Rapid Commun. Mass Spectrom.*, 2011)

Common Reference Standards

Standard	Ratio	Value (95% confidence)
SMOW	D/H	0.000 155 76 ± 0.000 000 10
	^{18}O/^{16}O	0.002 005 20 ± 0.000 000 43
	^{17}O/^{16}O	0.000 373 ± 0.000 015
PDB	^{13}C/^{12}C	0.011 237 2 ± 0.000 002 9
	^{18}O/^{16}O	0.002 067 1 ± 0.000 002 1
	^{17}O/^{16}O	0.000 379 ± 0.000 015
NBS19	^{13}C/^{12}C	0.011 202 ± 0.000 028
Air N_2	^{15}N/^{14}N	0.003 676 5 ± 0.000 008 1
Canyon Diablo Troilite (CDT)	^{34}S/^{32}S	0.045 004 5 ± 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 Relations

Multicomponent chemical system (Σ) with n parts/compartments
Overall system isotope ratio $R_\Sigma = N({}^i\mathrm{E})_\Sigma / N({}^j\mathrm{E})_\Sigma$

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

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

Material Balance Relations

Multicomponent chemical system (Σ) with n parts/compartments
Overall system isotope ratio $R_\Sigma = N(^i\mathrm{E})_\Sigma / N(^j\mathrm{E})_\Sigma$

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

$$R_\Sigma = \frac{N(^j\mathrm{E})_1}{N(^j\mathrm{E})_\Sigma}\left(\frac{N(^i\mathrm{E})_1}{N(^j\mathrm{E})_1}\right) + \cdots + \frac{N(^j\mathrm{E})_n}{N(^j\mathrm{E})_\Sigma}\left(\frac{N(^i\mathrm{E})_n}{N(^j\mathrm{E})_n}\right)$$

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

where χ_p is the system's mole fraction of the *reference isotope* $^j\mathrm{E}$ contained in part p

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

Do not confuse

- the *isotope-number fraction* of an isotope $^i\mathrm{E}$ in a substance P

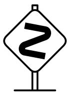
$$X(^i\mathrm{E})_\mathrm{P} = \frac{N(^i\mathrm{E})_\mathrm{P}}{\sum_k N(^k\mathrm{E})_\mathrm{P}}$$

$\rightarrow$ fraction of $^i\mathrm{E}$ atoms in all E atoms of a given P

- the *mole fraction* χ_p of isotope $^j\mathrm{E}$ of a part p in a system

$$\chi_p = \frac{N(^j\mathrm{E})_p}{N(^j\mathrm{E})_\Sigma} = \frac{N(^j\mathrm{E})_p}{\sum_p N(^j\mathrm{E})_p}$$

$\rightarrow$ fraction of $^j\mathrm{E}$ atoms in the system that are contained in p



Material Balance Relations With δ's

Since

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

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

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

which simplifies to

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

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."

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 $\mathrm{g\,cm^{-3}}$
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

$$\alpha_{\mathrm{A/B}} = \alpha_{(\mathrm{A-B})} = \frac{R_\mathrm{A}}{R_\mathrm{B}}$$

Example:

$$\mathrm{H_2O_{(l)} + HDS_{(g)} \rightleftharpoons HDO_{(l)} + H_2S_{(g)}}$$

- Phase A: $H_2O + HDO$ (water – ‘h2o’)
- Phase B: $H_2S + HDS$ (hydrogen sulfide – ‘h2s’)

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

Fractionation Constant

- Fractionation factors involving H isotopes highest
- Most often $\alpha_{(\mathrm{A-B})} \simeq 1$ and for practical usage we define

Fractionation Constant

$$\varepsilon_{(\mathrm{A-B})} = \alpha_{(\mathrm{A-B})} - 1$$

- Example:

$$^{12}\mathrm{CO}_{2\,(aq)} + \mathrm{H}^{13}\mathrm{CO}_3^- \leftrightharpoons {}^{13}\mathrm{CO}_{2\,(aq)} + \mathrm{H}^{12}\mathrm{CO}_3^-$$

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

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

Alternative Quantification of Isotope Effects

- Isotopic difference

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

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

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

  - for perfect gases, $\ln \alpha_{(\mathrm{A-B})}$ 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

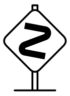
$$\begin{aligned}
\varepsilon_{\mathrm{(A-B)}} &= \alpha_{\mathrm{(A-B)}} - 1 \\
&= \frac{R_\mathrm{A}}{R_\mathrm{B}} - 1 \\
&= \frac{\delta_{\mathrm{A/std}} + 1}{\delta_{\mathrm{B/std}} + 1} - 1 \\
&= \frac{\delta_{\mathrm{A/std}} - \delta_{\mathrm{B/std}}}{\delta_{\mathrm{B/std}} + 1} \\
&= \frac{\Delta_{\mathrm{(A-B)/std}}}{\delta_{\mathrm{B/std}}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

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

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

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 $\delta_\mathrm{A} - \delta_\mathrm{B}$ 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

Kinetic Fractionation: Fractionation Factor $\alpha_{\mathrm{S/R}}$

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

$$\alpha_{\mathrm{S/P}} = \alpha_{(\mathrm{S-P})} = \frac{R_{\mathrm{S}}}{R_{\mathrm{P}}}$$

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

Mass Balance Equations

Reservoir with content $n \equiv n(\mathrm{E})$:

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

where

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

$$n(\mathrm{E}) = n({}^{j}\mathrm{E}) + \cdots + n({}^{i}\mathrm{E}) + \ldots$$

Question

How are the mass balance equations for ${}^{i}\mathrm{E}$, ${}^{j}\mathrm{E}$ and E related?

Problem to Solve

Solve a coupled differential equation problem:

- given
    - t_0 and t_{end} (time interval)
    - $n(t_0) = n_0$
    - $\delta^{13}\text{C}(t_0) = \delta_0$
    - 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

$$\begin{aligned}
n({}^j\text{E}) &= x({}^j\text{E}) \cdot n(\text{E}) \\
n({}^i\text{E}) &= x({}^i\text{E}) \cdot n(\text{E}) \\
n({}^i\text{E}) &= r({}^i\text{E}/{}^j\text{E}) \cdot n({}^j\text{E}) \\
J({}^j\text{E}) &= x({}^j\text{E})_J \cdot J(\text{E}) \\
J({}^i\text{E}) &= x({}^i\text{E})_J \cdot J(\text{E}) \\
J({}^i\text{E}) &= r({}^i\text{E}/{}^j\text{E})_J \cdot J({}^j\text{E})
\end{aligned}$$

Mass Balance Variables: Approximate Relationships

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

$$\begin{aligned} n(\mathrm{E}) &\simeq n({}^{j}\mathrm{E}) \\ x({}^{i}\mathrm{E}) &\simeq r({}^{i}\mathrm{E}/{}^{j}\mathrm{E}) \\ n({}^{i}\mathrm{E}) &\simeq r({}^{i}\mathrm{E}/{}^{j}\mathrm{E}) \cdot n(\mathrm{E}) \end{aligned}$$

$$\begin{aligned} J(\mathrm{E}) &\simeq J({}^{j}\mathrm{E}) \\ J({}^{i}\mathrm{E}) &\simeq r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_J \cdot J(\mathrm{E}) \end{aligned}$$

Mass Balance Equations for C-13

Exact relationships:

$$\begin{aligned} {}^{13}n &= {}^{13}x \cdot n(\mathrm{C}) \\ {}^{13}n &= {}^{13}r \cdot {}^{12}n \end{aligned}$$

$$\begin{aligned} {}^{13}J &= {}^{13}x_J \cdot J(\mathrm{C}) \\ {}^{13}J &= {}^{13}r_J \cdot {}^{12}J \end{aligned}$$

Approximations:

$$\begin{aligned} n(\mathrm{C}) &\simeq {}^{12}n \\ {}^{13}n &\simeq {}^{13}r \cdot n(\mathrm{C}) \end{aligned}$$

$$\begin{aligned} J(\mathrm{C}) &\simeq {}^{12}J \\ {}^{13}J &\simeq {}^{13}r_J \cdot J(\mathrm{C}) \end{aligned}$$

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

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

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

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

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

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

Approximate evolution equation for ${}^{13}n$:

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

The left-hand side develops as

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

Equating the two right-hand sides and rearranging leads to

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

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

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

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

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

where

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

Evolution Equation for ${}^{13}x$

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

${}^{13}x$ Equation (*exact*)

$$\frac{d\,{}^{13}x}{dt} = \Big(\sum({}^{13}x_{J_{\mathrm{in}}} - {}^{13}x) \cdot J_{\mathrm{in}}(\mathrm{C}) - \sum({}^{13}x_{J_{\mathrm{out}}} - {}^{13}x) \cdot J_{\mathrm{out}}(\mathrm{C}) \Big) \Big/ n$$

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

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

  and

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

In Practice: *Do's and Don'ts . . .*

From

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

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

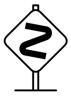
$$\frac{d\,^{13}r}{dt} \cdot n = \sum {}^{13}r_{J_{\mathrm{in}}} \cdot J_{\mathrm{in}}(\mathrm{C}) - \sum {}^{13}r_{J_{\mathrm{out}}} \cdot J_{\mathrm{out}}(\mathrm{C}) - {}^{13}r \cdot \frac{dn}{dt}$$

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

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

In Practice: *Do's and Don'ts . . .*

- Mathematically speaking, the two are identical
- However, numerically speaking, they are worlds apart:
  - Addition of many small terms in the "*Do*" version: terms in $J_{\mathrm{out}}(\mathrm{C})$ 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
    - ${}^{13}r_0 = {}^{13}r_{\mathrm{std}}(\delta_0 + 1)$
    - ${}^{13}x_0 = \dfrac{{}^{13}r_0}{1 + {}^{13}r_0}$
    - ${}^{13}n_0 = {}^{13}x_0 \cdot n_0$
2. Calculate $n(t)$ and ${}^{13}n(t)$
3. Whenever $\delta^{13}\mathrm{C}(t)$ is required
    - ${}^{13}x = \dfrac{{}^{13}n(t)}{n(t)}$
    - ${}^{13}r = \dfrac{{}^{13}x}{1 - {}^{13}x}$
    - $\delta^{13}\mathrm{C}(t) = \dfrac{{}^{13}r}{{}^{13}r_{\mathrm{std}}} - 1$

Useful References

- Coplen et al. (2002): *Isotope-abundance variations of selected elements (IUPAC Technical Report)*.
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