Appendix
Important Isotope Equations and Useful Conversions

Important Equations

1. Definition of δ (Section 2.1)

$$\delta^{H} X = [(R_{\text{SAMPLE}} / R_{\text{STANDARD}}) - 1] * 1000,$$

where X = H, C, N, O, or S, the superscript H gives the respective heavy isotope mass of that element (^{2}H, ^{13}C, ^{15}N, ^{18}O, or ^{34}S), and R is the ratio of the heavy isotope to the light isotope for the element, ^{2}H/^{1}H, ^{13}C/^{12}C, ^{15}N/^{14}N, ^{18}O/^{16}O, or ^{34}S/^{32}S.

International standards listed in Table 2.1 have these R_{STANDARD} values: 0.00015576 for δ^{2}H (SMOW), 0.0003799 for δ^{17}O (SMOW), 0.0020052 for δ^{18}O (SMOW), 0.01118 for δ^{13}C (VPDB), 0.0036765 for δ^{15}N (AIR), 0.0078772 for δ^{33}S (VCDT), and 0.0441626 for δ^{34}S (VCDT).

2. % Heavy Isotope, Atom % or ^{H}AP (Section 2.1)

The % heavy isotope is also known as atom % of the heavy isotope or ^{H}AP

$$^{H}AP = 100 * (\delta + 1000) / [(\delta + 1000 + (1000 / R_{\text{STANDARD}})]$$

(Conversion 4 below derives this equation from the δ definition. Also note that this equation is not strictly exact for O and S that have more than two stable isotopes, but the equation still provides an excellent approximation of ^{H}AP for ^{18}O and ^{34}S in almost all cases).

3. Fractionation (Sections 2.1, 4.6, 7.1–7.2, 7.5–7.7, Technical Supplement 2C)

α

is the fractionation factor given in terms of kinetic (k) rate constants for light (L) and heavy (H) isotope-substituted molecules,

$$\alpha = {}^{L}k/{}^{H}k.$$

Δ

is the fractionation factor in positive ‰ (permil) units,

$$\Delta = (\alpha - 1) * 1000.$$

Fractionation in All Reactions

(Sections 2.1, 4.6, 7.1, Technical Supplements 2C and 7B.)

$$\text{Approximate Instantaneous Fractionation: } \delta_{\text{PRODUCT}} = \delta_{\text{SOURCE}} - \Delta.$$

$$\text{Exact Instantaneous Fractionation: } R_{\text{PRODUCT}} = R_{\text{SUBSTRATE}}/\alpha.$$

Fractionation in a Closed System

(Sections 7.1–7.2, Technical Supplement 7B.) In a simple forward reaction with one product formed from substrate in a closed system with isotope fractionation Δ or α, there are approximate and exact isotope equations for residual substrate (*RS*), instantaneous product (*IP*), and accumulated product (*AP*), with isotope values expressed relative to initial substrate (INPUT). The isotope compositions are related to the fraction f of substrate converted to product, where f is the fraction reacted.

Approximate Equations

$$\delta_{RS} = \delta_{\text{INPUT}} - \Delta * \ln(1 - f)$$

$$\delta_{IP} = \delta_{\text{INPUT}} - \Delta * [1 + \ln(1 - f)]$$

$$\delta_{AP} = \delta_{\text{INPUT}} + \Delta * ((1 - f)/f) * \ln(1 - f).$$

Exact Equations

$$R_{RS} = R_{\text{INPUT}} * (1 - f)^{1/\alpha - 1}$$

$$R_{IP} = (1/\alpha) * R_{\text{INPUT}} * (1 - f)^{1/\alpha - 1}$$

$$R_{AP} = [R_{\text{INPUT}} - (1 - f) * R_{RS}]/f.$$

Fractionation in an Open System

(Sections 4.6, 7.1, 7.7.) In an open system, product is formed from substrate in a continual manner, with both product and residual substrate exiting the site of reaction.

Approximate Equations

$$\delta_{RS} = \delta_{\text{INPUT}} + \Delta * f$$

$$\delta_{\text{PRODUCT}} = \delta_{\text{INPUT}} - \Delta * (1 - f)$$

Exact Equations

$$R_{RS} = R_{\text{INPUT}} * (f * \alpha + 1 - f)$$

$$R_{\text{PRODUCT}} = R_{\text{INPUT}} * (f + (1 - f)/\alpha)$$

Fractionation in an Equilibrium Exchange Reaction

(Section 7.6.) Where two substances A and B are involved in an exchange reaction, and substance A becomes relatively enriched in heavy isotopes, the equilibrium fractionation factor for the overall reaction can be given exactly as α_{EQ} or approximately as Δ_{EQ}.

Approximate Equation

$$\Delta_{EQ} = \delta_{\text{A}} - \delta_{\text{B}}$$

Exact Equation

$$\alpha_{EQ} = R_{\text{A}}/R_{\text{B}} = (1000 + \delta_{\text{A}})/(1000 + \delta_{\text{B}})$$

4. I Chi Equations for a One-Box Open System Model (Sections 4.3, 4.6, 7.7)

I Chi equations give changes in mass and isotopes between time intervals t and $t + 1$. The equations specify gains with isotope mixing, and losses with isotope fractionation.

Gains

Where m terms are masses involved in the mixing

$$m_{t+1} = m_t + m_{\text{GAIN}}$$

Approximate Equation for Isotope Mixing during Gains

$$\delta_{t+1} = (\delta_t * m_t + m_{\text{GAIN}} * \delta_{\text{GAIN}})/m_{t+1}$$

Exact Equations for Isotope Mixing During Gains

The exact equations for δ_{t+1} during mixing gains require converting δ to ${}^{\text{H}}AP$, calculating mixing, then reconverting to δ. With ${}^{\text{H}}AP$ calculated from δ,

$${}^{\text{H}}AP = 100 * (\delta + 1000)/[(\delta + 1000 + (1000/R_{\text{STANDARD}})]$$

mixing is given by

$$^{\mathrm{H}}AP_{t+1} = \left({}^{\mathrm{H}}AP_t * m_t + m_{\mathrm{GAIN}} * {}^{\mathrm{H}}AP_{\mathrm{GAIN}} \right) / m_{t+1}$$

To convert $^{\mathrm{H}}\mathrm{AP}_{t+1}$ to δ_{t+1}, first solve for atom % for the light isotope, $^{\mathrm{L}}AP = 100 - {}^{\mathrm{H}}AP$, then

$$\delta_{t+1} = \left[\left({}^{\mathrm{H}}AP / {}^{\mathrm{L}}AP \right) / R_{\mathrm{STANDARD}} - 1 \right] * 1000$$

Losses

$$m_{t+1} = m_t - m_{\mathrm{LOSS}} \quad \text{and} \quad f = \text{fraction lost from the substrate pool}$$
$$f = m_{\mathrm{LOSS}} / m_t = 1 - m_{t+1} / m_t .$$

Approximate Equation for Isotope Fractionation during Loss

$$\delta_{t+1} = \delta_t + \Delta * f$$

Exact Equation for Isotope Fractionation During Loss

$$\delta_{t+1} = (\delta_t + 1000) * (f * \alpha + 1 - f) - 1000$$

5. Simple Two-Source Mixing (Section 5.3)

Two sources have different δ values and mix to produce a sample. The fractional contributions from the sources to the sample are $f_1 + f_2$ where

$$f_1 + f_2 = 1, \quad f_2 = 1 - f_1$$
$$f_1 = (\delta_{\mathrm{SAMPLE}} - \delta_{\mathrm{SOURCE2}}) / (\delta_{\mathrm{SOURCE1}} - \delta_{\mathrm{SOURCE2}})$$

6. Two-Source Mixing with One or More Spiked Samples (Technical Supplement 6B)

For samples that have been spiked with heavy isotope to very high levels, for example, $\delta^{13}\mathrm{C} > 4000$ or $\delta^{15}\mathrm{N} > 12{,}000‰$, the δ notation becomes inexact for mixing (see Technical Supplement 6B) and requires conversion to atom % or $^{\mathrm{H}}AP$:

$$^{\mathrm{H}}AP = 100 * (\delta + 1000) / [(\delta + 1000 + (1000 / R_{\mathrm{STANDARD}})]$$

The exact mixing equation for f_1, the fractional contribution of source 1, is always:

$$f_1 = \left({}^{\mathrm{H}}AP_{\mathrm{SAMPLE}} - {}^{\mathrm{H}}AP_{\mathrm{SOURCE2}} \right) / \left({}^{\mathrm{H}}AP_{\mathrm{SOURCE1}} - {}^{\mathrm{H}}AP_{\mathrm{SOURCE2}} \right)$$

7. Two-Source Mixing by Mass and Weighting (W) Factors (Section 5.4)

$$\delta_{\mathrm{SAMPLE}} = (m_1 * W_1 * \delta_{\mathrm{SOURCE1}} + m_2 * W_2 * \delta_{\mathrm{SOURCE2}}) / (m_1 * W_1 + m_2 * W_2)$$

8. Calculating Source Contributions when Two Sources Have Different Concentrations (Section 5.4)

When two sources combine to form a mixture, isotopes help monitor the source contributions at two levels. At the first level, isotopes budget the fractional contributions by element, for example, δ^{15}N measurements budget elemental N contributions by the equations given above:

$$f_1 = (\delta_{\mathrm{SAMPLE}} - \delta_{\mathrm{SOURCE2}}) / (\delta_{\mathrm{SOURCE1}} - \delta_{\mathrm{SOURCE2}}) \quad \text{and} \quad f_2 = 1 - f_1$$

But when sources have different concentrations of the element being budgeted, mixing calculations extend to a second, more general, level involving total masses being mixed, as is perhaps illustrated best by example. Suppose that δ^{15}N measurements show that two sources each contribute N equally to a mixed sample ($f_1 = f_2 = 0.5$), but source 2 contains a 2 times higher N concentration. In this case, only half as much mass from source 2 is needed to match the N contribution from source 1. The mixing is 1:1 for nitrogen, but because of the different N concentrations, the mixing is 2:1 by total mass. To calculate the contributions at this more general level of total masses involved, usually weightings (W) are assigned to reflect the different concentrations, for example, with W_1 and W_2 representing different % N values for the sources. The fractional contributions to the total mass (f_{TOTAL}) from the two sources is

$$f_{\mathrm{TOTAL1}} = f_1 * W_2 / (f_1 * W_2 + f_2 * W_1) \quad \text{and} \quad f_{\mathrm{TOTAL2}} = 1 - f_{\mathrm{TOTAL1}}$$

9. Blank Corrections for Contaminants Contributing to a Sample; Keeling Plots (Sections 3.5, 5.7)

Blanks contribute to observed results in many mixing situations such as laboratory analysis. The effects of a blank can be factored out using two-source mixing equations where the contaminating blank is fixed in both isotope value and amount. In this case, the mass balance mixing equations are:

$$m_{\mathrm{OBSERVED}} = m_{\mathrm{TRUE}} + m_{\mathrm{BLANK}}$$

and

$$\delta_{\text{OBSERVED}} * m_{\text{OBSERVED}} = \delta_{\text{TRUE}} * m_{\text{TRUE}} + \delta_{\text{BLANK}} * m_{\text{BLANK}}$$

where the observed δ values are a mixture of true sample and contaminating blank. This can be rearranged to:

$$\delta_{\text{OBSERVED}} = \delta_{\text{TRUE}} + (\delta_{\text{BLANK}} - \delta_{\text{TRUE}}) * (m_{\text{BLANK}} / m_{\text{TRUE}})$$

This rearrangement yields a straight line when laboratory data for different-sized replicates of the same sample is plotted as (x,y) data in the form (1/mass, δ) so that

$$y - \text{intercept} = \delta_{\text{TRUE}} \quad \text{and} \quad \text{Slope} = m_{\text{BLANK}} * (\delta_{\text{BLANK}} - \delta_{\text{TRUE}})$$

The mass of the blank, m_{BLANK}, usually can be obtained from direct measurement of blanks, allowing calculation of the δ_{BLANK} from the regression line:

$$\delta_{\text{BLANK}} = \delta_{\text{TRUE}} + \text{slope} / m_{\text{BLANK}}$$

Note: it is often difficult to directly measure the δ_{BLANK} for small samples, but the approach outlined here extrapolates δ_{BLANK}, essentially by observing effects of the blank on actual samples. Finally, with known values for m_{BLANK} and δ_{BLANK}, corrections can be made to all experimental data:

$$\delta_{\text{TRUE}} = (\delta_{\text{BLANK}} * m_{\text{BLANK}} + \delta_{\text{OBSERVED}} * m_{\text{OBSERVED}}) / (m_{\text{OBSERVED}} - m_{\text{BLANK}})$$

This approach has also been used in other instances of two-source mixing where the second source is not a contaminant, but just a source fixed in both mass and isotope values, for example, in Keeling plots and for estimating background corrections in sediment cores (Sections 3.5, 5.7).

10. Calculating Trophic Level (TL) based on $\delta^{15}N$ (Problem 10, Chapter 5)

In food webs where the $\delta^{15}N$ values of plants, herbivores and higher-level consumers are measured, the average trophic level (TL) of a consumer can be calculated as

$$TL = 1 + \left(\delta^{15}\text{N}_{\text{CONSUMER}} - \delta^{15}\text{N}_{\text{PLANT}}\right) / 3$$

using plants as the basal level of the food web, or

$$TL = 2 + \left(\delta^{15}\text{N}_{\text{CONSUMER}} - \delta^{15}\text{N}_{\text{HERBIVORE}}\right) / 3$$

using herbivores as the basal second level of the food web. The value "3" in the denominator in these equations represents the permil (‰) increase in ^{15}N per trophic level, most recently estimated as 2.2‰ for invertebrates and 3.4‰ for vertebrates (see Chapter 5.5 for references). The "3" used in the denominator of these equations is thus an approximate average value. Plants represent TL 1 in these equations.

11. Calculating Trophic Level (TL) Corrections to $\delta^{13}C$ Food Web Data (Problem 10, Chapter 5)

There is a small average increase in animal $\delta^{13}C$ values with each trophic level. Before using $\delta^{13}C$ to make source assessments, this ^{13}C trophic fractionation should be factored out, and "corrected $\delta^{13}C$" values used for the mixing models:

$$\text{Corrected } \delta^{13}C = \text{Measured Animal } \delta^{13}C - 0.5 * (TL - 1)$$

The *TL* is usually estimated as above from $\delta^{15}N$ but can also be estimated from gut content data. The 0.5‰ ^{13}C enrichment factor varies from 0–2‰, with 0.5‰ representing an average value (see Chapter 5.5 for references). Plants represent *TL* 1 in this equation.

Useful Conversions

Conversion 1

Two samples are measured versus a common standard. What is the true isotope difference between the two samples?

$$\delta_1 = [(R_1/R_0) - 1]1000$$
$$\delta_2 = [(R_2/R_0) - 1]1000$$
$$\delta_{1,2} = [(R_1/R_2) - 1]1000 = ?$$

Rearrange definitions to solve for R_1 and R_2:

$$R_1 = R_0 * (\delta_1 + 1000)/1000$$
$$R_2 = R_0 * (\delta_2 + 1000)/1000$$

Divide R_1 by R_2 and cancel R_0 and 1000 values:

$$R_1/R_2 = (\delta_1 + 1000)/(\delta_2 + 1000)$$

Subtract 1 and multiply by 1000:

$$\delta_{1,2} = \{[(\delta_1 + 1000)/(\delta_2 + 1000)] - 1\} * 1000 \quad \text{or}$$
$$\delta_{1,2} = [(\delta_1 - \delta_2)/(\delta_2 + 1000)] * 1000$$

for example, $\delta_1 = -6‰$, $\delta_2 = -16‰$, $\delta_{1,2} = 10.16‰$, not 10‰.

Note that this relationship is often given in a slightly modified form when the δ values are expressed as fractions instead of in ‰ units, for example, if $\delta_1 = -0.006$ not −6‰ and $\delta_2 = -0.016$ not −16‰ then:

$$\delta_{1,2} = (\delta_1 - \delta_2)/(\delta_2 + 1)$$

with the resulting $\delta_{1,2}$ value also expressed as a fraction, 0.01016. In this usage, permil values result when the scientist consciously multiplies by 1000, so that the fractional δ values of −0.006, −0.016, and 0.01016 become permil values of −6‰, −16‰, and 10.16‰ (*Annual Review of Plant Physiology and Plant Molecular Biology* 40:503–537; 1989)

Conversion 2

A sample is measured versus standard 1. How should you express the isotope value of this sample value versus standard 2, when the values of standards are known?

$$\delta_1 = [(R_{\text{SAMPLE}}/R_1) - 1]1000$$
$$\delta_2 = [(R_1/R_2) - 1]1000$$
$$\delta_3 = [(R_{\text{SAMPLE}}/R_2) - 1]1000 = ?$$

Rearrange definitions to solve for R_{SAMPLE} and R_2:

$$R_{\text{SAMPLE}} = R_1 * (\delta + 1000)/1000$$
$$R_2 = (1000 * R_1)/(\delta_2 + 1000)$$

Divide R_{SAMPLE} by R_2,

$$R_{\text{SAMPLE}}/R_2 = R_1 * (\delta_1 + 1000) * (\delta_2 + 1000)/(R_1 * 1{,}000{,}000)$$

Cancel R_1 values, subtract 1 and multiply by 1000,

$$\delta_3 = [(\delta_1 + 1000) * (\delta_2 + 1000) - 1{,}000{,}000]/1000$$

for example, $\delta_1 = -10$, $\delta_2 = -20$, $\delta_3 = -29.8$, not −30‰.

Conversion 3

This conversion deals with a common laboratory problem, calibrating a new tank of laboratory gas for use as a standard for δ measurements. To perform

the calibration, you use a known reference compound. These known reference compounds are available from agencies such as the National Institute of Standards (NIST) in the United States and the International Atomic Energy Agency (IAEA) in Austria. You measure the known reference compound versus the unknown tank gas, then calculate the isotope ratio (R_1) of the new tank gas. With this value, it is then possible to routinely use the new tank gas as a working standard. But to publish your results, you have to recalculate δ values of samples measured versus this tank gas in terms of the primary international standard, for example, VPDB in the case of carbon isotopes. This problem has two parts, (a) calibration of the unknown tank standard, and (b) recalculation of results versus an international standard.

a. You have an unknown lab standard gas and a reference compound whose δ value has been calibrated versus the international primary reference standard. You measure this reference compound versus the unknown tank gas. What is the isotope ratio R_1 for the tank gas?

$$\delta_1 = [(R_{\text{REFERENCE COMPOUND}}/R_1) - 1] * 1000 \quad \text{and}$$
$$\delta_2 = [(R_{\text{REFERENCE COMPOUND}}/\text{R}_{\text{INTERNATIONAL REFERENCE}}) - 1] * 1000$$
$$R_1 = ?$$

where $R_{\text{INTERNATIONAL REFERENCE}}$ is the known isotope ratio in an international standard reference material, for example, 0.01118 for carbon isotope measurements using the VPDB standard given in Table 2.1.

Rearrange equations for R_1 and $R_{\text{REFERENCE COMPOUND}}$:

$$R_1 = R_{\text{REFERENCE COMPOUND}} * 1000/(\delta_1 + 1000)$$
$$R_{\text{REFERENCE COMPOUND}} = R_{\text{INTERNATIONAL REFERENCE}} * (\delta_2 + 1000)/1000$$

substituting for $R_{\text{REFERENCE COMPOUND}}$,

$$R_1 = R_{\text{INTERNATIONAL REFERENCE}} * (\delta_2 + 1000)/(\delta_1 + 1000)$$

For example, $\delta_1 = -10$, $\delta_2 = -20$, $R_{\text{INTERNATIONAL REFERENCE}} = 0.01118$; then $R_1 = 0.011067$ and the δ value for your tank standard versus the international reference material = –10.10‰. You have now calibrated your unknown tank gas (a tertiary standard) using a known reference material (a secondary standard) that was calibrated originally against an international reference material (the primary standard).

b. And once you know R_1, the ratio value of your previously unknown tank gas, how do you convert δ values measured against this tank gas to δ values referenced to an international standard? For example, you measure a second sample versus this tank gas as $\delta_3 = [(R_{\text{SAMPLE2}}/R_1) - 1] * 1000$. What

is δ_4, the δ value of this second sample expressed versus the international standard?

So if

$$\delta_3 = [(R_{\text{SAMPLE2}}/R_1) - 1] * 1000$$
$$\delta_4 = [(R_{\text{SAMPLE2}}/R_{\text{INTERNATIONAL REFERENCE}}) - 1] * 1000 = ?$$

Rearrange the δ_3 equation for R_{SAMPLE2}:

$$R_{\text{SAMPLE2}} = R_1 * (\delta_3 + 1000)/1000$$

and substitute this value in the equation for δ_4:

$$\delta_4 = (\delta_3 + 1000) * (R_1/R_{\text{INTERNATIONAL REFERENCE}}) - 1000$$

For example, if $R_{\text{INTERNATIONAL REFERENCE}} = 0.01118$, $R_1 = 0.011067$ as determined above, and δ_3 measures –30‰, $\delta_4 = -39.8$‰. With these calculations, you can now use the newly calibrated tank gas and publish δ_4 values expressed relative to the primary international standard.

Conversion 4

How does one convert from δ to R_{SAMPLE}, ${}^{\text{H}}F$ and ${}^{\text{H}}AP$ (atom % of the heavy isotope) when $\delta = [(R_{\text{SAMPLE}}/R_{\text{STANDARD}}) - 1]1000$? And how does one convert back to δ from ${}^{\text{H}}AP$ values?

Calculate R_{SAMPLE}, the ratio of heavy-to-light isotope from rearranging the δ definition:

$$R_{\text{SAMPLE}} = [(\delta/1000) + 1] * R_{\text{STANDARD}}$$

(Note: see Table 2.1 for R_{STANDARD} values). To calculate ${}^{\text{H}}F$ and ${}^{\text{L}}F$, the respective fractions of heavy and light isotope in the sample, remember that R is the ratio of heavy-to-light isotopes, or:

$$R = {}^{\text{H}}F/{}^{\text{L}}F \quad \text{and that } {}^{\text{H}}F + {}^{\text{L}}F = 1, \quad \text{so that} \quad R = {}^{\text{H}}F/(1 - {}^{\text{H}}F)$$

Substituting for R_{SAMPLE} and rearranging, one obtains:

$${}^{\text{H}}F = (\delta + 1000)/[\delta + 1000 + (1000/R_{\text{STANDARD}})]$$

To calculate atom % for the heavy isotope, ${}^{\text{H}}AP$

$${}^{\text{H}}AP = 100 * {}^{\text{H}}F \quad \text{so that}$$
$${}^{\text{H}}AP = 100 * (\delta + 1000)/[(\delta + 1000 + (1000/R_{\text{STANDARD}})]$$

To convert from ${}^{H}AP$ to δ, solve for atom % for the light isotope,

$$ {}^{L}AP = 100 - {}^{H}AP, \quad \text{then}$$

$$ \delta = \left[\left({}^{H}AP / {}^{L}AP \right) / R_{\text{STANDARD}} - 1 \right] * 1000$$

Conversion 5

You find ratio (R) values for a standard, but want to know the fractional abundances or F values. For example, for an oxygen standard you find that ${}^{17}R = 0.000402$ and ${}^{18}R = 0.0020052$, what are F values?

You can write the following equalities.

$$ {}^{17}R = 0.000402 = {}^{17}F / {}^{16}F$$

$$ {}^{18}R = 0.0020052 = {}^{18}F / {}^{16}F$$

$$ {}^{16}F + {}^{17}F + {}^{18}F = 1$$

Simplify the equations by removing the R terms:

$$ {}^{17}F = 0.000402 * {}^{16}F$$

$$ {}^{18}F = 0.0020052 * {}^{16}F$$

$$ {}^{16}F + 0.000402 * {}^{16}F + 0.0020052 * {}^{16}F = 1 \quad \text{so that}$$

$$ {}^{16}F = 1 / (1 + 0.000402 + 0.0020052)$$

Solving the last equation for ${}^{16}F$ then substituting the ${}^{16}F$ value in the two previous equations, one obtains: ${}^{16}F = 0.997598581$, ${}^{17}\text{F} = 0.000401035$, and ${}^{18}\text{F} = 0.002000385$.

Index

T