Chapter 2

Fundamentals of Isotope Geochemistry

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2.1 Introduction

Of all the methods used to understand hydrologic processes in small catchments, applications of tracers--in particular isotope tracers--have been the most useful in terms of providing new insights into hydrologic processes. This is because they integrate small-scale variability to give an effective indication of catchment-scale processes (McDonnell and Kendall, 1992; Buttle, 1994). In contrast, internal watershed *point* measurements, such as those of water level or groundwater composition, cannot be used without extrapolation or additional assumptions about catchment behavior. Isotopes are also "applied" at the watershed scale (i.e., they are within all components of the hydrologic cycle). In particular, ^{18}O, ^{2}H, and ^{3}H are integral parts of natural water molecules that fall as rain or snow (meteoric water) each year over a watershed and, consequently, are ideal tracers of water. This no cost, long-term, and wide-spread *application* of these natural tracers allows hydrologists to study runoff generation on scales ranging from macropores to hillslopes to first- and higher- order streams (Sklash, 1990).

Environmental isotopes are natural and anthropogenic isotopes whose wide distribution in the hydrosphere can assist in the solution of hydrogeochemical problems. Typical uses of environmental isotopes in hydrology include:

- identification of mechanisms responsible for streamflow generation
- testing flowpath and water-budget models developed using hydrometric data
- characterization of flowpaths that water follows from the time precipitation hits the ground until discharge at the stream
- determination of weathering reactions that mobilize solutes along those flowpaths
- determination of the role of atmospheric deposition in controlling water chemistry
- identification of the sources of solutes in contaminated systems and
- assessment of biologic cycling of nutrients within an ecosystem.

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Environmental isotopes can be used as tracers of waters and solutes in catchments because:

- Waters recharged at different times, in different locations, or that followed different flowpaths are often isotopically distinct; in other words, they have distinctive "fingerprints".

- Unlike most chemical tracers, environmental isotopes are relatively conservative in reactions with catchment materials. This is especially true of oxygen and hydrogen isotopes in water; meteoric waters retain their distinctive fingerprints until they mix with waters of different compositions or, in the case of isotopes of dissolved species, there are reactions with minerals or other fluids.

- Solutes in catchment waters that are derived from atmospheric sources are commonly isotopically distinct from solutes derived from geologic and biologic sources within the catchment.

- Both biological cycling of solutes and water/rock reactions often change isotopic ratios of the solutes in predictable and recognizable directions; these interactions often can be reconstructed from the isotopic compositions.

- If water from an isotopically distinctive source (e.g., rain with an unusual isotopic composition) is found along a flowpath, it provides proof for a hydrologic connection, despite any hydraulic measurements or models to the contrary.

Given all these powerful applications, why do environmental hydrogeologists continue to under utilize isotopes? The most probable explanations are fear of the unknown and the sometimes awkward terminology used in this field. We hope to address and redress these problems in this book.

Before embarking on the fundamentals of isotope geochemistry, we would like to close this introduction with a cautionary note first presented in 1983 at a short-course on Isotope Hydrology co-taught by Tyler B. Coplen and Carol Kendall to scientists at the U.S. Geological Survey. This very appropriate note has been repeated at each subsequent USGS course we have taught:

> *Fretwell's Law:* "Warning! Stable isotope data may cause severe and contagious stomach upset if taken alone. To prevent upsetting reviewers' stomachs and your own, take stable isotope data with a healthy dose of other hydrologic, geologic, and geochemical information. Then, you will find stable isotope data very beneficial." (Marvin O. Fretwell, pers. comm. 1983).

Environmental isotopes *can* be a useful tool to help deduce geochemical processes. However, to avoid breaking Fretwell's Law, make sure that isotopic measurements are used along with measurements of major and minor trace elements and judicious amounts of hydrologic data to test hypotheses about hydrologic and geochemical mechanisms. In fact, one of the most powerful applications of isotopic measurements is their use in confirming or rejecting models derived from the use of other techniques. Isotopic measurements can also provide input for mass-balance calculations and quantitative constraints on reaction progress.

2.2 Fundamentals of Isotope Geochemistry

The following section presents a very brief discussion of the fundamentals of stable and radioisotope geochemistry, intended to provide readers with the necessary background information to understand the succeeding chapters. Many of the topics below are discussed in more detail in individual chapters. For more information on isotope systematics, the readers are encouraged to examine the following isotope reference books: Clark and Fritz (1997), Dickin (1995), Faure (1986), and Gat and Gonfiantini (1981). The first of these is a textbook intended for upper-division and graduate hydrogeology students, and contains problem sets.

2.2.1 Definitions

Isotopes are atoms of the same element that have different numbers of *neutrons*. Differences in the number of neutrons among the various isotopes of an element mean that the various isotopes have different masses. The superscript number to the left of the element designation is called the *mass number* and is the sum of the number of protons and neutrons in the isotope (Figure 2.1). For example, among the hydrogen isotopes, deuterium (denoted as D or ^{2}H) has one neutron and one proton. This mass number of 2 is approximately equal to twice the mass of protium (^{1}H), whereas tritium (^{3}H) has two neutrons and its mass is approximately three times the mass of protium. Isotopes of the same element have the same number of protons. For example, all isotopes of oxygen have 8 protons; however, an oxygen atom with a mass of 18 (denoted ^{18}O) has 2 more neutrons than oxygen with a mass of 16 (^{16}O). Isotope names are usually pronounced with the element name first, as in "oxygen-18" instead of "18-oxygen." In many texts, especially older ones typeset without superscripts, the mass number is shown to the right of the element abbreviation, as in C-13 or C^{13} for carbon-13.

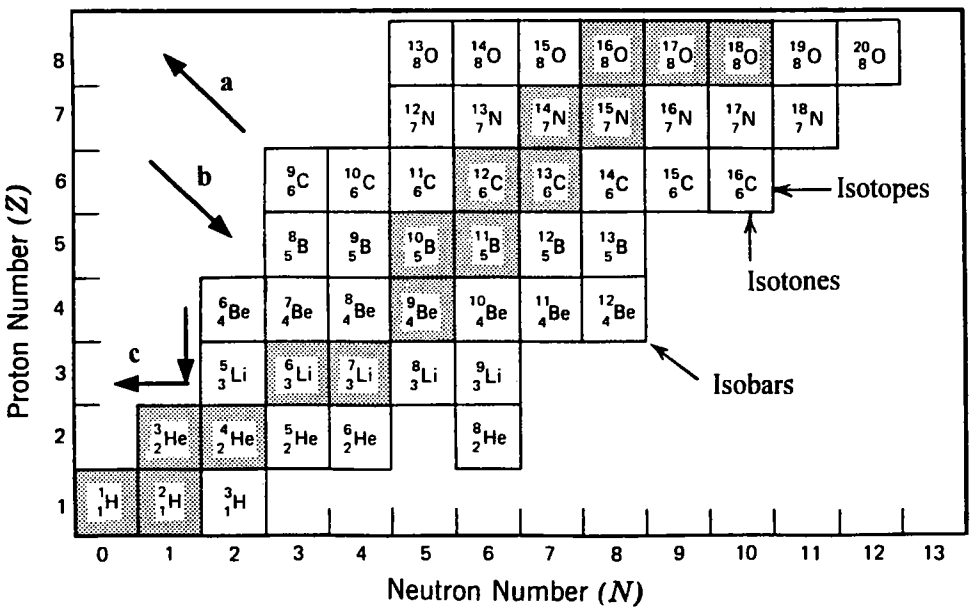


Figure 2.1. Partial chart of the elements. Each square represents a particular nuclide. The shaded squares are stable atoms and the unshaded squares are unstable or radioactive nuclides. Arrows at the left side of the diagram show the shifts in proton and neutron number caused by different decay mechanisms: beta decay (a), positron decay and beta capture (b), and alpha decay (c). Modified from Faure (1986).

The original isotopic compositions of planetary systems are a function of nuclear processes in stars. Over time, isotopic compositions in terrestrial environments change by the processes of radioactive decay, cosmic ray interactions, mass-dependent fractionations that accompany inorganic and biological reactions, and anthropogenic activities such as the processing of nuclear fuels, reactor accidents, and nuclear-weapons testing. *Radioactive* (unstable) isotopes are *nuclides* (isotope-specific atoms) that spontaneously disintegrate over time to form other isotopes. During the disintegration, radioactive isotopes emit *alpha* or *beta* particles and sometimes also *gamma rays*. *Stable* isotopes are nuclides that do not appear to decay to other isotopes on geologic time scales, but may themselves be produced by the decay of radioactive isotopes.

Naturally occurring nuclides define a path in the chart of nuclides, corresponding to the greatest stability of the neutron/proton (N/Z) ratio. For nuclides of low atomic mass, the greatest stability is achieved when the number of neutrons and protons are approximately equal ($N = Z$); these are the so-called *stable* isotopes (denoted as shaded nuclides in Figure 2.1). However, as the atomic mass increases, the stable neutron/proton ratio increases until $N/Z = 1.5$. Radioactive decay occurs when changes in N and Z of an unstable nuclide cause the transformation of an atom of one nuclide into that of another, more stable nuclide; these radioactive nuclides are called *unstable* nuclides (denoted as the non-shaded nuclides in Figure 2.1).

Atoms produced by the radioactive decay of other nuclides are termed *radiogenic*. A few nuclides are produced by cosmic ray bombardment of stable nuclides in the atmosphere and are termed *cosmogenic*. Other nuclides may be created by the addition of neutrons produced by the alpha decay of other nuclides (neutron activation). Alternatively, the neutron addition can displace a proton in the nucleus, creating a nuclide of the same atomic mass but lower atomic number. Nuclides produced by these two processes are termed *lithogenic*. If the daughter product is radioactive, it will decay to form an isotope of yet another element. This process will continue until a stable nuclide is produced. For example, uranium and thorium decay to form other radionuclides that are themselves radioactive and decay to other radionuclides, and so on until stable lead isotopes are formed (see Chapter 20 for uranium decay chains). Although the terms *parent* and *daughter* nuclides are commonly used, these terms can be misleading. Only *one* atom is involved during radioactive decay; that is, the daughter nuclide is the same nuclide as the parent atom. However, after radioactive decay it has a different number of neutrons in its nucleus.

The change in the number of neutrons can occur in a variety of ways (Figure 2.1). However, the four mechanisms described below are the most common and produce the radiogenic nuclides most relevant to hydrologic and geologic studies:

Beta decay occurs when nuclides deficient in protons transform a neutron into a proton and an electron, and expel the electron from the nucleus as a negative β particle (β^-), thereby increasing the atomic number by one while the number of neutrons is reduced by one.

Positron decay occurs when nuclides deficient in neutrons transform a proton into a neutron, an electron (β^+), and a neutrino, thereby decreasing the atomic number by one and increasing the neutron number by one. The daughters are *isobars* (nuclides of equal mass) of their parent and are isotopes of different elements.

Beta capture (or electron capture) occurs when nuclides deficient in neutrons transform a proton into a neutron plus neutrino by the capture of an electron by a proton, thereby decreasing the number of protons in the nucleus by one. Both this and positron decay yield a radiogenic nuclide that is an isobar of the parent nuclide.

Alpha decay occurs when heavy atoms above $Z = 83$ in the nuclide chart emit an alpha particle, which consists of a helium nuclei with two neutrons, two protons, and a 2^+ charge. This radiogenic daughter product in *not* an isobar of its parent nuclide because its mass is reduced by four (see Figure 2.1).

For example, the radioisotope (radioactive isotope) ^{14}C is produced in the atmosphere by cosmic ray neutron interaction with ^{14}N. ^{14}C has a half-life of about 5730 years, and decays back to stable ^{14}N by emission of a beta particle. The *decay equation* below expresses the change in the concentration (activity) of the nuclide over time:

$$A_t = A_o \cdot e^{-\lambda t} \tag{2.1}$$

where A_o is the initial activity of the parent nuclide, and A_t is its activity after some time "t." The decay constant "λ" is equal to $\ln (2/t^{1/2})$. Note that the decay rate is only a function of the activity of the nuclide and time, and that temperature and other environmental parameters appear to have no effect on the rate.

2.2.2 Terminology

Stable isotope compositions of low-mass (light) elements such as oxygen, hydrogen, carbon, nitrogen, and sulfur are normally reported as δ values. The term "δ" is spelled and pronounced **delta** not **del**. The word del describes either of two mathematical terms: an operator (∇) or a partial derivative (∂). δ values are reported in units of parts per thousand (denoted as ‰ or permil, or per mil, or per mille -- or even recently, per mill) relative to a standard of known composition. δ values are calculated by:

$$\delta \text{ (in ‰)} = (R_x / R_s - 1) \cdot 1000 \tag{2.2}$$

where R denotes the ratio of the heavy to light isotope (e.g., $^{34}S/^{32}S$), and R_x and R_s are the ratios in the sample and standard, respectively. For sulfur, carbon, nitrogen, and oxygen, the average terrestrial abundance ratio of the heavy to the light isotope ranges from 1:22 (sulfur) to 1:500 (oxygen); the ratio $^2H:^1H$ is much lower at 1:6410. A positive δ value means that the isotopic ratio of the sample is higher than that of the standard; a negative δ value means that the isotopic ratio of the sample is lower than that of the standard. For example, a $\delta^{15}N$ value of +30‰ means that the $^{15}N/^{14}N$ of the sample is 30 parts-per-thousand or 3% higher than the $^{15}N/^{14}N$ of the standard. Many isotope geochemists advocate always prefacing the δ value with a sign, even when the value is positive, to distinguish between a true positive δ value and a δ value that is merely missing its sign (a frequent occurrence with users unfamiliar with isotope terminology).

There are several commonly used ways for making comparisons between the δ values of two materials. The first two are preferred because of their clarity, and the fourth should be avoided:

(1) high vs. low values

(2) more/less positive vs. more/less negative (e.g., -10‰ is more positive than -20‰)

(3) heavier vs. lighter (the "heavy" material is the one with the higher δ value)

(4) enriched vs. depleted (always remember to state *what* isotope is in short supply, e.g., a material is enriched in ^{18}O or ^{16}O relative to some other material, *and* that the enrichment or depletion is a result of some reaction or process). For example, to say that "one sample is enriched in ^{34}S relative to another because of sulfate reduction" is proper usage. Phrases such as "a sample has an enriched $\delta^{15}N$ value" are misuses of terminology.

2.2.3 Standards

The isotopic compositions of materials analyzed on mass spectrometers are usually reported relative to some international *reference standard.* Samples are either analyzed at the same time as this reference standard or with some internal laboratory standard that has been calibrated relative to the international standard. Alternatively, the absolute ratios of isotopes can be reported. Small quantities of these reference standards are available for calibration purposes from either the National Institute of Standards and Technology (NIST) in the USA (Web site: **http://www.nist.gov/**), or the International Atomic Energy Agency (IAEA) in Vienna (Web site: **http://www.iaea.or.at/**).

Various isotope standards are used for reporting light stable-isotopic compositions (Table 2.1). The δ values of each of the standards have been defined as 0‰. δD and $\delta^{18}O$ values are normally reported relative to the SMOW standard (Standard Mean Ocean Water; Craig, 1961) or the equivalent VSMOW (Vienna-SMOW) standard. $\delta^{13}C$ values are reported relative to either the PDB (Pee Dee Belemnite) or the equivalent VPDB (Vienna-PDB) standard. $\delta^{18}O$ values of low-temperature carbonates are also commonly reported relative to PDB or VPDB.

Table 2.1. Abundance ratios and reference standards for some environmental isotopes.

Isotope	Ratio measured	Reference Standard	Abundance ratio of standard
^{2}H	$^{2}H/^{1}H$	VSMOW	$1.5575 \cdot 10^{-4}$
^{3}He	$^{3}He/^{4}He$	atmospheric He	$1.3 \cdot 10^{-6}$
^{6}Li	$^{6}Li/^{7}Li$	L-SVEC	$8.32 \cdot 10^{-2}$
^{11}B	$^{11}B/^{10}B$	NBS 951	4.04362
^{13}C	$^{13}C/^{12}C$	VPDB	$1.1237 \cdot 10^{-2}$
^{15}N	$^{15}N/^{14}N$	atmospheric N_2	$3.677 \cdot 10^{-3}$
^{18}O	$^{18}O/^{16}O$	VSMOW, or VPDB	$2.0052 \cdot 10^{-3}$ $2.0672 \cdot 10^{-3}$
^{34}S	$^{34}S/^{32}S$	CDT	$4.5005 \cdot 10^{-2}$
^{37}Cl	$^{37}Cl/^{35}Cl$	SMOC	0.324
^{87}Sr	$^{87}Sr/^{86}Sr$	Absolute ratio, or various materials	

VSMOW and VPDB are virtually identical to the SMOW and PDB standards. Use of VSMOW and VPDB is supposed to imply that the measurements were calibrated according to IAEA guidelines for expression of δ values relative to available reference materials on *normalized* permil scales (Coplen, 1994; 1995; 1996). Laboratories accustomed to analyzing synthetic compounds that are highly enriched in the heavy (or, less commonly, the light) isotope may report absolute isotope abundances in atomic-weight percent or ppm, instead of relative ratios in permil. In general, radioisotopes are reported as absolute concentrations or ratios. Tritium (^3H) values are typically reported as absolute concentrations, called Tritium Units (TU) where one TU corresponds to 1 tritium atom per 10^{18} hydrogen atoms. Tritium values may also be expressed in terms of activity (pico-Curies/liter, pCi/L) or decay (disintegrations per minute/liter, dpm/L), where 1 TU = 3.2 pCi/L = 7.2 dpm/L. ^{14}C contents are referenced to an international standard known as "modern carbon" and are typically expressed as a percent of modern carbon (pmc).

2.3 Stable Isotope Fractionation

2.3.1 Properties of isotopic molecules

The various isotopes of an element have slightly different chemical and physical properties because of their mass differences. Under the proper circumstances, such differences can manifest themselves as a *mass-dependent* isotope fractionation effect. Nuclear interactions, on the other hand, lead to a *non-mass-dependent* effect in the sense that they depend on the nuclear structure, rather than on the weight difference per se. In the first case, for example, the properties of molecules with ^{17}O will be intermediate between those of molecules with ^{16}O and ^{18}O; this is not necessarily the case for the non-mass-dependent effects. For elements of low atomic numbers, these mass differences are large enough for many physical, chemical, and biological processes or reactions to *fractionate* or change the relative proportions of different isotopes of the same element in various compounds. As a result of fractionation processes, waters and solutes often develop unique isotopic compositions (ratios of heavy to light isotopes) that may be indicative of their source or the processes that formed them.

Two main types of phenomena produce isotopic fractionations: *isotope exchange reactions* and *kinetic processes*. Isotope exchange reactions can be viewed as a subset of kinetic isotope reactions where the reactants and products remain in contact in a closed, well-mixed system such that back reactions can occur and chemical equilibrium can be established. Under such circumstances, isotopic equilibrium can be also established. Detailed discussions of isotope fractionations are found in O'Neil (1986), Gat and Gonfiantini (1981), Gat (1980), and other texts.

2.3.2 Fractionation accompanying chemical reactions and phase changes

The strength of chemical bonds involving different isotopic species will usually be different. Molecules containing heavy isotopes are more stable (i.e., have a higher dissociation energy) than molecules with lighter isotopes. Hence, isotopic fractionations between molecules can be explained by differences in their *zero point energies* (ZPE). For example, there is about a 2 kcal/mole difference in ZPE associated with the breaking of the H-H bond compared to the D-D bond (Figure 2.2). Hence, H-H bonds are broken more easily and D-D bonds are more stable. Chemical reaction rates where such a bond is broken will also show an isotope effect. These are quantum effects that become appreciable at low temperatures and disappear at higher temperatures.

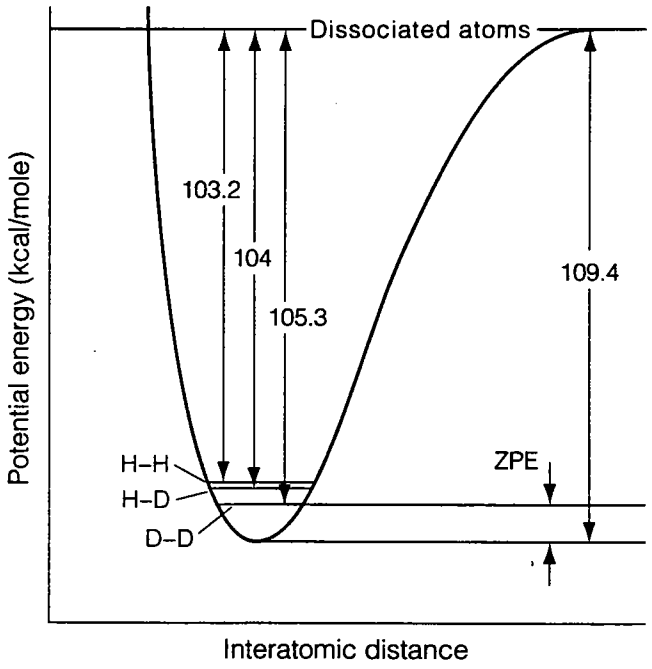


Figure 2.2. The interatomic distance - potential energy relationship for stable hydrogen isotopes of a molecule. Higher zero point energies (ZPE) result in molecules being less stable. Modified from O'Neil (1986).

The energy differences associated with isotope effects are about 1000 times smaller than the ΔG for chemical reactions, and hence cannot be the driving force for chemical equilibrium.

Equilibrium fractionations

Equilibrium isotope-exchange reactions involve the redistribution of isotopes of an element among various species or compounds (in a strict sense, this only occurs in a closed, well-mixed system at chemical equilibrium). At isotopic equilibrium, the forward and backward reaction rates of any particular isotope are identical. This does not mean that the isotopic compositions of two compounds at equilibrium are identical, but only that the ratios of the different isotopes in each compound are constant for a particular temperature.

During equilibrium reactions, the heavier isotope generally preferentially accumulates in the species or compound with the higher oxidation state. For example, sulfate becomes *enriched* in ^{34}S relative to sulfide (i.e., has a more positive $\delta^{34}S$ value); consequently, the residual sulfide becomes *depleted* in ^{34}S. As a "rule of thumb," among different phases of the same compound or different species of the same element, the more dense the material, the more it tends to be enriched in the heavier isotope. For example, for the various phases of water, at equilibrium, $\delta^{18}O_S > \delta^{18}O_L > \delta^{18}O_V$. Also, the $\delta^{13}C$ and $\delta^{18}O$ values of $CO_2 < HCO_3^- < CaCO_3$.

During phase changes, the ratio of heavy to light isotopes in the molecules in the two phases changes. For example, as water vapor condenses in rain clouds (a process typically viewed as an equilibrium process), the heavier water isotopes (^{18}O and ^{2}H) become enriched in the liquid phase while the lighter isotopes (^{16}O and ^{1}H) remain in the vapor phase. In general, the higher the temperature, the less the difference between the equilibrium isotopic compositions of any two species (because the differences in ZPE between the species become smaller).

The fractionation associated with the equilibrium exchange reaction between two substances *A* and *B* (i.e., the fractionation of *A* relative to *B*) can be expressed by use of the isotope fractionation factor α (alpha):

$$\alpha_{A\text{-}B} = R_A / R_B \tag{2.3}$$

where *R* = the ratio of the heavy isotope to the lighter isotope (i.e., D/H, $^{18}O/^{16}O$, $^{34}S/^{32}S$, etc.) in compounds *A* and *B*.

The value of such an *equilibrium* fractionation factor can be calculated on the basis of spectral data of the isotopic molecular species, at least for simple molecules. The α values generally differ by just a few percent from the equal-energy value of 1.00, except for exchange reactions involving hydrogen isotopes where α values may be as large as 4 at room temperature (see Friedman and O'Neil, 1977). The sign and magnitude of α are dependent on many factors, of which temperature is generally the most important. Other factors include chemical composition, crystal structure, and pressure.

The equilibrium fractionation factors ($\alpha_{l\text{-}v}$) for the water liquid-vapor phase transition are 1.0098 and 1.084 at 20°C and 1.0117 and 1.111 at 0°C for ^{18}O and ^{2}H, respectively (Majoube, 1971). In both cases, $\alpha_{l\text{-}v} > 1$, which means that the first phase (the liquid water) is "heavier" than the second phase (e.g., for $\alpha_{l\text{-}v} = 1.0098$, the $\delta^{18}O$ of water is +9.8‰ higher than the $\delta^{18}O$ value of vapor at equilibrium). For the ice-water transition (0°C), the values are 1.0035 and 1.0208, respectively (Arnason, 1969).

A useful equation that relates δ values and fractionation factors is:

$$\alpha_{A\text{-}B} = (1000 + \delta_A) / (1000 + \delta_B) . \tag{2.4}$$

Other common formulations for fractionation factors include:

$$\alpha^* = 1/\alpha = \alpha_{B\text{-}A} = R_B / R_A \tag{2.5}$$

and

$$\epsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1) \cdot 1000 . \tag{2.6}$$

For small values of ϵ (epsilon), $\epsilon_{A\text{-}B} \approx \delta_A - \delta_B$. For example, if $\delta_B = +10‰$ and if $\alpha_{A\text{-}B} = 1.020$, then $\epsilon = 20‰$ and $\delta_A \approx +30‰$. The difference in isotopic composition between two species *A* and *B* is defined as:

$$\epsilon_{A\text{-}B} \approx \delta_A - \delta_B \approx 1000 \ln \alpha_{A\text{-}B} . \tag{2.7}$$

Fractionation factors are commonly expressed as "$10^3 \ln \alpha$" because this expression is a very close approximation to the permil fractionation between the materials (ϵ), especially for the values of α near to unity typical of most elements of interest (O'Neil, 1986), and because the value "$10^3 \ln \alpha$" is nearly proportional to the inverse of temperature (1/T) at low temperatures (°K). Graphical plots of the temperature dependency of α are typically given as $10^3 \ln \alpha$ versus 1/T (Friedman and O'Neil, 1977).

Kinetic fractionations

Chemical, physical, and biological processes can be viewed as either reversible *equilibrium* reactions or irreversible unidirectional *kinetic* reactions. In systems out of chemical and isotopic equilibrium, forward and backward reaction rates are not identical, and isotope reactions may, in fact, be unidirectional if reaction products become physically isolated from the reactants. Such reaction rates are dependent on the ratios of the masses of the isotopes and their vibrational energies, and hence are called **kinetic** isotope fractionations.

The magnitude of a kinetic isotope fractionation depends on the reaction pathway, the reaction rate, and the relative bond energies of the bonds being severed or formed by the reaction. Kinetic fractionations, especially unidirectional ones, are usually larger than the equilibrium fractionation factor for the same reaction in most low-temperature environments. As a rule, bonds between the lighter isotopes are broken more easily than equivalent bonds of heavier isotopes. Hence, the light isotopes react faster and become concentrated in the products, causing the residual reactants to become enriched in the heavy isotopes. In contrast, reversible equilibrium reactions can produce products heavier or lighter than the original reactants.

Many reactions can take place either under purely equilibrium conditions or be affected by an additional kinetic isotope fractionation. For example, although isotopic exchange between water and vapor can take place under more-or-less equilibrium conditions (i.e., at 100% humidity when the air is still and the system is almost chemically closed), more typically the system is out of chemical equilibrium (i.e., < 100% humidity) or the products become partially isolated from the reactants (e.g., the resultant vapor is blown downwind). Under these conditions, the isotopic compositions of the water and vapor are affected by an additional kinetic isotope fractionation of variable magnitude (see below).

Isotope fractionation factors can be defined as:

$$\alpha = R_p / R_s \tag{2.8}$$

where R_p and R_s are the ratios of the heavy to light isotope in the *product* and *substrate* (reactant), respectively. An isotope enrichment factor, ϵ, can be defined as:

$$\epsilon_{p\text{-}s} = (\alpha - 1) \cdot 1000 \, . \tag{2.9}$$

If the reactant concentration is large and fractionations are small,

$$\epsilon_{p\text{-}s} \approx \Delta = \delta_p - \delta_s \tag{2.10}$$

where Δ (del) is another term for the enrichment factor. Note that Equations 2.8 - 2.10 for kinetic fractionations are the same as Equations 2.3, 2.6, and 2.7 (respectively) for equilibrium fractionations, except for the differences in subscripts. One should be especially careful with the superscripts, subscripts, and units of all fractionation factors; different authors may define them differently. The use of p and s (or r) for kinetic fractionations like Equation 2.10 reflects the unidirectional nature of these reactions.

The same formulations apply not only when part of the system is removed by a chemical or biological reaction, but also when material escapes by diffusion or outflow (e.g., by effusion through an aperture). In the latter cases the term *transport* fractionation factor may be preferred.

The transport fractionation, like the *equilibrium* factors, is temperature dependent. However, unlike true *kinetic* fractionation factors, which can be quite appreciable, transport fractionations have only slight (positive) temperature coefficients.

2.3.3 The Rayleigh equations

The isotopic literature abounds with different approximations of the **Rayleigh equations**, including the three equations below. These equations are so-named because the original equation was derived by Lord Rayleigh (pronounced "raylee") for the case of *fractional distillation of mixed liquids*. This is an exponential relation that describes the partitioning of isotopes between two reservoirs as one reservoir decreases in size. The equations can be used to describe an isotope fractionation process if: (1) material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g., water with ^{18}O and ^{16}O, or sulfate with ^{34}S and ^{32}S), (2) the fractionation accompanying the removal process at any instance is described by the fractionation factor α, and (3) α does not change during the process. Under these conditions, the evolution of the isotopic composition in the residual (reactant) material is described by:

$$(R / R_\circ) = (X_l / X_{l\circ})^{\alpha-1} \tag{2.11}$$

where R = ratio of the isotopes (e.g., $^{18}O/^{16}O$) in the reactant, $R_\circ$ = initial ratio, X_l = the concentration or amount of the more abundant (lighter) isotope (e.g., ^{16}O), and $X_{l\circ}$ = initial concentration. Because the concentration of $X_l >> X_h$, X_l is approximately equal to the amount of original material in the phase. Hence, if $f = X_l/X_{l\circ}$ = fraction of material remaining, then:

$$R = R_\circ f^{(\alpha-1)}. \tag{2.12}$$

Another form of the equation in δ-units is:

$$\delta \approx \delta_\circ f^{(\alpha-1)} \tag{2.13}$$

which is valid for α values near 1, $\delta_\circ$ values near 0, and ϵ values less than about 10.

In a strict sense, the term "Rayleigh fractionation" should only be used for chemically *open* systems where the isotopic species removed at every instant were in thermodynamic and isotopic equilibrium with those remaining in the system at the moment of removal. Furthermore, such an "ideal" Rayleigh distillation is one where the reactant reservoir is finite and well mixed, and does not re-react with the product (Clark and Fritz, 1997). However, the term "Rayleigh fractionation" is commonly applied to equilibrium closed systems and kinetic fractionations as well (as described below) because the situations may be computationally identical.

2.3.4 Isotopic fractionation in open and closed systems

The Rayleigh equation applies to an open system from which material is removed continuously under condition of a constant fractionation factor. However, such processes can proceed under different boundary conditions, even when the fractionation factors are the same. One such

system is the so-called "closed" system (or 2-phase equilibrium model), where the material removed from one reservoir accumulates in a second reservoir in such a manner that isotopic equilibrium is maintained throughout the process (Gat and Gonfiantini, 1981). An example is the condensation of vapor to droplets in a cloud where there is continuous exchange between the isotopes in the vapor and water droplets.

The isotope enrichment achieved can be very different in closed vs. open systems. For example, Figure 2.3 shows the changes in the $\delta^{18}O$ of water and vapor during evaporation (an *open*-system process) where the vapor is continuously removed (i.e., isolated from the water) with a constant fractionation factor $\alpha_{l\text{-}v} = 1.010$ (i.e., the newly formed vapor is always 10‰ lighter than the residual water). As evaporation progresses (i.e., $f \rightarrow 0$), the $\delta^{18}O$ of the remaining water (solid line A), becomes heavier and heavier. The $\delta^{18}O$ of the instantaneously formed vapor (solid line B) describes a curve parallel to that of the remaining water, but lower than it (for all values of f) by the precise amount dictated by the fractionation factor for ambient temperature, in this case by 10‰. For higher temperatures, the α value would be smaller and the curves closer together. The integrated curve, giving the isotopic composition of the accumulated vapor thus removed, is shown as solid line C. Mass balance considerations require that the isotope content of the total accumulated vapor approaches the initial water $\delta^{18}O$ value as $f \rightarrow 0$; hence, any process should be carried out to completion (with 100% yield) to avoid isotopic fractionation.

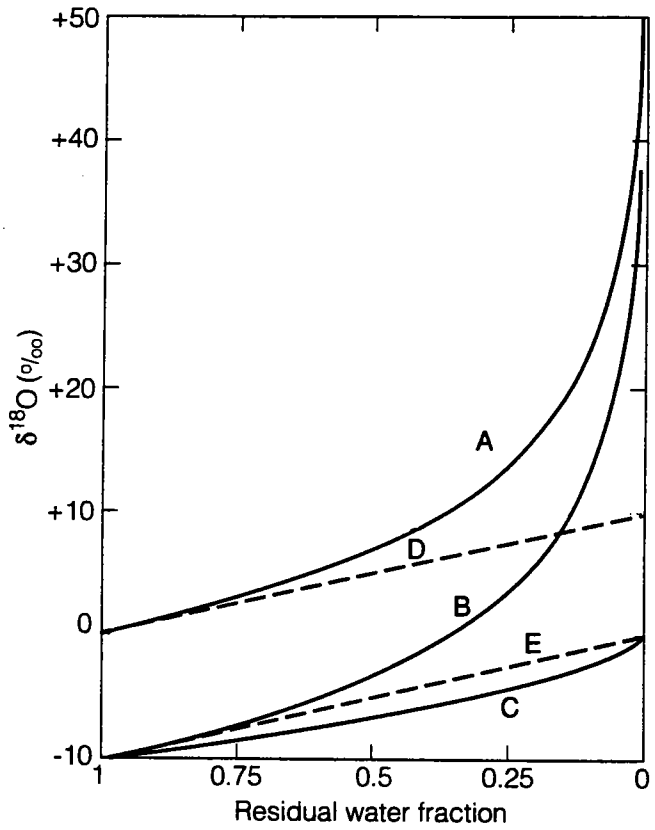


Figure 2.3. Isotopic change under open- and closed-system Rayleigh conditions for evaporation with a fractionation factor $\alpha = 1.01$ for an initial liquid composition of $\delta^{18}O = 0$. The $\delta^{18}O$ of the **remaining water** (solid line A), the **instantaneous vapor** being removed (solid line B), and the **accumulated vapor** being removed (solid line C) all increase during single-phase, open-system, evaporation under equilibrium conditions. The $\delta^{18}O$ of water (dashed line D) and vapor (dashed line E) in a two-phase closed system also increase during evaporation, but much less than in an open system; for a closed system, the δ values of the instantaneous and cumulative vapor are identical. Modified from Gat and Gonfiantini (1981).

The dashed lines in Figure 2.3 show the $\delta^{18}O$ of vapor (E) and water (D) during equilibrium evaporation in a *closed* system (i.e., where the vapor and water are in contact for the entire phase change). Note that the $\delta^{18}O$ of vapor in the *open* system where the vapor is continuously removed (line B) is always heavier than the $\delta^{18}O$ of vapor in a *closed* system where the vapor (line E) and water (line D) remain in contact. In both cases, the evaporation takes place under equilibrium conditions with $\alpha = 1.010$, but the cumulative vapor in the closed system *remains* in equilibrium with the water during the entire phase change. As a rule, fractionations in a true "open-system" Rayleigh process create a much larger range in the isotopic compositions of the products and reactants than in closed systems. This is because of the lack of back reactions in open systems. Natural processes will produce fractionations between these two "ideal" cases.

Other non-equilibrium fractionations may behave like Rayleigh fractionations in that there may be negligible back reaction between the reactant and product, regardless of whether the system is open or closed, because of kinetics. Such fractionations typically result in larger ranges of composition than for equivalent equilibrium reactions. An example of this process is biologically mediated denitrification (reduction) of nitrate to N_2 in groundwater; the N_2 is lost so it can't re-equilibrate with the nitrate, even if there was a back reaction by this organism, which there isn't. Figure 2.4 shows how Rayleigh-type fractionations affect the compositions of residual substrate, instantaneous product, and cumulative product (curved lines) during a *closed*-system kinetic reaction (e.g., denitrification, uptake of N by plants, or nitrification). Note that at all times, the δ values of instantaneous product are "ϵ ‰" less than the corresponding δ values of residual substrate. The parallel straight lines are the compositions for an *open*-system kinetic reaction where the supply of substrate is infinite and, hence, is not affected by the conversion of some substrate to product with a constant fractionation of ϵ.

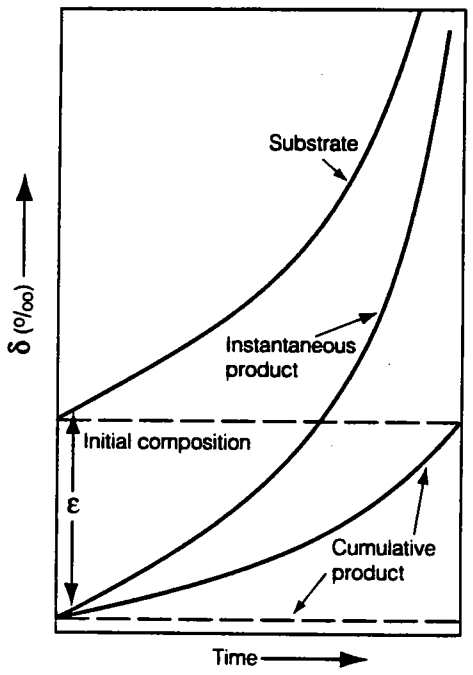


Figure 2.4. Relative changes in δ values of substrate, instantaneous product and cumulative product during closed-system (solid curved lines) and open-system (dashed straight lines) kinetic fractionation processes. In an open system, the supply of reactant is infinite; in a closed system, it is finite. At all times, the compositions of the instantaneous product and substrate differ by ϵ, the enrichment factor. For the open system, both the instantaneous and the cumulative product fall along the same line, parallel to the substrate-composition line but lower than it by ϵ. Modified from Högberg, 1997.

The curved lines on Figure 2.4 are very similar to the curved lines on Figure 2.3, which is reasonable since they are both solutions of the same Rayleigh equations. However, the ones in Figure 2.3 describe an *open*-system equilibrium process whereas the ones in Figure 2.4 describe a *closed*-system kinetic process. Furthermore, the straight lines in Figure 2.3 depict a *closed* system and the dissimilar but also straight lines in Figure 2.4 depict an *open* system. What is going on here? How can the same Rayleigh equations be used to produce fractionation curves described so differently?

The answer lies with where the *boundary lines* are drawn between the system being studied and the rest of the universe. In the case of the *equilibrium* fractionations illustrated in Figure 2.3, "open" means that the product, once formed at equilibrium, escapes to outside the system and does not interact again with the residual substrate (and, consequently, is no longer in equilibrium with the substrate). And "closed" means that the reactant and product remain in close contact, in their own closed (finite) system during the entire reaction, so that the two reservoirs are always in chemical and isotopic equilibrium. For the *kinetic* fractionations illustrated in Figure 2.4, "open" means that the supply of substrate is infinite (which it can't be in a closed system). The use of "closed" for kinetic reactions suggests that there is a limited supply of reactant, which is undergoing irreversible, quantitative, conversion to product in an isolated system.

Thusfar, a constant fractionation factor was assumed to apply throughout the process. However, this is not always the case. For example, rainout from an air mass is usually the result of a continuous cooling of the air parcel. The cooling increases the fractionation factor for the vapor-to-water (or vapor-to-ice) transition. Another conspicuous example of a changing "effective" fractionation factor is that of the evaporation of water from a surface water body to the atmosphere. As will be shown, the change in this situation is the result of the changing conditions (in this case, of the isotopic gradient) at the water-atmosphere boundary, rather than a change of the fractionation factors themselves.

Almost everyone finds the Rayleigh equations a bit confusing. Hence, we will now give some examples of how to calculate open- and closed-system fractionations, and how they affect the compositions of the residual substrate and the newly formed products of a reaction. Because much of the book focuses on *water* and its isotopes, we will demonstrate how to apply the Rayleigh equations by using the fractionations during water phase changes (i.e., during the condensation of vapor and the evaporation of water) as examples. For a more rigorous discussion of the topic, see Gat and Gonfiantini (1981) or Gat (1996); chapter 2 of Clark and Fritz (1997) provides a well-illustrated and exceptionally clear discussion of this fascinating topic. Many other reactions (e.g., sulfate reduction, methane oxidation, ammonia volatilization, and nitrification) can also be modeled with Rayleigh-type models; the same principles described here apply to these kinetic reactions.

Condensation of water

The isotopic composition of moisture in the marine atmosphere is controlled by the air-sea interaction processes as described by Craig and Gordon (1965), Merlivat and Jouzel (1979), and others. As air masses move across continents and lose water by rainout, they become *depleted* in the heavy isotopic species ($H_2{}^{18}O$ and HDO) because the liquid phase is *enriched* in the heavy isotopic species relative to the vapor phase (see Chapter 3). The evolution of the isotopic composition is adequately described by a Rayleigh process (in this case it is condensation) in those cases where rainout is the only factor in the atmospheric-moisture budget (Dansgaard, 1964; Gat, 1980). A Rayleigh fractionation plot for condensation would

be very similar to Figure 2.3, except that all the curves would bend down instead of up because the residual vapor and water condensed would become progressively *lighter* over time, not heavier (as they do for evaporation).

When the isotopic compositions of precipitation samples from all over the world are plotted relative to each other on $\delta^{18}O$ versus δD plots, the data form a linear band of data that can be described by the equation (Craig, 1961):

$$\delta D = 8\,\delta^{18}O + 10 \qquad (2.14)$$

and is called the *Global Meteoric Water Line* (GMWL) or just the *MWL*, or even the *Craig Line*. The slope is 8 (actually, different data sets give slightly different values) because this is approximately the value produced by equilibrium Rayleigh condensation of rain at about 100% humidity. The value of 8 is also close to the ratio of the equilibrium fractionation factors for H and O isotopes at 25-30°C. At equilibrium, the δ values of the rain and the vapor both plot along the MWL, but separated by the ^{18}O and ^{2}H enrichment values corresponding to the temperature of the cloud base where rainout occurred.

The y-intercept value of 10 in the GMWL equation is called the *deuterium excess* (or d-excess, or d parameter) value for this equation. The term only applies to the calculated y-intercept for sets of meteoric data "fitted" to a slope of 8; typical d-excess values range from 0 to 20 (see Chapter 3). The fact that the intercept of the GMWL is 10 instead of 0 means that the GMWL does not intersect $\delta^{18}O = \delta D = 0$, which is the composition of average ocean water (VSMOW). The GMWL does not intersect the composition of the ocean, the source of most of the water vapor that produces rain, because of the ≈10‰ kinetic enrichment in D of vapor evaporating from the ocean at an average humidity of 85%.

The Rayleigh law is formulated in approximate differential form and using δ notation as:

$$d\delta \approx \epsilon^{*} \cdot d\ln f \qquad (2.15)$$

where $f = N_f/N_0$ is the fraction of remaining water (N_0 and N_f being the water content of the air mass before and after the rain, respectively) so that $(N_0 - N_f)$ is the total water loss (rainout) from the air mass. The term ϵ^{*} is related to α^{*}, the unit equilibrium isotope fractionation factor between water and its vapor at the ambient near-surface air temperature, as follows:

$$\epsilon^{+} = (\alpha^{+} - 1) \cdot 10^{3}\,. \qquad (2.16)$$

Note that this equation is the same as Equation 2.6, except for the superscripts. Why the change? Because of some historical choices made to simplify mathematical expressions.

The equilibrium fractionation factor α between liquid and vapor can be defined in two ways, which are mathematical inverses: $\alpha = R_l/R_v$ or $\alpha = R_l/R_v$, where R_l and R_v are the isotopic ratios of the liquid and vapor, respectively. However, Craig and Gordon (1965) defined equilibrium fractionation factors such that $\alpha^{+} = 1/\alpha^{*}$, so that $\alpha^{+} = R_l/R_v > 1$ and $\alpha^{*} = R_v/R_l < 1$ (and, consequently, $\epsilon^{+} > 0$ and $\epsilon^{+} \approx -\epsilon^{*}$). This usage has become traditional when discussing atmospheric processes. In general, α^{+} (often abbreviated to simply α) is used for condensation problems, whereas α^{*} is commonly preferred for evaporation problems. Values for α^{+} can be calculated from Majoube (1971). Although the use of α^{+} vs. α^{*} may simplify calculations, many other people find it more convenient to use the definition of fractionation factor that produces $\alpha > 1$, despite tradition.

As rain condenses, the heavier isotopes of water (mainly $HD^{16}O$ and $H_2{}^{18}O$) are preferentially removed from the air mass (and into the rain), and the air mass consequently becomes progressively lighter in isotopic composition (i.e., higher concentrations of $H_2{}^{16}O$). Hence, the isotopic compositions of successive aliquots of rain become progressively lighter in the heavier isotope due to continuing rainout of the heavy isotopes. As will be described in Chapter 3, this is why the δ values of rain become lighter as storms move inland from the ocean. At any point along the storm trajectory (i.e., for some specific fraction f of the total original vapor mass), the $\delta^{18}O$ of the residual fraction of vapor in the air mass can be calculated by:

$$\delta \approx \delta_o + \epsilon \ln (f) \tag{2.17}$$

$$\delta^{18}O_v \approx \delta_o{}^{18}O_v + \epsilon_{l\text{-}v} \cdot \ln f \tag{2.18}$$

where $\delta_o{}^{18}O_v$ is the initial δ value of the vapor (remember that ln x <0 for x <1, so that the residual vapor is lighter than the initial vapor). The $\delta^{18}O$ of the of the rain produced at this point can be determined by:

$$\delta^{18}O_l \approx \delta^{18}O_v + \epsilon_{l\text{-}v} \tag{2.19}$$

where $\epsilon_{l\text{-}v}$ (the enrichment of liquid relative to vapor, equivalent to ϵ^+ in the discussion above) is constant. For a system with changing temperature, the relation has to be integrated to account for the change in ϵ as a function of temperature.

Another commonly used formulation of the Rayleigh equation for systems with a constant fractionation factor is: $\delta \approx \delta_o - \epsilon \ln (f)$. In this case, the enrichment factor in the Rayleigh equation has a negative sign, instead of the positive sign shown earlier (Equation 2.17), because of different definitions for α (and hence for ϵ values). The choice of either α^* or its reciprocal value α^+ for the equilibrium fractionation factor is dictated only by convenience; there is no "right" way. If there is any confusion about how the fractionation terms are defined in some paper, just try a few test calculations to make sure the δ values for a reaction change in the "right" direction (e.g., with biological reactions, residual reactants get heavier; during condensation of rain, residual vapor gets lighter; etc); if the δ values don't change as expected, this probably means that the fractionation factor being used is the inverse of what should be used in the equation.

Evaporation of water

Evaporation from an open-water surface fractionates the isotopes of hydrogen and oxygen in a manner which depends on a number of environmental parameters, the most important of which is the ambient humidity. This is illustrated for various relative humidities in Figure 2.5. The higher the humidity, the smaller the change in $\delta^{18}O$ and δD during evaporation. For example, at 95% humidity, the δ values are constant for evaporation of the last 85% of the water. Evaporation results in lines with slopes <8 on a $\delta^{18}O$ vs. δD plot (i.e., the data plot on lines *below* the MWL that intersect the MWL at the composition of the original water).

Evaporation at 0% humidity describes open-system evaporation ("open" in terms of the definitions for Figure 2.3). Note that the two upper diagrams on Figure 2.5 are Rayleigh-type plots, similar to Figure 2.3 but with larger changes in $\delta^{18}O$ during open-system evaporation on Figure 2.5. The δ values on the curved fractionation lines on the upper diagrams plot along nearly straight lines on the lower $\delta^{18}O$ vs. δD plot. The "length" of the evaporation lines on the

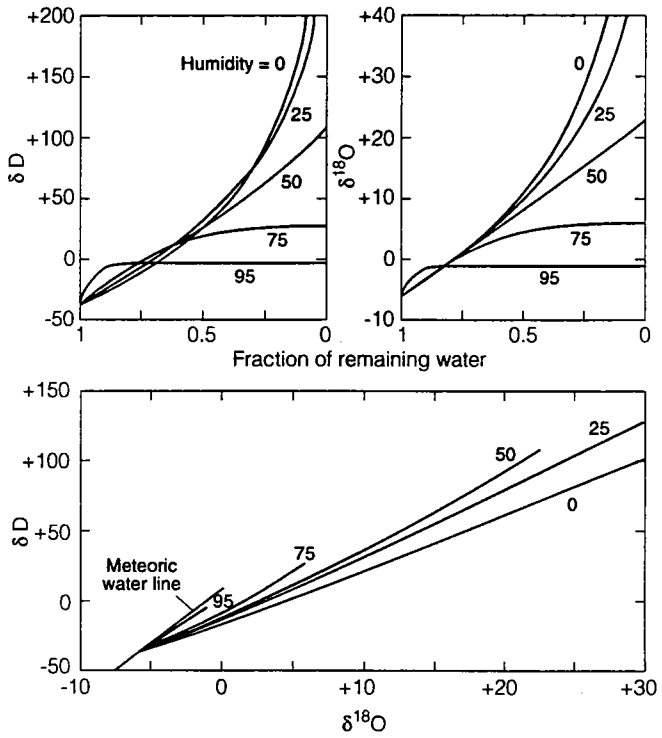


Figure 2.5. The effect of humidity on the $\delta^{18}O$ and δD values of the residual water fraction during evaporation. Higher humidities result in less fractionation because of back exchange between the water and the vapor, and evaporation lines with higher slopes. Modified from Gat and Gonfiantini (1981).

$\delta^{18}O$ vs. δD plot reflect the range of values of water produced during total evaporation under different humidities. For example, the short line for 95% humidity indicates that the water changes little during the entire evaporation process.

Evaporation under almost 100% humidity conditions is more-or-less equivalent to evaporation under closed-system conditions (i.e., isotopic equilibrium is possible), and data for waters plot along a slope of 8 (ie., along the MWL). However, the shapes of the curves in the upper diagrams for 95% humidity are not the same as for closed-system *equilibrium* fractionation (Figure 2.3); instead, they are similar to the infinite-reservoir *kinetic* fractionation shown on Figure 2.4. This is because the curves in Figure 2.5 were calculated using both an equilibrium fractionation for the phase change and a kinetic fractionation (Equation 2.20) for the diffusion of water vapor across the water-atmosphere interface (Gat and Gonfiantini, 1981). This is also the explanation for the larger open-system fractionations on Figure 2.5 than on Figure 2.3.

The most useful model for the isotope fractionation during evaporation is that of Craig and Gordon (1965). It is schematically shown in Figure 2.6 (redrawn from Gat, 1996). This model assumes that equilibrium conditions apply at the air/water interface (where the humidity is 100%), that there is a constant vertical flux, and that there is no fractionation during fully turbulent transport. For a detailed derivation, see Craig and Gordon (1965) or Gat (1996).

At the water-air interface, there is a balance between two opposing water fluxes: one upward from the water surface and one downward consisting of atmospheric moisture. When the humidity is 100% (i.e., the air is saturated), the upward and downward physical fluxes can

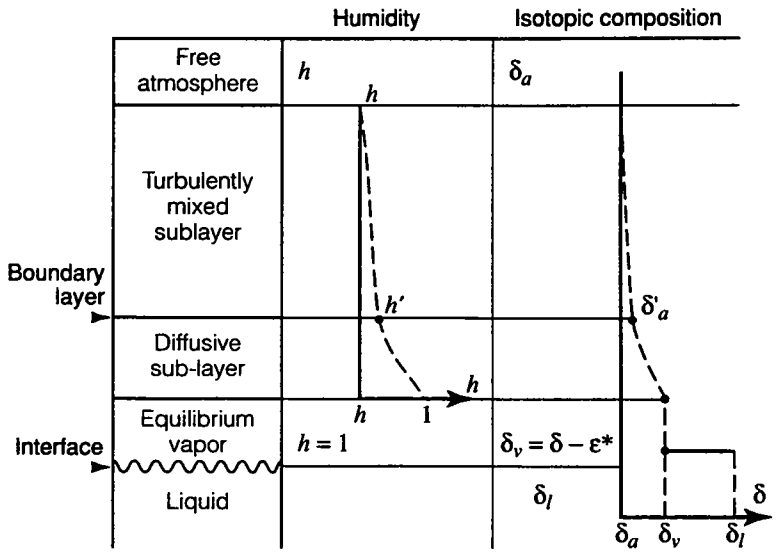


Figure 2.6. The Craig-Gordon model for isotopic fractionation during the evaporation of water, showing how isotopic composition and humidity change across different layers above the water. Modified from Gat (1996).

become equivalent and their isotopic compositions may then reach equilibrium (note that equilibrium does ***not*** mean that the δ values of the two reservoirs are identical, only that they differ by the equilibrium enrichment factor); see Clark and Fritz (1997) pages 26-27.

The changes in humidity and corresponding changes in the isotopic composition of vapor across the transition between the water and the free atmosphere are given as dashed lines in Figure 2.6. Note that where h = 1 (in the so-called "equilibrium vapor" layer between the interface and the boundary layer where the humidity is 100%), the vapor is in equilibrium with the liquid (i.e., $\delta_v = \delta - \epsilon^*$). When the air is undersaturated (i.e., h < 1), a net evaporative flux is produced. The rate determining step for evaporation is the diffusion of water vapor across the air boundary layer, which occurs in response to the humidity gradient between the surface and the fully turbulent ambient air (Figure 2.6).

The isotopic composition of the evaporated moisture (for either oxygen or hydrogen isotopes) can be formulated as:

$$\delta_E = (\alpha^* \delta_w - h\delta_a - \epsilon) / [(1-h) + \Delta\epsilon/1000] \approx (\delta_w - h\delta_a - \epsilon) / (1-h) \qquad (2.20)$$

where $\epsilon = \epsilon^* + \Delta\epsilon$, $\epsilon^* = (1-\alpha^*)\cdot 10^3$, $\alpha^* < 1$, and the variable $\Delta\epsilon$ is an additional diffusive (kinetic) isotope fractionation which results from the different diffusivities of the water molecules of various isotopic compositions in the liquid-air boundary layer (i.e., an additional fractionation caused by diffusion across the humidity gradient between the "equilibrium vapor layer" and the turbulently mixed vapor sublayer on Figure 2.6). Hence, the total fractionation ϵ equals the sum of the equilibrium and kinetic fractionations. δ_w and δ_a are the isotopic compositions of the surface water and the atmospheric moisture (vapor), respectively, with all parameters in ‰ units. Relative humidity, *h*, is normalized to the saturated vapor pressure at the temperature of the lake surface water, and is written as a fraction < 1. According to the Craig and Gordon (1965) model, $\Delta\epsilon$ has the form:

$$\Delta\epsilon = (1-h) \cdot \theta \cdot n \cdot \epsilon_k \tag{2.21}$$

where ϵ_k is a "kinetic" constant with values of 25.1‰ and 28.5‰ for δ^2H and $\delta^{18}O$, respectively (Merlivat, 1978), and $0.5 \leq n \leq 1$. The weighting term θ can be assumed equal to 1 for small bodies of water whose evaporation flux does not perturb the ambient moisture significantly (Gat, 1995), but has been shown to have a value of 0.88 for the North American Great Lakes (Gat et al., 1994) and a value of about 0.5 for evaporation in the eastern Mediterranean Sea (Gat et al., 1996). For an open water body, a value of $n = 0.5$ seems appropriate (Gat, 1996). However, for evaporation of water through a stagnant air layer such as in soils (Barnes and Allison, 1988) or leaves (Allison et al., 1985), a value of $n \approx 1$ fits the data reasonably well. See Chapters 5 and 6 for discussion of evaporation in soils and plants. Note that in some articles the ϵ_k values in Equation 2.21 are modified by multiplication by 1000 (or need to be) because the values for ϵ_k may not be in ‰.

The values of δ_E and δ_w define a line in $\delta^{18}O$ vs. δD space called the *evaporation line* (Figures 2.5 and 2.7) whose slope is given by:

$$S = [h(\delta_a - \delta_w) + \epsilon]_{2H} / [h(\delta_a - \delta_w) + \epsilon]_{18O} . \tag{2.22}$$

To preserve mass balance, the initial water composition, the evaporated moisture, and the residual water (such as lake waters or soil waters) must all plot along this same line. The slope of the evaporation line is determined by the air humidity (Figure 2.5), and the equilibrium and kinetic fractionations (ϵ^* and $\Delta\epsilon$), which are dependent themselves on temperature and boundary conditions, respectively. The slopes of evaporation lines on Figure 2.5 range from 3.9 (for humidity = 0) to 6.8 (for humidity = 95%). The δ_E value plots above the MWL (Figure 2.7). This evaporated vapor will mix with ambient vapor δ_a to produce vapor with a higher d-excess value than the original vapor, and can affect the δ values of later rain from the airmass.

When part of the rained-out moisture is returned to the atmosphere by means of evapotranspiration, then a simple Rayleigh law no longer applies. The downwind effect of the evapotranspiration flux on the isotopic composition of the atmospheric moisture and precipitation

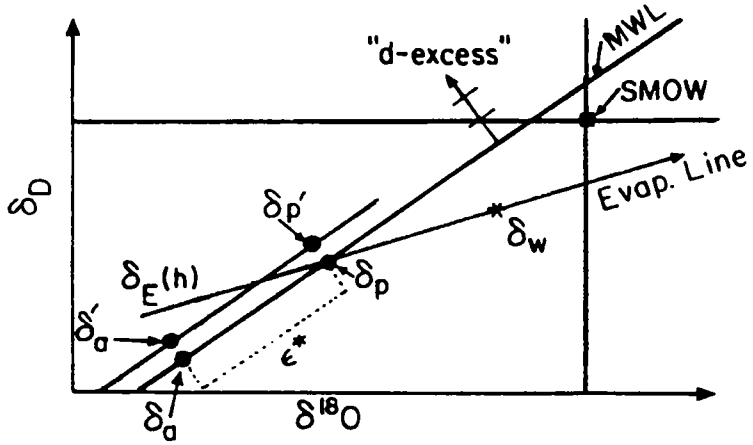


Figure 2.7. The isotopic compositions of evaporated surface water (δ_w), the original precipitation prior to evaporation (δ_p), and the evaporated vapor (δ_E) all plot along the same evaporation line. Both the precipitation (δ_p) and the atmospheric vapor (δ_a) in equilibrium with it plot along the MWL, separated by the enrichment factor for the environmental temperature (ϵ^*). When the evaporate (δ_E) mixes with the local atmospheric vapor (δ_a), a new vapor (δ'_a) is formed that plots above the MWL. If rain later condenses from this vapor, it would plot along a new line parallel to the MWL but with a higher *d-excess* value. (From Gat et al., 1994).

depends on the details of the evapo-transpiration process. Transpiration returns precipitated water essentially unfractionated to the atmosphere, despite the complex fractionations in leaf water (see Chapter 6). Thus, transpiration cancels out the effect of the rainout process. In other words, admixture of transpired waters moves the isotopic composition of the atmospheric moisture back towards more positive δ values (i.e., enriched in the heavy isotopic species), as if rain never took place. Under such circumstances, the change in the isotope composition along the air-mass trajectory measures only the net loss of water from the air mass, rather than being a measure of the integrated total rainout. On the other hand, evaporated vapor (δ_E) is usually depleted in the heavy isotopic species relative to that of transpired water (δ_T) and is actually closer to the composition of the atmospheric moisture. Hence mixing of moisture derived from the evaporation of lake water back into the atmospheric moisture reservoir has a somewhat smaller effect than the addition of transpired water in restoring isotopic composition of the original air mass.

2.3.5 Biological fractionations

Biological processes are generally unidirectional and are excellent examples of *kinetic* isotope reactions. Organisms preferentially use the lighter isotopic species because of the lower energy "costs" associated with breaking the bonds in these molecules, resulting in significant fractionations between the substrate (heavier) and the biologically mediated product (lighter). Kinetic isotopic fractionations of biologically-mediated processes vary in magnitude, depending on reaction rates, concentrations of products and reactants, environmental conditions, and -- in the case of metabolic transformations -- species of the organism. The variability of the fractionations makes interpretation of isotopic data difficult, particularly for nitrogen and sulfur. The fractionations are very different from, and typically larger than, the equivalent equilibrium reaction. The magnitude of the fractionation depends on the reaction pathway utilized (i.e., which is the rate-limiting step) and the relative energies of the bonds severed and formed by the reaction. In general, slower reaction steps show greater isotopic fractionation than faster steps because the organism has time to be more selective (i.e., the organism saves internal energy by preferentially breaking light-isotope bonds).

If the substrate concentration is large enough that the isotopic composition of the reservoir is insignificantly changed by the reaction (O'Leary, 1981) or if the isotopic ratio of the product is measured within an infinitely short time period (Mariotti et al., 1981), the fractionation factor can be defined as in Equation 2.8 (i.e., the straight lines on Figure 2.4 for the "open system model"). For unidirectional reactions (Figure 2.4, curved lines), the change in the isotope ratio of the substrate relative to the fraction of the unreacted substrate can be described by the Rayleigh equation:

$$R_s / R_{so} = f^{(\alpha-1)} \tag{2.23}$$

where R_s and R_{so} are the ratios of the unreacted and initial substrate, respectively, and f is the fraction of unreacted substrate. Figure 2.8 shows the changes in compositions of residual NO_3, incremental N_2 produced, and cumulative N_2 for denitrification with a fractionation factors of $\beta = 1.005$, 1.010, and 1.020 (i.e., the organism preferentially utilizes the lighter isotope), which are equivalent to $\alpha = 0.995$, 0.99, and 0.98, respectively. In the final stages of the reaction, when the NO_3 is almost gone, the isotopic compositions of the residual reactant and incremental product increase dramatically, reaching very high values when the reaction is almost complete (see Chapter 16).

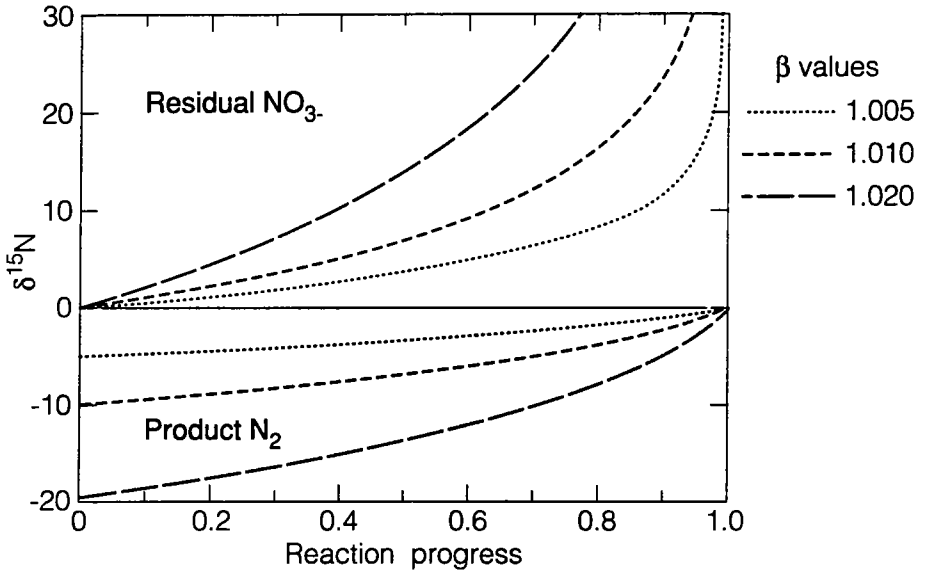


Figure 2.8. Reaction progress vs. the $\delta^{15}N$ values of residual reactant (NO_3) and cumulative product (N_2) resulting from denitrification with fractionation factors (β) of 1.005, 1.010, and 1.020. The higher the β value, the higher the $\delta^{15}N$ of the NO_3 and the lower the $\delta^{15}N$ of the N_2.

Readers of this book and articles dealing with isotope fractionations must be careful: both fractionation and enrichment factors are defined in various ways by different authors, especially in the biological literature. Kinetic fractionation factors are typically described in terms of enrichment or discrimination factors, using such symbols as β, ϵ, or D. In particular, the enrichment factor is sometimes defined in reverse (i.e., $\epsilon_{s\text{-}p}$), and some researchers define a "discrimination factor" $D_{s/p} = (\alpha_{s/p} - 1)1000$, where *s/p* denotes "substrate relative to products." Good discussions of fractionations associated with biological processes include Hübner (1986) and Fogel and Cifuentes (1993).

A good example of the complexities of kinetic reactions is given by the fractionation between CO_2 and photosynthetic organic carbon. The fractionation can be described by the model (Fogel and Cifuentes, 1993):

$$\Delta = A + (C_i / C_a)(B - A) \tag{2.24}$$

where Δ is the isotopic fractionation, *A* is the isotope effect caused by diffusion of CO_2 into the plant (-4.4‰), *B* is the isotope effect caused by enzymatic (photosynthetic) fixation of carbon (-27‰), and C_i/C_a is the ratio of internal to atmospheric CO_2 contents. The magnitude of the fractionation depends on the values of the above parameters. For example, when there is unlimited CO_2 (i.e., $C_i/C_a = 1$), the enzymatic fractionation controls the $\delta^{13}C$ of the plant, with plant $\delta^{13}C$ values as low as -36‰ (Fogel and Cifuentes, 1993). Alternatively, if the CO_2 content is limiting ($C_i/C_a << 1$) and the diffusion of CO_2 into the cell is rate determining, $\delta^{13}C$ values will be strongly affected by the smaller diffusional isotope effect, resulting in more positive $\delta^{13}C$ values (-20 to -30‰).

2.4 Sample Collection, Analysis, and Quality Assurance

2.4.1 Sampling guidelines

Considerable field effort is often required to collect a sample that adequately represents the average composition of the medium being sampled, at the time it is sampled. For small streams, this can be as simple as collecting water as it flows over a weir or rock ledge. For large rivers, lakes, soils, and organisms, mass-integrated composites may be required. Adequate coverage of this vital topic is beyond the scope of this chapter. The reader is advised to look at the references given in subsequent chapters, or consult colleagues who routinely collect such samples. Other useful sources of information include: Clark and Fritz (1997; chapter 10: "Field methods for sampling"), Mazor (1997), and the Web pages of various isotope laboratories.

Below is a potpourri of guidelines and suggestions related to collecting, bottling, and preserving samples for analysis of the most commonly-used environmental isotopes. The reader should keep in mind that the optimum methods often depend on the laboratory chosen for analysis and their preferred preparation methods, and should always inquire before planning the field campaign. Collection of duplicates is alway advisable -- in case of breakage of samples during transport and to use as checks of the reproducibility of the laboratory (i.e., submit 5-10% of these as "blind duplicates," with different sample ID numbers than their duplicates).

$\delta^{18}O/\delta^{2}H$ of water

Natural waters are easy to collect. The water sample is put in a clean dry bottle, which is filled almost completely to the top, and capped tightly. The main objective is to protect the sample from evaporation and exchange with atmospheric water vapor. Samples should not be filtered unless they contain oil (e.g., mineral oil added to rain collectors to help prevent evaporation) or contain abundant particulate matter. Bottle rinsing, chilling, and addition of preservatives are unnecessary. Freezing does not affect the composition of the water but can break the bottles in transit; for this reason, many users prefer plastic bottles. Our experience suggests that caps with conical plastic inserts (e.g., "poly-seal" caps) are the most reliable, followed by teflon-lined caps. For extended storage, use of glass bottles and waxing of the caps is advisable. Sample-size is lab-dependent; typical volumes range from 10-60 mL. In some laboratories, samples as small as a few µL can be analyzed.

Determinations of both hydrogen and oxygen isotope ratios are usually made on the same bottle of water. It is wise to collect many more samples than one can afford to analyze at the present; samples have a long shelf life if bottled correctly, and can be archived for future analysis. One should make sure that the laboratory chosen to analyze the samples normalizes their values according to IAEA guidelines (Coplen, 1994), and reports values relative to VSMOW. If the samples are saline, one should check whether the lab is preparing samples by an equilibration or quantitative-conversion method (see below). Waters with high contents of volatile organic matter may require distillation.

For many purposes, especially hydrograph separations (see Chapter 1), analysis for all samples for both oxygen and hydrogen isotopes is unnecessary because of the high correlation coefficient between these isotopes (see Chapter 3). A sensible alternative is to have some smaller percentage analyzed for both isotopes, either initially or after the data for the first

isotope are evaluated. For hydrograph studies in arid environments or studies that involve evaporated water in ponds or wetlands, analysis of samples for both isotopes is probably advisable. Because most labs have fewer problems analyzing waters for $\delta^{18}O$ than for $\delta^{2}H$, if the samples are not analyzed in duplicate and will only be analyzed for one isotope, it is usually better to choose $\delta^{18}O$.

Solid and vapor samples are more difficult to collect for $\delta^{18}O$ and $\delta^{2}H$. Snow and ice samples can be collected in tightly sealed bags or jars, melted overnight, and then poured into bottles. Plant and soil samples should be collected in air-tight containers matched to the sample size. Common procedures include waxing of soil cores, use of heat-sealed bags, or insertion into tiny tree-core-size vials. Water vapor samples are collected by pumping vapor through a cold-trap where the vapor is quantitatively retained. For more information on various sampling procedures, see Chapters 3-6.

Tritium

The amount of water needed for tritium analysis depends on the age of the water (old waters contain little tritium) and the sensitivity of analysis needed. Typical sample sizes range from 10 mL to 1L. Samples are collected in unrinsed glass or high-density polyethylene bottles and should not be filtered. The bottles should then be sealed and returned to the laboratory for analysis. The collection date should be noted on the bottle to obtain an accurate determination of the tritium concentration for the time of collection.

$\delta^{13}C$ and ^{14}C of dissolved inorganic carbon

There are two main methods in common use for the collection of DIC (dissolved inorganic carbon) for the measurement of ^{13}C or ^{14}C, depending on which of two laboratory preparation methods is being used: gas stripping or carbonate precipitation. Both preparation methods insure quantitative removal of the DIC and provide a $\delta^{13}C$ or ^{14}C value for total DIC. Analysis for $\delta^{13}C$ generally requires 10-100 μM of carbon. Analysis of ^{14}C by conventional beta-counting methods requires as much as 1 g of C; analysis by AMS usually requires about 1 mg of C.

For laboratories that use a gas-stripping method to extract the CO_2, samples are usually collected in sample-rinsed glass bottles with septa-caps, or in vessels with stopcocks or valves. Such samples should be filtered to remove particulate carbon, and perhaps poisoned (using mercuric chloride, acid, or organic biocide) to prevent biological activity; the bottles should be kept chilled until analyzed to prevent biological fractionations.

The alternative technique is the precipitation method. Samples should be pre-filtered if there might be suspended carbonate particulate material in the water. The carbonate is precipitated by adding a strongly basic solution of strontium or barium chloride (Gleason et al., 1969) to the sample in a sample-rinsed bottle. The base increases the pH to 10-11 where all the inorganic carbon is CO_3^{-2}, and the Ba or Sr precipitates all the DIC in the water. This reagent and the treated samples must be protected against contamination by atmospheric CO_2. Glass bottles are best because CO_2 diffuses through most plastic bottles. Bottles should have poly-seal caps that are taped securely. Bottles should be individually wrapped in bubble paper and shipped in insulated boxes or coolers filled with artificial "peanuts" to insure against breakage.

$\delta^{15}N$ of dissolved inorganic nitrogen

A number of different preparation methods are in common use; inquire what collection method is preferred by the contract laboratory for their particular preparation method. In particular, it

is important to verify that the laboratory is accustomed to analyzing *natural abundance* samples. Laboratories that primarily analyze agricultural samples often use methods that are appropriate for labeled (^{15}N-spiked) samples but have unacceptable analytical precisions for natural abundance studies. Check that the laboratory has a good track record for natural samples. Samples can be analyzed for the $\delta^{15}N$ of ammonium and/or nitrate; analysis of total nitrogen is probably worthless. Generally, samples are filtered through 0.1 micron filters, put in rinsed glass bottles, poisoned (with sulfuric acid, mercuric chloride, or chloroform), chilled or frozen, wrapped in insulating packing material, and sent to the laboratory in ice chests. Sample-size requirements are in the range of 10-100 μM of N. Nitrate samples can also be analyzed for $\delta^{18}O$ in a few laboratories.

An alternate method is to concentrate the NO_3 or NH_4 on anion or cation exchange resins (Garten, 1992; Silva et al., submitted; Chang et al., in review). Collection of nitrate on anion exchange resins eliminates the need to send large quantities of chilled water back to the laboratory, eliminates the need for hazardous preservatives, makes it easier to archive samples, and allows analysis of extremely low-nitrate waters.

$\delta^{34}S$ of dissolved sulfate

Depending on the sulfate concentration, samples are filtered directly into glass bottles or are first pre-concentrated on an exchange resin. Sulfate from dilute waters should be collected on ion exchange resin in the field if the concentration of sulfate in the water is believed to be less than 20 mg/L. Similar to collection methods for NO_3 or NH_4 on ion exchange resins, collection of sulfate on exchange resins avoids problems of incomplete precipitation of $BaSO_4$ in dilute samples, eliminates the need to send large quantities of chilled water back to the lab, eliminates the need for hazardous preservatives, makes it easier to archive samples, and allows analysis of extremely low-sulfate waters.

Low-sulfate water samples are first acidified before passing through ion exchange columns. The sulfate is then eluted from the resin using a relatively small volume of concentrated barium chloride solution. The final volume of the solution is much less than that of the original water sample and the sulfate from the sample is thus concentrated in this much smaller volume (generally 10-500 μM of SO_4 is required). The solution is reacidified and sulfate is precipitated by adding $BaCl_2$. $BaSO_4$ is then collected by filtration and analyzed for $\delta^{34}S$. Sulfate can also be analyzed for $\delta^{18}O$ in some laboratories. Large quantities of sulfate can also be analyzed for ^{35}S, a natural radioisotope with a half-life of 87 days, using liquid scintillation counting.

C, H, N, O, and S isotopes of solid samples

Solid organic and inorganic samples (e.g., animals, plants, minerals, and soils) and liquids (such as oils) can also be analyzed for their isotopic composition. Particulate matter in water can be captured on fiberglass filters and processed similar to methods used for other solid samples. Requirements for solid samples are similar to the requirements for solute samples of the same element (i.e., 1-100 μM of the element of interest). Biologically labile samples (e.g., leaves, fish, manure) should be kept cold until processed. Freeze-drying is an ideal means for preserving the samples; air-drying results in loss of volatile organic matter and probably some isotopic fractionation.

Lithogenic (metals and semi-metals) isotopes

The sample size is dependent on the species being analyzed. Analysis of Sr, Li, or B requires a minimum of 1 μg; Pb and Nd require a minimum of 0.1 μg. Aqueous samples should be

filtered; 0.1 micron filters are best for Nd and Pb, and 0.45 micron filters are best for Sr, Li, and B (Thomas D. Bullen, pers. comm. 1997). Aqueous samples are collected in rinsed plastic bottles and acidified to pH ≈ 2 using Ultrex HNO_3. Blanks should be sent to the laboratory along with your samples, including the triple distilled water used for filtering and the clean water run through the processing equipment. One must be careful about possible contamination with lithium grease, borate soaps or detergents, and strontium chloride reagents.

2.4.2 Analytical methods and instrumentation

Stable isotopes are analyzed either on *gas-* or *solid-source* mass spectrometers, depending on both the masses of the isotopes and the existence of appropriate gaseous compounds stable at room temperature. Radioisotopes can be analyzed by counting the number of disintegrations per unit time on gamma ray or beta particle counters, or analyzed on mass spectrometers.

Gas-source mass spectrometers

Many methods are used to prepare gases for C, H, N, O, and S (CHNOS) stable isotope content, but in all the cases the basic steps are the same. Sample preparation involves the quantitative conversion or production of pure gas from solely the compound of interest, cryogenic or chromatographic purification of the gas, introduction of the gas into the mass spectrometer, ionization to produce positively charged species, dispersion of different masses in a magnetic field, impaction of different masses on different collector cups, and measurement of the ratios of the isotopes in the ionized gas. In general, hydrogen is analyzed as H_2, oxygen and carbon are both analyzed as CO_2, nitrogen is analyzed as N_2, and sulfur is usually analyzed as SO_2. The analytical precisions are small relative to the ranges in δ values that occur in natural earth systems. Typical one standard deviation analytical precisions for oxygen, carbon, nitrogen, and sulfur isotopes are in the range of 0.05 to 0.2‰; typical precisions for hydrogen isotopes are poorer, from 0.2 to 1.0‰, because of the lower ^2H:^1H ratio.

Although the topic is rarely discussed, the activity coefficients of isotopic species are not all equal to 1 (i.e., the isotope *concentration* of a sample is not necessarily equal to the isotope *activity*). The activity coefficient for a particular isotope can be positive or negative, depending on solute type, molality, and temperature. The isotopic compositions of waters and solutes can be significantly affected by the concentration and types of salts because the isotopic compositions of waters in the hydration spheres of salts and in regions farther from the salts are different (see Horita (1989) for a good discussion of this topic). In general, the only times when it is important to consider isotope activities is for low pH, high SO_4, and/or high Mg brines because the activity and concentration δ values of these waters (δ_a and δ_c) are significantly different. For example, the difference (δD_a- δD_c) between the activity and concentration δ values for sulfuric acid solutions in mine tailings is about +16‰ for 2 molal solutions. For normal saline waters (e.g., seawater), the activity coefficients for $\delta^{18}O$ and δ^2H are essentially equal to 1.

Virtually all laboratories report $\delta^{18}O$ activities (not concentrations) for water samples. The δ^2H of waters may be reported in either concentration or activity δ values, depending on the method used for preparing the samples for analysis. Methods that involve *quantitative conversion* of the H in H_2O to H_2, produce δ_c values. Methods that *equilibrate* H_2O with H_2 (or H_2O with CO_2) produce δ_a values. "Equilibrate" in this case means letting the liquid and gas reach isotopic equilibrium at a constant, known temperature. To avoid confusion, laboratories and research papers should always report the method used.

Most conventional CHNOS mass spectrometers are *dual inlet* machines that have both a sample and a standard inlet or introduction port. In such instruments, the ratios of the isotopes of interest (e.g., $^{13}C/^{12}C$) in the sample gas are measured relative to the same ratios in a gaseous standard that is analyzed more-or-less simultaneously. Such instruments usually have either "double collectors" or "triple collectors," meaning that either two or three masses of the ionized gas can be measured simultaneously. For example, N_2 contains three species: $^{14}N^{14}N$, $^{14}N^{15}N$ and $^{15}N^{15}N$ (i.e., masses 28, 29, and 30). A triple-collecting mass spectrometer would measure the abundances of all these species relative to the abundances in a gaseous standard introduced through the "standard" inlet. A double-collecting mass spectrometer would only measure the 28 and 29 masses (actually m/e is measured since the molecules are ionized, with positive charges).

Another type of stable isotope mass spectrometer is the so-called *continuous flow* mass spectrometer. Such instruments may lack a dual inlet, and usually have triple collectors. These instruments represent a "marriage" of chromatography and mass spectrometry, and are similar to conventional organic mass spectrometers in that gas samples are introduced into the mass spectrometer within a stream of helium gas, usually from an automated sample preparation unit (e.g., an elemental analyzer or gas chromatograph). In general, the analytical precision available for continuous flow mass spectrometers is slightly poorer than with conventional methods, but this may change in the next few years. The main advantage of the continuous flow method is that such instruments are very easily combined with various on-line preparation systems, dramatically lowering the manpower cost of isotope analyses. For an exceptionally thorough discussion of modern stable isotope mass spectrometry see Barrie and Prosser (1996).

Solid-source mass spectrometers

Elements analyzed as solids (e.g., strontium, lithium, boron, lead, etc.) are prepared by precipitating selected compounds on wire filaments, loading the filaments into the source of a thermal ionization (solid-source) mass spectrometer, ionizing the compounds to produce gases (negative or positive charged), and measuring the abundances of selected isotopes in the gas on multiple collectors. Some light-mass solids (e.g., boron and lithium) are reported in the standard δ units. Generally, the heavier-mass elements are reported in terms of the relative abundances of two isotopes (e.g., $^{207}Pb/^{206}Pb$); however, strontium isotope abundances ($^{87}Sr/^{86}Sr$) are occasionally reported in δ notation relative to some arbitrary standard. Solid-source mass spectrometry has been shown to give a more accurate analysis of certain radium and uranium isotopes that conventionally were measured by decay counting methods.

Gas and liquid scintillation counters

Radioactive isotopes can be measured by a number of methods, depending on the mass, abundance, type of decay involved, accuracy desired, and money available. Some, of course, can be analyzed on solid source mass spectrometers (e.g., uranium-series isotopes). Otherwise, radioisotopes are analyzed on liquid scintillation counters (LSC) and gas proportional counters (both with enrichment), and on accelerator mass spectrometers (see below). Liquid scintillation and gas proportional systems are the most common systems used for light isotopes with beta decays. Gas proportional counting usually requires that the isotope being analyzed form a suitable counting gas, so that elements with high electronegativities, such as chlorine and sulphur, are not suitable for this type of analysis. The two isotopes most commonly used in hydrology, tritium and ^{14}C, have generally been analyzed using liquid scintillation or gas proportional counting. Radon is analyzed either by gas Geiger or proportional counting in the field, or sent to a laboratory for liquid scintillation counting, depending on the accuracy desired. For isotopes that decay by gamma and alpha emission, and beta emissions where the

target isotope cannot be reduced to a suitable chemical form for LCS or gas counting, the use of solid scintillation-counting using crystals, or more advanced systems like lithium-germanium drift counters, have been utilized.

Accelerator mass spectrometry

Accelerator mass spectrometers (AMS), sometimes called "tandem" accelerators, are very large (> 10m), expensive, high-resolution, mass spectrometers (with either gas or solid-sources) that accelerate charged particles through very high (mega-volt) electrical fields to separate different isobars and isotopes (Figure 2.1). These instruments can analyze some radioactive species more rapidly, with greater accuracy, and/or with much smaller sample sizes (e.g., mg rather than g samples) than previous counting methods. For example, tritium can now be analyzed using the helium ingrowth method, although it frequently requires long delays (6 months) to accrue enough ^{3}He to obtain an accurate analysis. AMS has become the method of choice for some isotopes, such as ^{14}C, ^{36}Cl and ^{129}I. It will give accuracies close to those obtained by traditional methods, and samples can be analyzed much more rapidly by AMS.

2.4.3 Quality assurance of contract laboratories

How does one find a good contract laboratory for analyzing samples? Choices include university laboratories, private commercial companies, and government laboratories that can accept contract (or collaborative) work. A primary selection criterion should be that the laboratory has been making the desired type of analysis for several years on a routine basis (e.g., samples submitted to some university laboratories may be analyzed by temporary student help, who do not perform analyses on a routine basis). Make inquiries among colleagues about the long-term track record of the laboratory. Good laboratories have active QA/QC programs, with documentation generally available on request. In our opinion, the laboratory should analyze about 5-15% of the samples in duplicate, as an internal verification that "everything" is operating correctly. Furthermore, laboratories with automated preparation systems and computer-controlled data management systems probably produce better and more reliable data on a long-term basis than laboratories where everything is done manually. The reader is cautioned to beware of bargains (*caveat emptor*); quality work usually costs more than the average price. Furthermore, the potential long-term cost of **wrong** interpretations, due to bad data, should be factored into the total cost of the analyses when evaluating laboratory choices.

One should also consider collecting duplicates in case the sample bottle is broken or lost in transit. Most laboratories routinely analyze each sample only once; if high precision data are required, either request duplicate analysis of each sample (and triplicates if the duplicates do not agree within some predetermined range) or send in "blind" duplicates. Sending in 10-15% blind duplicates is advisable, in any case. If any result seems questionable, immediately request a repeat. Most laboratories keep analyzed samples for a couple months before discarding them and will reanalyze modest numbers of samples at no additional cost.

For water samples, immediately plot the data on a δD vs. $\delta^{18}O$ diagram; outliers, especially ones that plot appreciably above the GMWL (the line defined by "$\delta D = 8\ \delta^{18}O + 10$" -- see Figure 2.7), should be viewed with skepticism and possibly reanalyzed. Few natural processes produce waters that plot significantly above the GMWL; exceptions include methanogenesis in landfills (Baedecker and Back, 1979) and silicate hydrolysis.

2.5 Applications of Isotope Tracers in Catchment Hydrology

The applications of environmental isotopes as hydrologic tracers in low temperature (< 40°C) systems fall into two main categories:

- tracers of the water itself: *water isotope hydrology*
- tracers of the solutes in the water: *solute isotope biogeochemistry.*

These classifications are by no means universal but they are conceptually useful and often eliminate confusion when comparing results using different tracers. This book uses this classification for dividing chapters into Part III (Chapters 10 - 14) and Part IV (Chapters 15 - 20). Because the main emphasis of this book is watershed *hydrology* not *biogeochemistry*, much of the discussion in Part II (Chapters 3 - 9) focuses on uses of environmental isotopes to understand sources, ages, and transport of **water**, with extra attention given to understanding the sources of variability in water isotopes because of their leading role as tracers of water. Part V contains two synthesis chapters, one which reviews the "art and science of modeling of environmental isotope and hydrochemical data in catchment hydrology," and one which describes the uses of isotope techniques for understanding environmental change.

Chapters 10 - 22 provide an overview of some of the myriad applications of environmental isotopes to catchment hydrobiogeochemistry. Most of the chapters focus on a particular type of catchment and how isotopes can be used to understand the functioning of the catchment, or on specific kinds of uses of isotopes in catchments (e.g., on determining flowpaths or obtaining climatic information). For general information on uses of isotopes of some particular element, especially for applications "beyond the catchment," useful Web sources of information include:

http://www.iaea.or.at/ The Web site for the IAEA (International Atomic Energy Agency). This page contains information on IAEA publications, how to order isotope reference materials, and how to access the IAEA isotope databases.

http://www.nist.gov/ The Web site for the National Institute of Standards and Technology (formerly NBS) provides information on ordering isotope reference materials.

http://wwwrcamnl.wr.usgs.gov/isoig/ The Web site of the USGS Isotope Interest Group (IsoIG). This page contains a variety of links to isotope-related resources, including short notes on isotope fundamentals and applications, information about isotope reference standards, links to several search engines for finding publications, and a link to the Web site for the **ISOGEOCHEM** email discussion group. The **ISOGEOCHEM** listserver primarily focuses on the stable isotope community, contains links to many isotope laboratories, and contains an archive of previous emails with a full search engine. If any of the other URLs listed here have changed, check the IsoIG Web site for updated links.

http://wwwrcamnl.wr.usgs.gov/isoig/period/ This Web site contains a "clickable" periodic table that provides information about many isotopes, including lists of noteworthy publications, and descriptions of the uses of these isotopes to hydrology, geology, and biology; it contains a search engine.

http://wwwrcamnl.wr.usgs.gov/isoig/isopubs/ The Web site for this book.

The sections below are intended as a brief introduction to the many uses of environmental isotopes in catchment hydrology, for readers who might be unfamiliar with what various isotopes have to offer, and a lead-in to the more thorough discussions in succeeding chapters.

2.5.1 Water isotope hydrology

Isotope Hydrology addresses the application of the measurements of isotopes that form water molecules: the oxygen isotopes (oxygen-16, oxygen-17, and oxygen-18) and the hydrogen isotopes (protium, deuterium, and tritium). These isotopes are ideal tracers of water sources and movement because they are integral constituents of water molecules, not something that is dissolved *in* the water like other tracers that are commonly used in hydrology (e.g., dissolved species such as chloride). Water isotopes can sometimes be useful tracers of water flowpaths, especially in groundwater systems where a source of water with a distinctive isotopic composition forms a "plume" in the subsurface (see Chapter 18 or Bullen et al., 1996).

In most low-temperature environments, stable hydrogen and oxygen isotopes behave conservatively in the sense that as they move through a catchment, any interactions with oxygen and hydrogen in the organic and geologic materials in the catchment will have a negligible effect on the ratios of isotopes in the water molecule. Although tritium also exhibits insignificant reaction with geologic materials, it does change in concentration over time because it is radioactive and decays with a half-life of about 12.4 years. The main processes that dictate the oxygen and hydrogen isotopic compositions of waters in a catchment are: (1) phase changes that affect the water above or near the ground surface (evaporation, condensation, melting), and (2) simple mixing at or below the ground surface.

Stable oxygen and hydrogen isotopes can be used to determine the contributions of old and new water to a stream (and to other components of the catchment) during periods of high runoff because the rain or snowmelt (new water) that triggers the runoff is often isotopically different from the water already in the catchment (old water). Chapters 3-7 discuss the sources of variability in the isotopic compositions of water in rain, snow, soil water, plants, and groundwater (respectively) and explain why the old and new water components often have different isotopic compositions. Tritium (^3H) is an excellent tracer for determining time scales for the mixing and flow of waters, and is ideally suited for studying processes that occur on a time scale of less than 100 years (see Chapters 3, 7, and 9). Chapters 10-14 explore how isotopes can be used to investigate hydrologic processes in various catchment types (rain-dominated temperate and tropical catchments, snowmelt-dominated catchments, arid basins, and lake-dominated systems, respectively).

2.5.2 Solute isotope biogeochemistry

Isotope Biogeochemistry addresses the application of isotopes of constituents that are dissolved in the water or are carried in the gas phase. Isotopes commonly used in solute isotope **bio**chemistry research include the isotopes of: sulfur (Chapter 15), nitrogen (Chapter 16), and carbon (Chapters 17 and 18). Less commonly applied isotopes in **geo**chemical research include those of: strontium, lead, uranium, radon, helium, radium, lithium, and boron (see Chapters 8, 9, 18, 19, and 20).

Unlike the isotopes in the water molecules, the ratios of solute isotopes can be significantly altered by reaction with biological and/or geological materials as the water moves through the catchment. Although the literature contains numerous case studies involving the use of solutes (and sometimes solute isotopes) to trace *water* sources and flowpaths, such applications include an implicit assumption that these solutes are transported conservatively *with* the water. In a strict sense, *solute isotopes only trace solutes*. Solute isotopes also provide information on the

reactions that are responsible for their presence in the water and the flowpaths implied by their presence.

As discussed above, water isotopes often provide relatively unambiguous information about residence times and relative contributions from different water sources; these data can then be used to make hypotheses about water flowpaths. Solute isotopes can provide an alternative, independent isotopic method for determining the relative amounts of water flowing along various subsurface flowpaths. However, the least ambiguous use of solute isotopes in catchment research is tracing the relative contributions of potential solute sources to groundwater and surface water. Although there has been extensive use of carbon, nitrogen, and sulfur isotopes in studies of forest growth and agricultural productivity, solute isotopes are not yet commonly used for determining weathering reactions and sources of solutes in catchment research. This book attempts to remedy that situation.

2.5.3 Mixing

Isotopic compositions mix conservatively. In other words, the isotopic compositions of mixtures are intermediate between the compositions of the endmembers. Despite the awkward terminology (i.e., the δ notation and units of ‰) and negative signs, the compositions can be treated just like any other chemical constituent (e.g., chloride content) for making mixing calculations. For example, if two streams with known discharges (Q_1, Q_2) and known $\delta^{18}O$ values ($\delta^{18}O_1$, $\delta^{18}O_2$) merge and become well mixed, the $\delta^{18}O$ of the combined flow (Q_T) can be calculated from:

$$Q_T = Q_1 + Q_2 \tag{2.25}$$

$$\delta^{18}O_T Q_T = \delta^{18}O_1 Q_1 + \delta^{18}O_2 Q_2 \,. \tag{2.26}$$

Another example: any mixing proportions of two waters with known $\delta^{18}O$ and δD values will fall along a tie line between the compositions of the endmembers on a $\delta^{18}O$ vs. δD plot.

What is *not* so obvious is that on many types of X-Y plots, mixtures of two endmembers will not necessarily plot along lines but instead along *hyperbolic curves* (Figure 2.9a). This is explained very elegantly by Faure (1986) using the example of $^{87}Sr/^{86}Sr$ ratios. The basic principle is that mixtures of two components that have different *isotope ratios* (e.g., $^{87}Sr/^{86}Sr$ or $^{15}N/^{14}N$) and different *concentrations* of the element in question (e.g., Sr or N) form hyperbolas when plotted on diagrams with coordinates of isotope ratios versus concentration. As the difference between the elemental concentrations of two components (endmembers) approaches 0, the hyperbolas flatten to lines. The hyperbolas are concave or convex depending on whether the component with the higher isotope ratio has a higher or lower concentration than the other component. Mixing hyperbolas can be transformed into a straight lines by plotting isotope ratios versus the inverse of concentration (1/C), as shown in Figure 2.9b.

Graphical methods are commonly used for determining whether the data support an interpretation of *mixing* of two potential sources or *fractionation of a single source*. Implicit in such efforts is often the idea that mixing will produce a "line" connecting the compositions of the two proposed endmembers whereas fractionation will produce a "curve." However, as shown in Figure 2.10a, both mixing and fractionation (in this case, denitrification) can produce curves (Mariotti et al., 1988), although both relations can look linear for small ranges of

concentrations. However, the equations describing mixing and fractionation processes are different and under favorable conditions, the process responsible for the curve can be identified. This is because Rayleigh fractionations are *exponential* relations (Equation 2.13), and plotting δ values versus the natural log of concentration will produce a straight line (Figure 2.10b). If an exponential relation is not observed and a straight line is produced on a δ vs 1/C plot (like Figure 2.9b), this supports the contention that the data are produced by simple mixing of two endmembers.

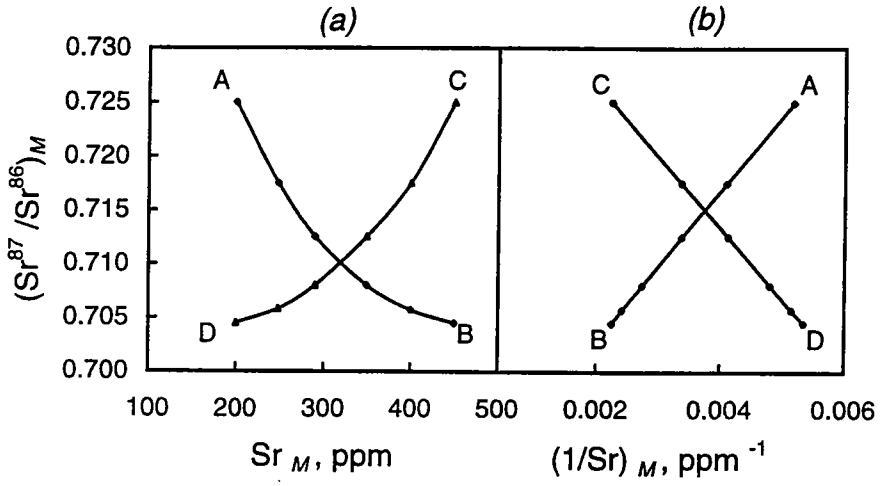


Figure 2.9. (*a*) Hyperbolas formed by the mixing of components (waters or minerals) *A* and *B* with different Sr concentrations and Sr isotope ratios ($^{87}Sr/^{86}Sr$). If the concentrations of Sr in *A* and *B* are identical, the mixing relation would be a straight line; otherwise, the mixing relations are either concave or convex curves, as shown. (*b*) Plotting the reciprocals of the strontium concentrations transforms the mixing hyperbolas into straight lines. If the curves in (*a*) were the result of some fractionation process (e.g., radioactive decay) that is an exponential relation, plotting the reciprocals of the Sr concentrations would not produce lines. Modified from Faure (1986).

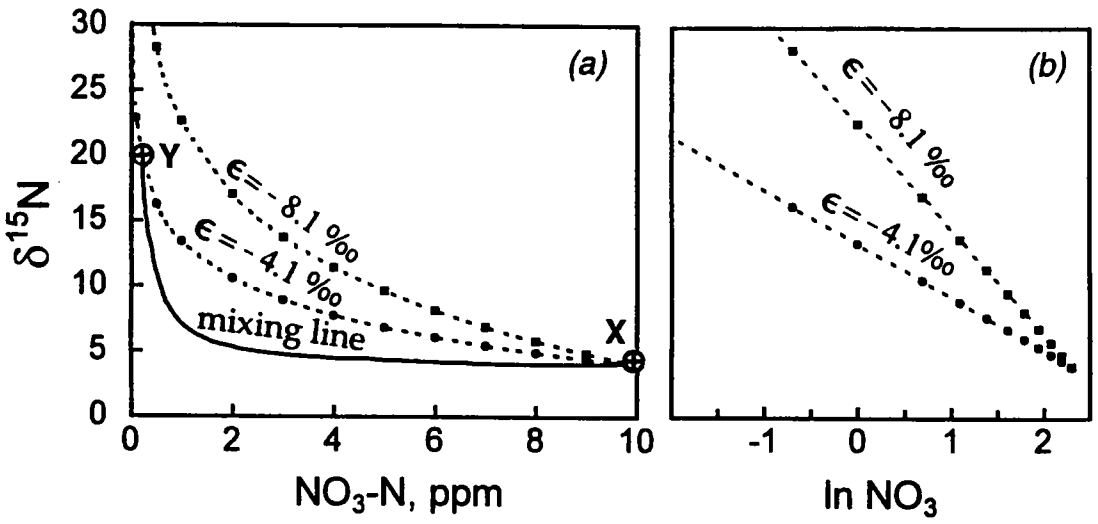


Figure 2.10. (*a*) Theoretical evolution of the $\delta^{15}N$ and the nitrate-N concentration during mixing (solid line) of two waters X and Y, and during an isotope fractionating process (e.g., denitrification of water X with a NO_3 concentration of 10 ppm). Denitrification for ϵ = -4.1‰ results in a curve (dashed line) that ends at Y. Two different enrichment factors are compared: ϵ = -4.1‰ and ϵ = -8.1‰. The data points represent successive 0.1 increments of mixing or denitrification progress. (*b*) Plotting the natural log of the concentrations for a fractionation process yields straight lines, different for different ϵ values. Modified from Mariotti et al. (1988).

2.5.4 Isotopically labeled materials

Man-made materials with isotopic compositions that are not observed in nature are called "spiked" or isotopically labeled materials. There are many commercial suppliers of isotopically labeled liquids, gases, and solids -- some with multiple-labeled atoms (e.g., water with unusual $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios, or organic molecules with various percentages of the elements of specific functional groups labeled with uncommon isotopic compositions). The most common watershed use of spiked tracers is for agricultural studies of plant uptake of nutrients. Other applications include whole-catchment experiments where labeled NH_4, NO_3, or SO_4 is sprinkled in artificial rain (see Chapters 15 and 16), and plot studies where labeled H_2O is applied to the land surface to make it easier to trace to movement of "new" water into the subsurface.

Materials can be enriched in either the common or less common isotope. Advantages of the former include low price, ready availability, and absence of potential contamination problems. The main disadvantage is that the lowest possible δ value for a material is -1000‰. In contrast, materials enriched in the less common isotope with δ values greater than $+10 \cdot 10^6$ ‰ are commonly available. Why the the lower limit of the permil scale is -1000‰ is illustrated by the following example for a water with no deuterium (i.e., all the hydrogen is protium):

$$\delta^2H = [(^2H / {}^1H)_x / (^2H / {}^1H)_s - 1)] \cdot 1000 \tag{2.27}$$

$$\delta^2H = [(0/{}^1H)_x / (^2H / {}^1H)_s - 1)] \cdot 1000 = (0 - 1) \cdot 1000 = -1000‰ . \tag{2.28}$$

The isotopic compositions in "labeled tracer" catalogs are generally in units of atom weight percent (at.%). For accurate conversion of these values to δ values, one must know the R_s value of the appropriate standard used for that isotope. Unfortunately, the absolute R_s values are not known for all international standards; the average terrestrial abundance ratios can be used for rough estimates. For example, the δ^2H value of a bottle of "95 at.% ^2H" water is calculated as follows (using the absolute ratio of VSMOW from Table 2.1):

$$\delta^2H = [(95/5) / (156 \cdot 10^{-6}) - 1)] \cdot 1000 = +122 \cdot 10^6 ‰ . \tag{2.29}$$

Although δ values are additive for natural abundance studies, mass balance calculations for labeled materials should be done using fractional isotopic abundances where $F = R/(1 + R)$ and R is the ratio of isotopes of interest. For the general case where the *concentrations* of labeled material in the waters mixed together might be different (e.g., a water with 20 mg/L of 75 at.% ^{15}N-labeled NO_3 added to water with 5 mg/L of NO_3 with a $\delta^{15}N$ value of +2‰), the isotopic composition of the solute in the mixed solution is:

$$F_T C_T n_T = F_1 C_1 n_1 + F_2 C_2 n_2 \tag{2.30}$$

where C is the concentration of the species of interest, n is the number of liters of solution, and the subscripts T, 1, and 2 refer to the total, 1st, and 2nd waters, respectively.

2.5.5 Stable isotopes in geochemical modeling

In chemical reaction modeling, usually several reaction models can be found that satisfy the data. For each model reaction path, calculations are used to predict the chemical and isotopic composition of the aqueous phase as well as the amounts of minerals dissolving or precipitated

along a flow path. The power of the stable isotope technique in groundwater modeling lies in the fact that we have added one more thermodynamic component to our system for each isotope ratio that is measured (Plummer et al., 1983). These isotopic compositions can be used along with chemical data in geochemical mass balance and reaction path models (e.g., BALANCE, PHREEQE, NETPATH, etc.) to deduce geochemical processes, test hypotheses on hydrology and geochemical mechanisms, and eliminate possible reaction paths (Plummer et al., 1991).

For example, the $\delta^{13}C$ of total dissolved inorganic carbon (DIC) is generally a function of the $\delta^{13}C$ of the rocks and extent of reaction with the rocks in a system. Thus, $\delta^{13}C$ can be a good indicator of which geochemical reactions are occurring (Chapter 18). Sulfur is similar to carbon in this respect, and changes in $\delta^{13}C$ along a flowpath sometimes can reflect reactions that also cause changes in $\delta^{34}S$ (e.g., progressive calcite precipitation along a flowpath in response to degassing of CO_2 causes gypsum to dissolve). Changes in ^{14}C content along a flowpath are useful for indicating changes in residence time. On the other hand, there is little change in δD and $\delta^{18}O$ of water during reactions with minerals along shallow, low-temperature flowpaths. Therefore, sulfur and carbon isotope data along a flowpath can sometimes be used to eliminate one or more plausible reaction models developed from chemical data, by comparing the observed changes in isotopic compositions with reaction progress (Figure 2.8) along a flowpath. Other useful stable isotope tracers include $\delta^{15}N$ and $\delta^{18}O$ of nitrates (Chapter 16) and $\delta^{34}S$ and $\delta^{18}O$ of sulfates (Chapter 15). Useful radiogenic isotopes include carbon-14, strontium-87, and various uranium-series isotopes (Chapter 7-9, 18, and 20).

2.5.6 Use of a multi-isotope approach for the determination of flowpaths

Flowpaths are the individual pathways contributing to surface flow in a catchment (see Chapter 1). These result from runoff mechanisms that include, but are not limited to, saturation-excess overland flow, Hortonian overland flow, near-stream groundwater ridging, hillslope subsurface flow through the soil matrix or macropores, and shallow organic-layer flow. Knowledge of hydrologic flowpaths in catchments is critical to the preservation of public water supplies and the understanding of the transport of point and non-point source pollutants (Peters, 1994). The need to incorporate flowpath dynamics is recognized as a key ingredient in producing reliable chemical models (Robson et al., 1992). In other words, if the model used gets the hydrology wrong, it is unlikely to correctly predict the geochemical response.

Stable isotopes such as ^{18}O and ^{2}H are shown throughout this book to be an improved alternative to traditional non-conservative chemical tracers because waters are often uniquely labeled by their isotopic compositions (Sklash and Farvolden, 1979), often allowing the separation of waters from different sources (e.g., "new" rain vs. "old" pre-storm water). However, studies have shown that flowpaths commonly cannot be identified to a high degree of certainty using $\delta^{18}O$ or δD data and simple hydrograph separation techniques because waters within the same flowpath can be derived from several different sources (Ogunkoya and Jenkins, 1991). Furthermore, an underlying theme of many of the chapters in Part 2 of this book is that the isotopic composition of rain, throughfall, meltwater, soil water, and groundwater are commonly variable in time and space. If such variability is significant at the catchment scale (i.e., if hillslope waters that are variable in composition actually reach the stream during the storm event) or if transit times are long and/or variable, then simple two- and three-component, constant composition, mixing models may not provide realistic interpretations of the system hydrology.

One solution is to include alternative, independent isotopic methods for determining the relative amounts of water flowing along different subsurface flowpaths into hydrologic models. Reactive solute isotopes such as ^{13}C, ^{34}S, and ^{87}Sr can provide valuable information about flowpaths (not water sources) useful for geochemical and hydrologic modeling precisely because they ***can*** reflect the reactions characteristic of and taking place along specific flowpaths (see Bullen et al., 1996; Chapter 18). In many instances, the waters flowing along mineralogically distinctive horizons can be distinctively labeled by their chemical composition and by the isotopic compositions of solute isotopes like ^{13}C, ^{87}Sr, ^{34}S, ^{15}N, etc. For example, waters flowing through the soil zone often have $\delta^{13}C$ values that are depleted in ^{13}C relative to deeper groundwaters because of biogenic production of carbonic acid in organic soils; these same shallow waters can also have distinctive Pb and Sr isotopic compositions.

2.6 Summary

The dominant use of isotopes in catchment research in the last few decades has been to trace sources of waters and solutes. Generally, such data were evaluated with simple mixing models to determine how much was derived from either of two (sometimes three) constant-composition sources. The world does not seem this simple anymore. With the expansion of the field of isotope hydrology in the last decade, made possible by the development and increased availability of automated preparation and analysis systems for mass spectrometers, we have documented considerable heterogeneity in the isotopic compositions of rain, soil water, groundwater, and solute sources. We are still grappling with how to deal with this heterogeneity in our hydrologic and geochemical models. A major challenge is to use the variability as ***signal***, not noise, in our models (Kendall et al., 1995); the isotopic and chemical compositions are providing very detailed information about sources and reactions in shallow systems, if only we can develop appropriate models to use the data. This integration of chemical and isotopic data with complex hydrologic models constitutes an important frontier of catchment research.

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